AP • Advanced Placement • College Board

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

8020 ENGLISH

AP 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.

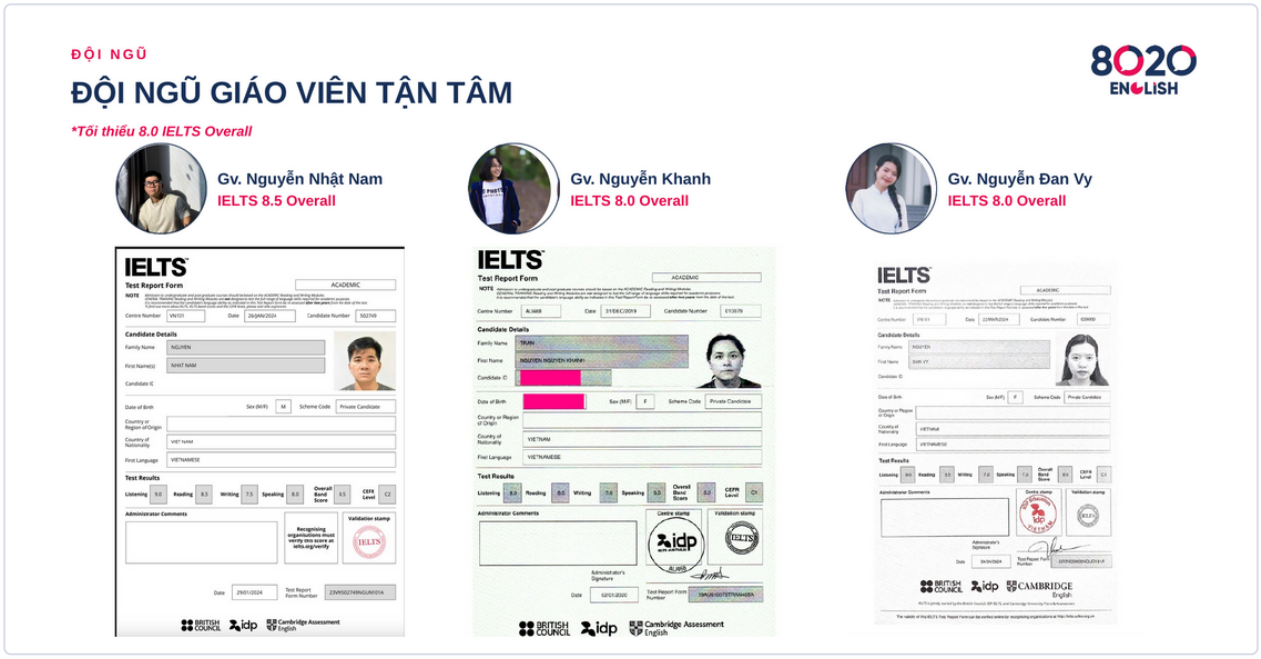
Kết quả học viên — điểm thi thật: IELTS 8.0–9.0 · SAT 1550 / 1570 / 1590 · AP 5/5 (Calculus BC, Microeconomics) · IB 90/100 (Economics) · Duolingo 110 · PTE 90 · TOEFL 120. **Bảng vàng SAT:** Khánh Đăng 1510 · Thảo Nguyên 1520 · Tâm Anh 1530.

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

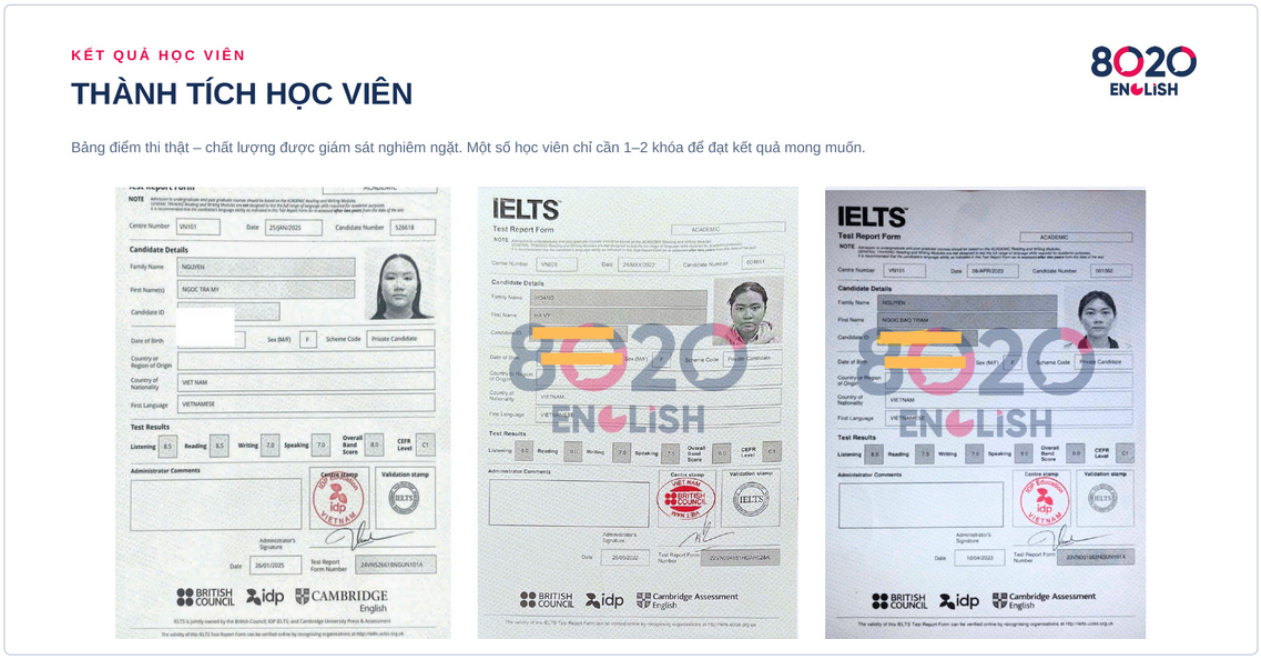
Cách dùng sách hiệu quả: mỗi Unit gồm (1) **Lý thuyết trọng tâm** tiếng Anh kèm **giải thích tiếng Việt**; (2) **Ví dụ mẫu** có lời giải; (3) **Hệ thống bài tập** kèm **lời giải chi tiết**. Hãy tự làm bài trước khi xem lời giải để đạt hiệu quả tối đa.

THÀNH TÍCH THỰC TẾ · 8020 ENGLISH

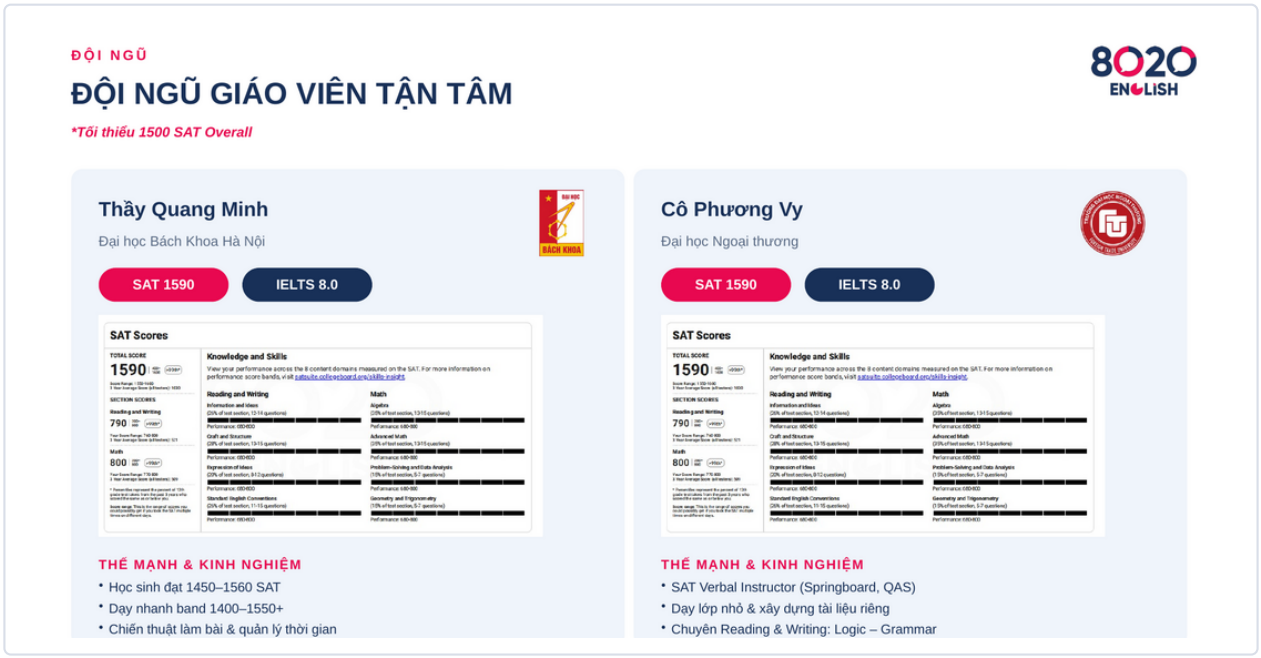
Điểm thi thật · Bằng & bảng điểm thật của giảng viên và học viên 8020 English — **Điểm thật · Thầy thật · Kết quả thật**



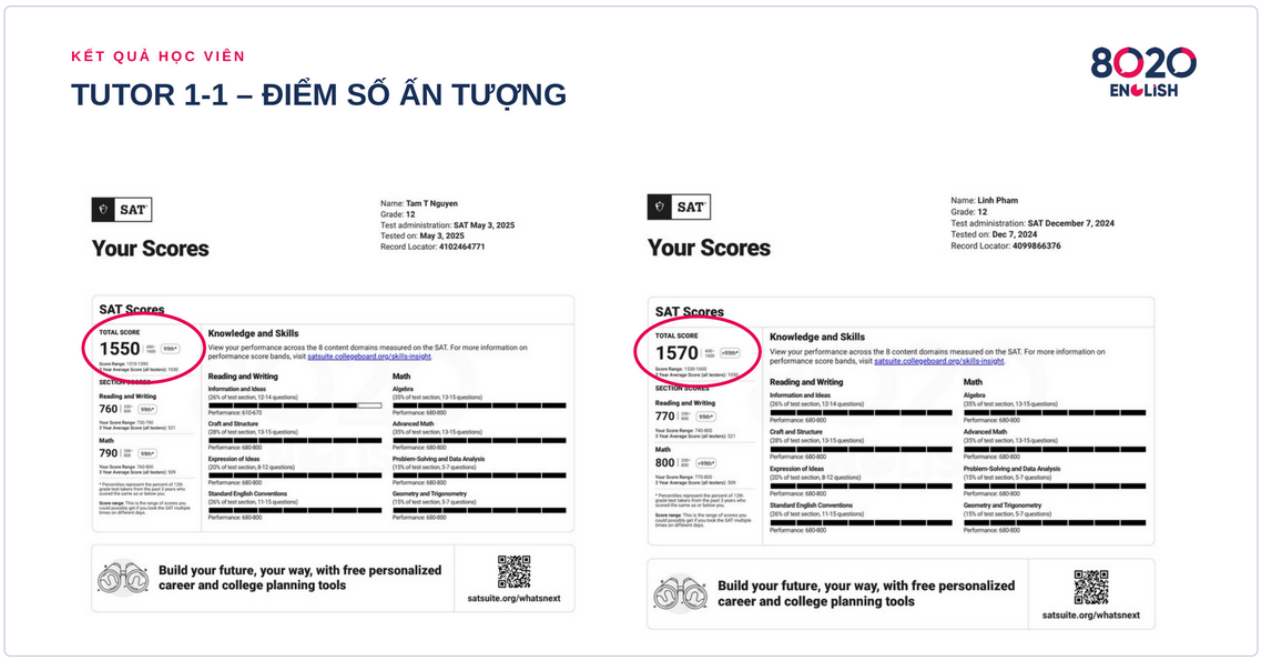
Giảng viên 8020 — IELTS 8.5 & 8.0 Overall (British Council · IDP · Cambridge)



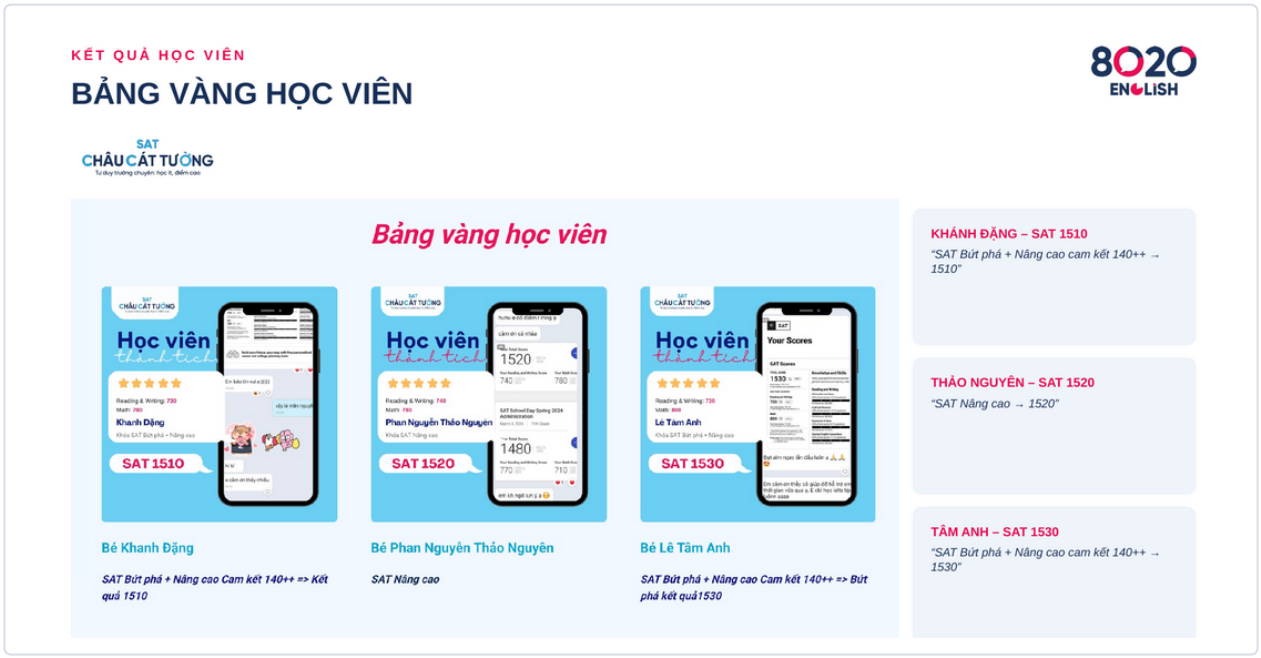
Học viên 8020 — IELTS 8.0 Overall (bảng điểm thật)



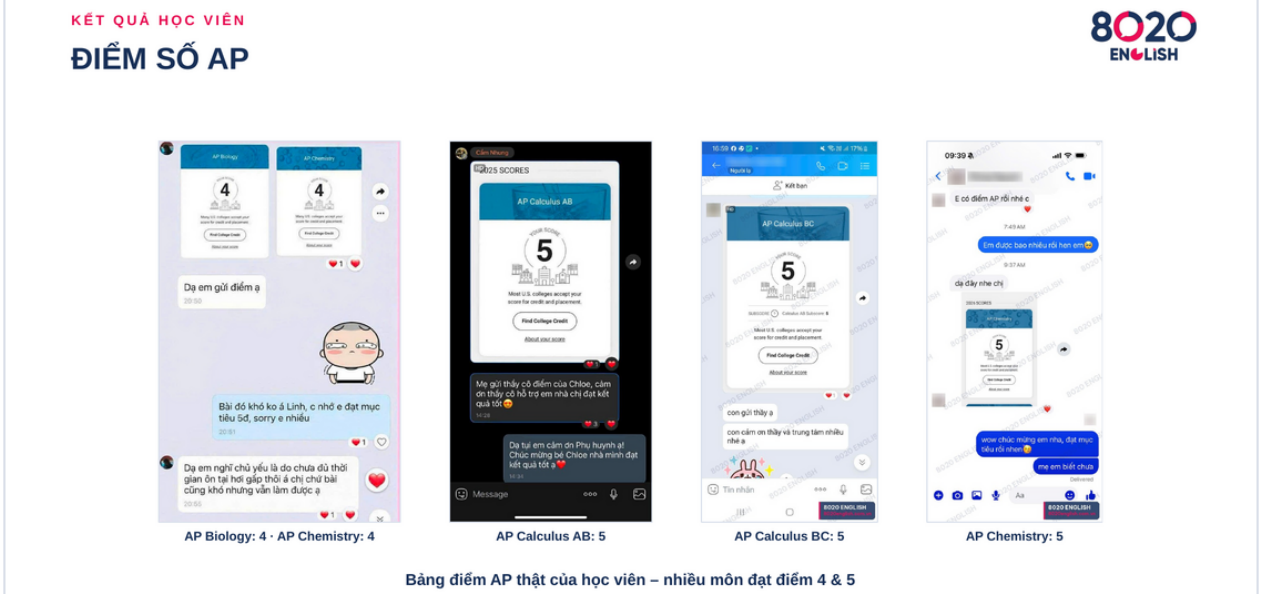
Giảng viên 8020 — SAT 1590 (ĐH Bách Khoa Hà Nội & ĐH Ngoại thương)



Học viên 8020 — SAT 1550 & 1570 (College Board)



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



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

Mục lục · Contents

Atomic Structure and Properties

Mục tiêu Unit: Sau khi học xong Unit này, học sinh có thể: (1) chuyển đổi thành thạo giữa khối lượng, số mol và số hạt (nguyên tử/phân tử/ion); (2) đọc phổ khối (mass spectrum) và tính khối lượng nguyên tử trung bình có trọng số; (3) xác định công thức thực nghiệm và công thức phân tử từ phần trăm khối lượng; (4) tính phần trăm thành phần của một chất trong hỗn hợp; (5) viết cấu hình electron đầy đủ, kể cả các trường hợp ngoại lệ Cr và Cu; (6) đọc phổ quang electron (PES) để suy ra cấu hình electron và xác định nguyên tố; (7) giải thích và vận dụng các xu hướng tuần hoàn thông qua điện tích hạt nhân hiệu dụng Z_{eff} và định luật Coulomb; (8) dự đoán công thức hợp chất ion từ điện tích, so sánh bán kính của các ion đẳng electron (isoelectronic) và xu hướng năng lượng mạng tinh thể.

1.1 Moles and molar mass

The **mole (mol)** is the SI base unit for amount of substance. One mole of any particle (atom, molecule, ion, formula unit) contains exactly **Avogadro's number**, $N_A = 6.022 \times 10^{23}$ particles per mole. The mole lets chemists convert between the microscopic world (individual atoms and molecules, far too small to weigh directly) and the macroscopic world (grams, measured on a balance).

Mole, molar mass, and the mole bridge

The **molar mass** M of a substance (units g/mol) is numerically equal to its average atomic mass (for an element) or the sum of average atomic masses of all atoms in a formula unit (for a compound), both read directly off the periodic table. Molar mass is the conversion factor between mass and moles:

$$n = \frac{m}{M} \qquad \text{(moles = mass} \div \text{molar mass).}$$

Moles convert to number of particles by multiplying by N_A:

$$N = n \times N_A.$$

Chaining these two relationships gives the **mole bridge**, the single most-used tool in quantitative chemistry: mass $\rightleftharpoons$ moles $\rightleftharpoons$ number of particles. Every stoichiometry calculation in this course passes through moles at some point.

VN **GIẢI THÍCH TIẾNG VIỆT**

Mol là "đơn vị đếm" của hoá học, giống như "chục", "tá" trong đời sống — chỉ khác là con số ở đây cực lớn: 6.022×10^{23} (số Avogadro). Khối lượng mol (M, đơn vị g/mol) chính là khối lượng nguyên tử/phân tử trung bình đọc trên bảng tuần hoàn, nhưng đổi đơn vị từ "amu cho 1 hạt" sang "gam cho 1 mol hạt". Sơ đồ ghi nhớ: khối lượng (g) $\xrightarrow{\div M}$ số mol $\xrightarrow{\times N_A}$ số hạt, và ngược lại theo chiều mũi tên đảo ngược.

Ví dụ mẫu · Mass → moles → particles → atoms

How many molecules of glucose, $C_6H_{12}O_6$, are in a 25.0 g sample, and how many total atoms of all elements does this represent?

Step 1 — molar mass:

$$M(C_6H_{12}O_6) = 6(12.01) + 12(1.008) + 6(16.00) = 72.06 + 12.10 + 96.00 = 180.16 \text{ g/mol}.$$

Step 2 — moles:

$$n = \frac{25.0 \text{ g}}{180.16 \text{ g/mol}} = 0.1388 \text{ mol}.$$

Step 3 — molecules:

$$N = 0.1388 \text{ mol} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 8.36 \times 10^{22} \text{ molecules}.$$

Step 4 — total atoms: each glucose molecule has $6 + 12 + 6 = 24$ atoms, so

$$8.36 \times 10^{22} \times 24 = 2.01 \times 10^{24} \text{ atoms (all elements combined)}.$$

Ví dụ mẫu · Particles → mass of one element in a compound

A sample contains exactly 3.011×10^{23} formula units of calcium chloride, $CaCl_2$. Find (a) the total mass of the sample and (b) the mass of chlorine alone.

(a) $n = \dfrac{3.011 \times 10^{23}}{6.022 \times 10^{23}} = 0.5000$ mol $CaCl_2$. $M(CaCl_2) = 40.08 + 2(35.45) = 110.98$ g/mol, so

$$m = 0.5000 \times 110.98 = 55.49 \text{ g}.$$

(b) Each formula unit contains 2 Cl atoms, so moles of Cl $= 2 \times 0.5000 = 1.000$ mol:

$$m(\text{Cl}) = 1.000 \times 35.45 = 35.45 \text{ g of chlorine}.$$

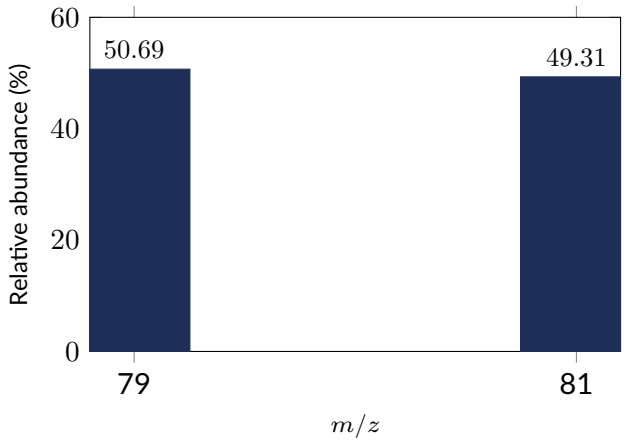
Mole bridge: mass (g) $\xrightarrow[\times M]{\div M}$ moles $\xrightarrow[\div N_A]{\times N_A}$ number of particles. To move from mass of one element in a compound to mass of another, always pass through the *mole ratio* given by the chemical formula's subscripts.

1.2 Mass spectrometry of elements

Most elements exist in nature as a mixture of **isotopes**: atoms with the same number of protons (Z, defining the element) but different numbers of neutrons, hence different mass numbers A. A **mass spectrometer** identifies and quantifies isotopes in four stages: (1) the sample is vaporized and **ionized**, usually to a $+1$ cation, by bombardment with high-energy electrons; (2) the ions are **accelerated** through an electric field; (3) the ion beam passes through a **magnetic field**, which deflects each ion by an amount inversely related to its mass-to-charge ratio (m/z) — lighter ions deflect more; (4) a **detector** records the position (hence m/z) and intensity (proportional to the relative number of ions, i.e. relative abundance) of each isotope. The output is a bar-graph spectrum: m/z on the horizontal axis, relative abundance on the vertical axis.

The **average atomic mass** listed on the periodic table is the abundance-weighted mean of all naturally occurring isotope masses:

$$\bar{m} = \sum_i (\text{fractional abundance}_i) \times (\text{isotope mass}_i).$$



Mass spectrum of elemental bromine: two isotopes, ^{79}Br (78.918 amu, 50.69%) and ^{81}Br (80.916 amu, 49.31%), giving the near-even double peak characteristic of bromine-containing compounds.

VN **GIẢI THÍCH TIẾNG VIỆT**

Máy phổ khối (mass spectrometer) tách các đồng vị dựa trên tỉ lệ khối lượng/điện tích (m/z): ion càng nhẹ càng bị từ trường bẻ cong nhiều, ion càng nặng càng bị bẻ cong ít. Chiều cao mỗi vạch trên phổ tỉ lệ với số lượng ion (% phong phú/abundance) của đồng vị đó. Khối lượng nguyên tử trung bình ghi trên bảng tuần hoàn là **trung bình có trọng số** — KHÔNG phải trung bình cộng đơn giản — của khối lượng các đồng vị, với trọng số là % phong phú của mỗi đồng vị.

Ví dụ mẫu · Weighted-average atomic mass of copper

Copper has two naturally occurring isotopes: ^{63}Cu (mass 62.930 amu, abundance 69.15%) and ^{65}Cu (mass 64.928 amu, abundance 30.85%). Calculate the average atomic mass.

$$\bar{m} = (0.6915)(62.930) + (0.3085)(64.928) = 43.52 + 20.03 = 63.55 \text{ amu}.$$

This matches the standard atomic weight of copper used throughout this book, 63.55 g/mol.

(!) Lỗi thường gặp: Average atomic mass is a **weighted** average, not $\dfrac{m_1 + m_2}{2}$. A common error is to average the two isotope masses directly, ignoring abundance. For copper, a naive simple average of 62.930 and 64.928 gives 63.93 amu — noticeably wrong, because it ignores that the lighter isotope (^{63}Cu) is more than twice as abundant and therefore pulls the true average *down* toward 63.55 amu.

Ví dụ mẫu · Solving for isotopic abundance

Boron has two isotopes, ^{10}B (mass 10.013 amu) and ^{11}B (mass 11.009 amu). The average atomic mass of boron is 10.81 amu. Find the percent abundance of each isotope.

Let x = fractional abundance of ^{10}B; then $(1 - x)$ = fractional abundance of ^{11}B:

$$10.013x + 11.009(1 - x) = 10.81.$$

$$10.013x + 11.009 - 11.009x = 10.81 \;\Rightarrow\; -0.996x = -0.199 \;\Rightarrow\; x = 0.1998.$$

So ^{10}B is $\approx\ 20.0\%$ abundant and ^{11}B is $\approx\ 80.0\%$ abundant — consistent with why boron's average atomic mass sits much closer to 11 than to 10.

1.3 Elemental composition of pure substances

For a pure compound with a fixed chemical formula, the **percent composition by mass** of each element is fixed and can be computed directly from the formula and atomic masses:

$$\%\,\text{element} = \frac{(\text{number of atoms of that element}) \times (\text{its atomic mass})}{\text{molar mass of the whole compound}} \times 100\%.$$

Running this process in reverse — starting from experimentally measured percent composition — gives the **empirical formula**, the simplest whole-number ratio of atoms in a compound. Because percent composition only fixes a *ratio*, several different molecular formulas can share the same empirical formula (e.g. CH_2O is the empirical formula of both formaldehyde, CH_2O, and glucose, $C_6H_{12}O_6$). The true **molecular formula** is recovered by comparing the empirical formula mass to the compound's actual molar mass (determined separately, e.g. by mass spectrometry or colligative properties):

$$n = \frac{M_{\text{molecular}}}{M_{\text{empirical}}}\ (\text{rounded to the nearest integer}), \qquad \text{molecular formula} = (\text{empirical formula}) \times n.$$

Ví dụ mẫu · Percent composition from a formula

Find the percent composition by mass of aluminum sulfate, $Al_2(SO_4)_3$.

$$M = 2(26.98) + 3\big[32.07 + 4(16.00)\big] = 53.96 + 3(96.07) = 53.96 + 288.21 = 342.17\ \text{g/mol}.$$

$$\%\text{Al} = \frac{53.96}{342.17}\times 100 = 15.77\%, \qquad \%\text{S} = \frac{96.21}{342.17}\times 100 = 28.12\%, \qquad \%\text{O} = \frac{192.00}{342.17}\times 100 = 56.11\%.$$

Check: $15.77 + 28.12 + 56.11 = 100.00\%$. ✓

Ví dụ mẫu · Empirical and molecular formula of vitamin C

Combustion analysis of ascorbic acid (vitamin C) gives 40.92% C, 4.58% H, and 54.50% O by mass; separately, its molar mass is found to be 176.12 g/mol. Determine the molecular formula.

Step 1 — assume 100 g of sample, convert to moles:

$$n(\text{C}) = \frac{40.92}{12.01} = 3.407\ \text{mol}, \quad n(\text{H}) = \frac{4.58}{1.008} = 4.544\ \text{mol}, \quad n(\text{O}) = \frac{54.50}{16.00} = 3.406\ \text{mol}.$$

Step 2 — divide every value by the smallest (3.406):

$$\text{C} : 1.000, \qquad \text{H} : 1.334\ (\approx \tfrac{4}{3}), \qquad \text{O} : 1.000.$$

Since $1.334 \approx \frac{4}{3}$ is not close to a whole number, multiply all three ratios by 3:

$$\text{C} : 3, \qquad \text{H} : 4.00, \qquad \text{O} : 3 \ \Rightarrow\ \text{empirical formula } C_3H_4O_3.$$

Step 3 — empirical formula mass:

$$M_{\text{empirical}} = 3(12.01) + 4(1.008) + 3(16.00) = 36.03 + 4.03 + 48.00 = 88.06\ \text{g/mol}.$$

Step 4 — multiplier and molecular formula:

$$n = \frac{176.12}{88.06} = 2.00 \ \Rightarrow\ \text{molecular formula} = C_3H_4O_3 \times 2 = C_6H_8O_6.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Công thức thực nghiệm (empirical formula) chỉ cho biết **tỉ lệ** nguyên tử đơn giản nhất, không cho biết số nguyên tử thật sự trong phân tử. Nhiều hợp chất khác nhau có thể có cùng công thức thực nghiệm (ví dụ CH_2O là công thức thực nghiệm của cả formaldehyde lẫn glucose). Muốn tìm công thức phân tử thật, ta cần biết thêm khối lượng mol thực tế của chất đó, rồi so sánh với khối lượng mol của công thức thực nghiệm để tìm hệ số nhân n.

1.4 Composition of mixtures

Unlike a pure compound, a **mixture** has no fixed formula, so its percent composition is not calculated from atomic masses alone — it must be measured experimentally, sample by sample. Typical laboratory strategies for finding percent composition of a mixture include: **gravimetric precipitation** (react one component selectively to form an insoluble solid, weigh the precipitate, and work back through mole ratios to the original component); **gas evolution** (react one component to release a measurable mass or volume of gas); and **mass-loss on heating or reaction** (compare mass before and after a component is selectively removed or converted). In every case, the calculation still passes through the mole bridge — the difference from Section 1.3 is that the "compound" being quantified is only part of an impure or multi-substance sample.

Ví dụ mẫu · Percent purity by gravimetric analysis

A 12.50 g sample of impure table salt is dissolved in water and treated with excess silver nitrate solution:

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

The silver chloride precipitate is filtered, dried, and weighed: $m(\mathrm{AgCl}) = 27.05$ g. Assuming the impurity does not contain chlorine and does not react, find the percent NaCl by mass in the original sample.

$$M(\mathrm{AgCl}) = 107.87 + 35.45 = 143.32 \text{ g/mol}, \qquad n(\mathrm{AgCl}) = \frac{27.05}{143.32} = 0.1887 \text{ mol}.$$

By the $1{:}1$ stoichiometry of $\mathrm{Cl^-}$, $n(\mathrm{NaCl}) = n(\mathrm{AgCl}) = 0.1887$ mol. With $M(\mathrm{NaCl}) = 22.99 + 35.45 = 58.44$ g/mol:

$$m(\mathrm{NaCl}) = 0.1887 \times 58.44 = 11.03 \text{ g} \;\Rightarrow\; \%\mathrm{NaCl} = \frac{11.03}{12.50} \times 100 = 88.2\%.$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Điểm khác biệt cốt lõi giữa % thành phần của hợp chất tinh khiết (Mục 1.3) và % thành phần trong hỗn hợp (Mục 1.4): với hợp chất tinh khiết, công thức hoá học cố định nên % khối lượng luôn tính được trực tiếp từ khối lượng mol; với hỗn hợp, tỉ lệ các chất có thể thay đổi theo từng mẫu, nên phải đo đạc thực nghiệm (thường qua phản ứng kết tủa, giải phóng khí, hoặc chênh lệch khối lượng trước/sau xử lý) rồi mới quy đổi qua số mol để tìm phần trăm.

1.5 Atomic structure and electron configuration

The location and energy of every electron in an atom is described by a set of four **quantum numbers**.

The four quantum numbers

Symbol	Name / meaning	Allowed values
n	Principal — shell size and energy	positive integers: $1, 2, 3, \ldots$
l	Angular momentum — subshell shape	0 to $n-1$; labeled s (l=0), p (l=1), d (l=2), f (l=3)
m_l	Magnetic — orbital orientation	$-l$ to $+l$ in integer steps (gives $2l+1$ orbitals per subshell)
m_s	Spin — electron spin direction	$+\frac{1}{2}$ or $-\frac{1}{2}$ only

Each orbital (n, l, m_l fixed) holds at most 2 electrons, of opposite spin. Subshell capacities follow from $2l+1$ orbitals $\times\, 2$ electrons: s holds 2, p holds 6, d holds 10, f holds 14.

Three filling rules

Aufbau principle: electrons occupy the lowest-energy available orbitals first, following the order $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, \ldots$ (note that $4s$ fills *before* $3d$).

Pauli exclusion principle: no two electrons in the same atom can share all four quantum numbers; equivalently, an orbital holds at most 2 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 orbital receives a second electron. This minimizes electron–electron repulsion and maximizes total spin.

GIẢI THÍCH TIẾNG VIỆT

VN

Bốn số lượng tử giống như "địa chỉ" đầy đủ của một electron: n = tầng (lớp), l = hình dạng phân lớp (s, p, d, f), m_l = orbital cụ thể trong phân lớp đó, m_s = chiều spin. Nguyên lý Pauli nói rằng không electron nào có "địa chỉ" hoàn toàn trùng nhau. Quy tắc Hund giải thích tại sao electron "giãn ra" chiếm các orbital trống trước khi ghép đôi — giống như hành khách chọn ghế trống trước khi ngồi chung ghế với người khác, giúp giảm lực đẩy giữa các electron.

Ví dụ mẫu · The chromium and copper exceptions

Predict the ground-state electron configurations of chromium (Cr, $Z = 24$) and copper (Cu, $Z = 29$), and explain why each deviates from the naive Aufbau prediction.

Naive Aufbau prediction for Cr: $[\text{Ar}]4s^2 3d^4$. **Actual ground state:**

$$\text{Cr}: \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1\,3d^5 \quad = [\text{Ar}]4s^1 3d^5.$$

Naive Aufbau prediction for Cu: $[\text{Ar}]4s^2 3d^9$. **Actual ground state:**

$$\text{Cu}: \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1\,3d^{10} \quad = [\text{Ar}]4s^1 3d^{10}.$$

In both cases one $4s$ electron shifts into the $3d$ subshell because a **half-filled** (d^5) or **completely filled** (d^{10}) subshell has extra stability: the symmetric, singly-occupied (or fully-paired-and-symmetric) arrangement minimizes electron–electron repulsion and maximizes exchange energy. The $4s$ and $3d$ subshells are close enough in energy that this small stabilization is enough to favor the exception.

Ví dụ mẫu · Electron configuration of a transition-metal ion

Write the ground-state electron configuration of Fe^{3+} (Fe, $Z = 26$).

Neutral iron: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^6 = [Ar]4s^2 3d^6$. When a transition metal ionizes, electrons are always removed from the **highest-n subshell first** — i.e. $4s$ electrons leave *before* $3d$ electrons, even though $4s$ filled first. Removing 3 electrons (two from $4s$, one from $3d$):

$$Fe^{3+}: \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5 = [Ar]3d^5.$$

Note the result is a stable, half-filled $3d^5$ configuration — one reason Fe^{3+} is a common, relatively stable oxidation state.

(!) Lỗi thường gặp: It is tempting to write ions of transition metals by simply removing electrons from the *last-filled* subshell in the Aufbau order (which would mean removing from $3d$ first, since it fills after $4s$). This is backwards. Once occupied, $4s$ electrons are actually higher in energy than $3d$ electrons in the ion (the relative ordering shifts once $3d$ starts filling), so ns **electrons are always removed before** $(n-1)d$ **electrons** when forming a transition-metal cation.

1.6 Photoelectron spectroscopy

Photoelectron spectroscopy (PES) probes electron structure experimentally. A sample is irradiated with photons of known, fixed high energy; each photon can eject one electron from the sample, provided the photon energy exceeds that electron's **binding energy (BE)** — the energy holding the electron to the atom. The ejected electron's kinetic energy (KE) is measured, and since photon energy $h\nu$ is known,

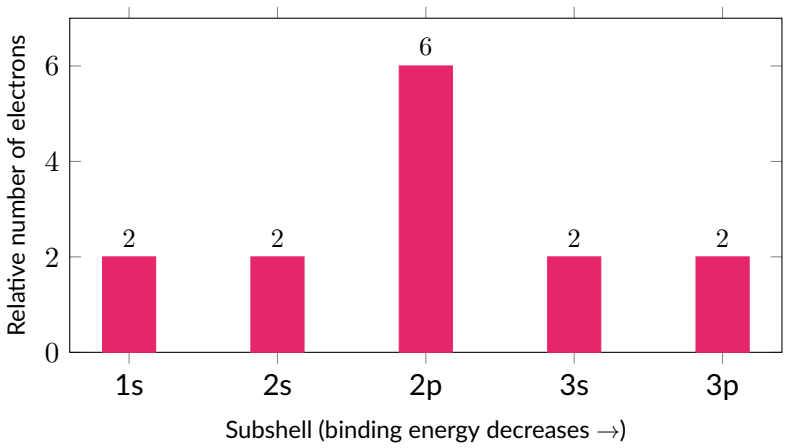
$$\text{BE} = h\nu - \text{KE}.$$

Every electron in a given subshell (e.g. all six $2p$ electrons in oxygen) has essentially the same binding energy, so the spectrometer output is a series of discrete peaks rather than a continuum.

Reading a PES spectrum

- **Number of peaks** = number of chemically distinct subshells occupied by electrons (each n, l combination gives one peak; e.g. $2p$ is one peak even though it holds up to 6 electrons across 3 orbitals).
- **Peak position (binding energy)** tracks distance/shielding from the nucleus: electrons closer to the nucleus and less shielded are held more tightly, so BE decreases as n increases and, within the same n, as l increases: $1s > 2s > 2p > 3s > 3p > \cdots$. For a fixed subshell, BE also increases with atomic number Z (more protons pull harder on every electron).
- **Peak height (relative intensity)** is directly proportional to the number of electrons occupying that subshell.

By reading off the number of peaks, their relative heights, and (if given numerically) their binding energies, an unknown element's full electron configuration — and therefore its identity — can be determined.



Photoelectron spectrum of silicon ($1s^2 2s^2 2p^6 3s^2 3p^2$). Approximate binding energies (MJ/mol): $1s \approx 178$, $2s \approx 15.9$, $2p \approx 10.3$, $3s \approx 1.46$, $3p \approx 0.786$. Five peaks with height ratio $2 : 2 : 6 : 2 : 2$ (total 14 electrons) identify silicon uniquely.

VN **GIẢI THÍCH TIẾNG VIỆT**

Đọc phổ PES theo ba bước: **(1)** đếm số đỉnh → số phân lớp electron khác nhau; **(2)** sắp xếp vị trí đỉnh theo năng lượng liên kết giảm dần ($1s > 2s > 2p > 3s > 3p > \ldots$) → xác định đỉnh nào ứng với phân lớp nào; **(3)** đọc chiều cao (tỉ lệ) mỗi đỉnh → số electron trong phân lớp đó. Ghép các phân lớp và số electron lại, ta có cấu hình electron đầy đủ, từ đó suy ra tổng số electron = số hiệu nguyên tử Z → xác định nguyên tố.

Ví dụ mẫu · Identifying an element from its PES spectrum

An unknown element's PES spectrum shows four peaks. From highest to lowest binding energy, the relative peak heights are $2 : 2 : 6 : 1$. Identify the element.

Four peaks ⇒ four distinct subshells occupied. In order of decreasing binding energy these must be $1s, 2s, 2p, 3s$. Assigning the given heights:

$$1s^2\ 2s^2\ 2p^6\ 3s^1.$$

Total electrons $= 2 + 2 + 6 + 1 = 13$, so $Z = 13$: the element is **aluminum** (Al), configuration $[\text{Ne}]3s^2$... *wait — recount*: $2 + 2 + 6 + 1 = 11$. Total electrons $= 11$, so $Z = 11$: the element is **sodium** (Na), configuration $1s^2 2s^2 2p^6 3s^1 = [\text{Ne}]3s^1$.

Ví dụ mẫu · Confirming identity using binding-energy magnitudes

A different unknown element shows three peaks at approximate binding energies 19.3, 1.36, and 0.80 MJ/mol (highest to lowest), with relative heights $2 : 2 : 1$. Identify the element and check the assignment against tabulated data.

Three peaks ⇒ subshells $1s, 2s, 2p$ in order of decreasing BE. Heights $2 : 2 : 1$ give configuration $1s^2\ 2s^2\ 2p^1$, total electrons $= 5$, so $Z = 5$: **boron** (B). The stated binding energies ($1s \approx 19.3$, $2s \approx 1.36$, $2p \approx 0.80$ MJ/mol) match tabulated experimental PES data for boron, confirming the assignment. Note that boron's $1s$ binding energy (19.3 MJ/mol) is much larger than hydrogen's (1.31 MJ/mol, single $1s$ peak) — binding energy for the same subshell type grows with nuclear charge Z.

1.7 Periodic trends and effective nuclear charge

Every periodic trend in this unit — atomic radius, ionic radius, ionization energy, electron affinity, electronegativity — is a consequence of two competing effects: the pull of the nucleus and the shielding of inner electrons, combined through **Coulomb's law**.

Effective nuclear charge and Coulomb's law

The full nuclear charge Z is not what a valence electron actually experiences, because inner (core) electrons partially block, or **shield**, the nuclear attraction. The simplified model used throughout this course is

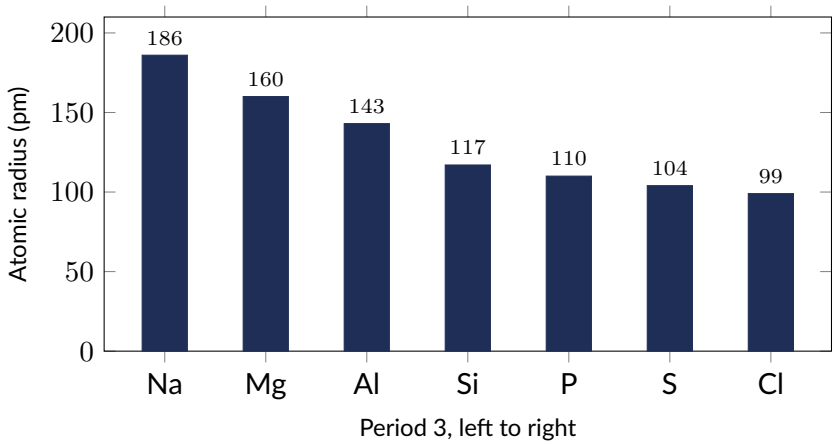
$$Z_{\text{eff}} \approx Z - S,$$

where S is taken as the number of **core (inner-shell) electrons** — i.e. all electrons in shells below the outermost occupied shell. Valence electrons in the same shell are assumed not to shield each other significantly in this simplified picture.
The force of attraction between the nucleus (effective charge $+Z_{\text{eff}}e$) and a valence electron (charge $-e$) separated by distance r follows **Coulomb's law**:

$$F = k\,\frac{Q_1 Q_2}{r^2}, \qquad k = 8.99 \times 10^9\ \text{N}\cdot\text{m}^2/\text{C}^2.$$

Attraction increases with the magnitude of the charges and decreases sharply (inverse-square) with distance. Every periodic trend below is a statement about how Z_{eff} and r change, and therefore how strongly the nucleus holds onto (or could pull in) an electron.

Property	Across a period (L→R)	Down a group	Driven by
Atomic radius	decreases	increases	Z_{eff} ↑ vs. new shell
Cation radius (vs. parent atom)	always smaller	—	lost shell / Z_{eff} ↑ per e^-
Anion radius (vs. parent atom)	always larger	—	extra repulsion / Z_{eff} ↓ per e^-
First ionization energy	increases (with exceptions)	decreases	Z_{eff} ↑, r ↓
Electron affinity (magnitude)	generally increases	generally decreases	Z_{eff} ↑, r ↓
Electronegativity	increases	decreases	Z_{eff} ↑, r ↓
Metallic character	decreases	increases	inverse of IE/EN



Atomic radius decreases steadily across Period 3 as Z_{eff} (core shielding fixed at 10 electrons; nuclear charge rising from 11 to 17) pulls the same $n = 3$ shell in tighter.

Ví dụ mẫu · Estimating Z_{eff} and applying Coulomb's law

(a) Estimate Z_{eff} for the outermost electron of sodium ($Z = 11$), magnesium ($Z = 12$), and aluminum ($Z = 13$), using the simplified core-shielding model.

All three have the same core: $1s^2 2s^2 2p^6$ (10 core electrons), so $S = 10$ for each:

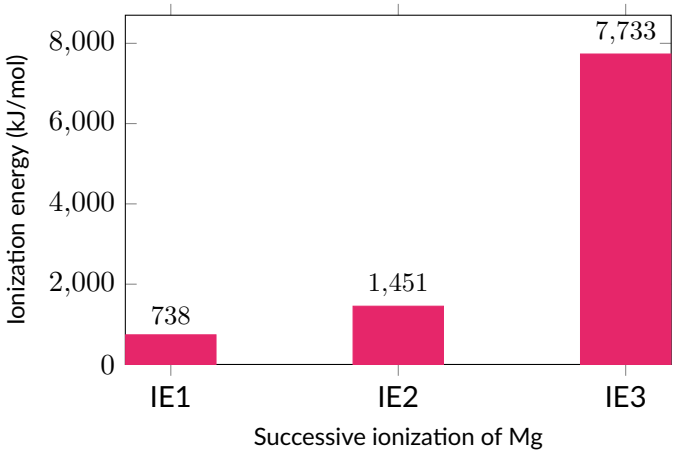
$$Z_{\text{eff}}(\text{Na}) = 11 - 10 = 1, \qquad Z_{\text{eff}}(\text{Mg}) = 12 - 10 = 2, \qquad Z_{\text{eff}}(\text{Al}) = 13 - 10 = 3.$$

This rising Z_{eff} (with the valence shell staying at $n = 3$ throughout) is why atomic radius drops steadily from Na to Al, and why the first ionization energy generally rises.

(b) A valence electron sits at $r_1 = 100$ pm from a nucleus of net attractive charge $+1e$. A second, larger atom holds its valence electron at $r_2 = 200$ pm with the same net charge $+1e$. Compare the Coulombic attractive forces.

$$\frac{F_1}{F_2} = \frac{kQ_1Q_2/r_1^2}{kQ_1Q_2/r_2^2} = \left(\frac{r_2}{r_1}\right)^2 = \left(\frac{200}{100}\right)^2 = 4.$$

Doubling the electron–nucleus distance cuts the attractive force to one-quarter. This inverse-square sensitivity to r is why smaller atoms/ions (smaller r, or larger Z_{eff}) bind their electrons far more tightly, giving higher ionization energies and larger electronegativities.



Successive ionization energies of magnesium ([Ne]$3s^2$). Removing the two $3s$ valence electrons costs 738 and 1451 kJ/mol; removing a third electron requires breaking into the filled, lower-n [Ne] core, causing a $> 5\times$ jump to 7733 kJ/mol.

Ví dụ mẫu · Interpreting successive ionization energies

An unknown main-group element Q has successive ionization energies (kJ/mol): $\text{IE}_1 = 738$, $\text{IE}_2 = 1451$, $\text{IE}_3 = 7733$, $\text{IE}_4 = 10540$. Based on this pattern, how many valence electrons does Q have, and to which group does it likely belong?

Ionization energy rises steadily but modestly from IE_1 to IE_2 (removing valence electrons from the same shell). Then there is a very large jump — more than $5\times$ — from IE_2 to IE_3. This jump marks the point where all valence electrons have been removed and the next electron must come from a full, lower-energy **core shell**, which is held far more tightly. Since the jump occurs

after the second ionization, Q has 2 **valence electrons** and belongs to **Group 2** (alkaline earth metals) — these values are in fact those of magnesium.

(!) Lỗi thường gặp: Ionization energy does not increase perfectly monotonically across a period — two exceptions recur constantly on exams. **(1) Group 2 vs. Group 13** (e.g. Mg vs. Al): Mg ($\text{IE}_1 = 738$ kJ/mol, filled $3s^2$) has a *higher* first ionization energy than Al ($\text{IE}_1 = 578$ kJ/mol, single $3p^1$), even though Al has one more proton. Removing Al's lone $3p$ electron is easier than breaking into Mg's stable, filled $3s^2$ subshell. **(2) Group 15 vs. Group 16** (e.g. N vs. O): N ($\text{IE}_1 = 1402$ kJ/mol, half-filled $2p^3$, one electron per orbital) has a *higher* first ionization energy than O ($\text{IE}_1 = 1314$ kJ/mol, $2p^4$, one orbital now doubly occupied). The extra electron–electron repulsion from pairing up in O's $2p$ subshell makes that electron easier to remove, despite O having greater nuclear charge.

VN **GIẢI THÍCH TIẾNG VIỆT**

Z_{eff} (điện tích hạt nhân hiệu dụng) là lực hút "thực sự" mà một electron hoá trị cảm nhận được sau khi trừ đi hiệu ứng chắn của các electron lớp trong. Theo mô hình đơn giản dùng trong chương trình: $Z_{\text{eff}} \approx Z - (\text{số electron lõi})$. Trong một chu kỳ, số electron lõi không đổi trong khi Z tăng dần $\rightarrow Z_{\text{eff}}$ tăng $\rightarrow$ bán kính giảm, năng lượng ion hoá và độ âm điện tăng. Xuống một nhóm, electron hoá trị nhảy sang lớp n lớn hơn hẳn (khoảng cách r tăng mạnh) $\rightarrow$ theo định luật Coulomb ($F \propto 1/r^2$), lực hút giảm nhanh hơn nhiều so với mức tăng của Z_{eff}, nên bán kính vẫn tăng và năng lượng ion hoá vẫn giảm khi đi xuống nhóm.

1.8 Valence electrons and ionic compounds

Main-group elements gain or lose valence electrons to reach the stable, low-energy electron configuration of the nearest noble gas. Metals on the left of the periodic table **lose** electrons to form cations; nonmetals on the right **gain** electrons to form anions. Species with identical electron configurations (though different Z) are called **isoelectronic**.

Isoelectronic radius ranking and ionic formula prediction

Within an isoelectronic series, every species has the *same* number of electrons and the *same* shielding pattern, so the only variable is nuclear charge Z: **more protons pull the same electron cloud in tighter**, giving a smaller radius. Radius therefore decreases monotonically as Z increases across an isoelectronic series.

To predict the empirical formula of an ionic compound from the charges of its ions, use the **criss-cross method**: the magnitude of each ion's charge becomes the subscript of the *other* ion, then the ratio is reduced to lowest whole numbers so that total positive charge = total negative charge.

Qualitatively, **lattice energy** (the energy released when gaseous ions come together into a solid ionic lattice) follows the same Coulombic logic as ionization energy:

$$|\,\text{Lattice energy}\,| \;\propto\; \frac{|Q_1|\,|Q_2|}{r_+ + r_-}.$$

Larger ionic charges and smaller ionic radii both increase the magnitude of lattice energy (more exothermic, stronger ionic solid).

Ion	Protons (Z)	Electrons	Radius trend
S^{2-}	16	18	largest
Cl^{-}	17	18	↓
K^{+}	19	18	↓
Ca^{2+}	20	18	smallest

All four ions are isoelectronic with argon (18 electrons); radius decreases as nuclear charge increases.

Ví dụ mẫu · Ranking isoelectronic ionic radii

Rank the following isoelectronic ions (all 18 electrons, argon configuration) from largest to smallest radius: Ca^{2+}, S^{2-}, Cl^{-}, K^{+}.

Same electron count and shielding for all four, so radius is governed purely by nuclear charge: S ($Z = 16$) < Cl ($Z = 17$) < K ($Z = 19$) < Ca ($Z = 20$). More protons ⇒ stronger pull ⇒ smaller radius, so ranking largest to smallest is

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

Ví dụ mẫu · Predicting ionic compound formulas

Predict the empirical formula formed between (a) aluminum (Al^{3+}) and oxide (O^{2-}), and (b) barium (Ba^{2+}) and nitride (N^{3-}).

(a) Criss-cross the charge magnitudes: Al gets subscript 2 (from O's charge), O gets subscript 3 (from Al's charge): Al_2O_3. Check: $2(+3) + 3(-2) = +6 - 6 = 0$. ✓

(b) Ba gets subscript 3, N gets subscript 2: Ba_3N_2. Check: $3(+2) + 2(-3) = +6 - 6 = 0$. ✓

Ví dụ mẫu · Lattice energy trend

Rank sodium fluoride (NaF) and magnesium oxide (MgO) by expected lattice energy magnitude, and check against literature values.

Na^{+} and F^{-} are singly charged ($|Q_1||Q_2| = 1$); Mg^{2+} and O^{2-} are doubly charged ($|Q_1||Q_2| = 4$), and Mg^{2+}/O^{2-} are also smaller ions than Na^{+}/F^{-} radius-for-radius in their respective rows. Both effects point the same direction:

$$|\text{Lattice energy}(\text{MgO})| \gg |\text{Lattice energy}(\text{NaF})|.$$

Literature values confirm the prediction: NaF ≈ 923 kJ/mol versus MgO ≈ 3795 kJ/mol — over four times larger, dominated by the Q_1Q_2 term in Coulomb's law.

GIẢI THÍCH TIẾNG VIỆT VN

Kim loại nhóm chính mất electron hoá trị để đạt cấu hình khí hiếm gần nhất (bền vững), phi kim nhận electron để làm điều tương tự — đây là động lực hình thành liên kết ion. Các ion "đẳng electron" (isoelectronic) có cùng số electron nhưng khác số proton; proton càng nhiều thì lực hút hạt nhân lên đám mây electron giống hệt nhau càng mạnh, khiến bán kính càng nhỏ. Phương pháp "bắt chéo" điện tích (criss-cross) giúp suy nhanh công thức hợp chất ion: lấy trị tuyệt đối điện tích ion này làm chỉ số dưới của ion kia, rồi rút gọn. Năng lượng mạng tinh thể tỉ lệ thuận với tích điện tích và tỉ lệ nghịch với tổng bán kính ion — điện tích càng lớn, bán kính càng nhỏ, tinh thể ion càng bền (năng lượng mạng càng âm).

1.9 End-of-unit practice problems

Bài tập luyện tập

How many moles of CO_2 are contained in an 88.0 g sample of dry ice?

(A) 1.00 mol
(B) 2.00 mol
(C) 3.88 mol
(D) 0.500 mol

Lời giải chi tiết

$M(CO_2) = 12.01 + 2(16.00) = 44.01$ g/mol. $n = \dfrac{88.0}{44.01} = 2.00$ mol. **(B)**.

Bài tập luyện tập

A 15.0 g sample of aluminum sulfide, Al_2S_3, is analyzed. Find (a) the number of moles of Al_2S_3, (b) the number of Al^{3+} ions present, and (c) the mass of sulfur contained in the sample.

Lời giải chi tiết

$M(Al_2S_3) = 2(26.98) + 3(32.07) = 53.96 + 96.21 = 150.17$ g/mol.
(a) $n = \dfrac{15.0}{150.17} = 0.0999$ mol.
(b) Each formula unit has 2 Al^{3+} ions: $N(Al^{3+}) = 0.0999 \times 2 \times 6.022 \times 10^{23} = 1.20 \times 10^{23}$ ions.
(c) Moles of S $= 0.0999 \times 3 = 0.2997$ mol; $m(S) = 0.2997 \times 32.07 = 9.61$ g.

Bài tập luyện tập

An ionic compound with formula XCl_2 has 0.250 mol weighing 27.75 g. Identify element X.

(A) Mg
(B) Ca
(C) Fe
(D) Zn

Lời giải chi tiết

$M = \dfrac{27.75}{0.250} = 111.0$ g/mol. $M(X) = 111.0 - 2(35.45) = 111.0 - 70.90 = 40.1$ g/mol, matching calcium (40.08). **(B)**.

Bài tập luyện tập

Naturally occurring silicon consists of three isotopes: ^{28}Si (27.977 amu, 92.23%), ^{29}Si (28.976 amu, 4.68%), and ^{30}Si (29.974 amu, 3.09%). Calculate the average atomic mass of silicon.

Lời giải chi tiết

$$\bar{m} = (0.9223)(27.977) + (0.0468)(28.976) + (0.0309)(29.974)$$
$$= 25.808 + 1.356 + 0.926 = 28.09 \text{ amu}.$$

This matches the periodic-table value for silicon.

Bài tập luyện tập

Gallium has two isotopes, ^{69}Ga (mass 68.926 amu) and ^{71}Ga (mass 70.925 amu). The average atomic mass of gallium is 69.72 amu. Find the percent abundance of each isotope.

Lời giải chi tiết

Let a = fractional abundance of ^{69}Ga:

$$68.926a + 70.925(1 - a) = 69.72.$$

$$68.926a + 70.925 - 70.925a = 69.72 \;\Rightarrow\; -1.999a = -1.205 \;\Rightarrow\; a = 0.603.$$

So ^{69}Ga is $\approx 60.3\%$ abundant and ^{71}Ga is $\approx 39.7\%$ abundant.

Bài tập luyện tập

A mass spectrometer is used to analyze a sample of pure neon gas. Sample A shows only two peaks, at $m/z = 20$ and $m/z = 22$. Sample B shows three peaks, at $m/z = 20$, 21, and 22. Given that naturally occurring neon has three isotopes (^{20}Ne, ^{21}Ne, ^{22}Ne), which sample's spectrum is consistent with a pure, natural sample of neon, and why?

(A) Sample A, because most neon atoms are ^{20}Ne or ^{22}Ne

(B) Sample B, because a natural sample contains all isotopes present in nature, each producing its own peak

(C) Both are equally valid readings of the same gas

(D) Neither, because neon is monoisotopic

Lời giải chi tiết

A mass spectrometer resolves *every* isotope present in the sample as a separate peak at its own m/z. Since natural neon truly contains three isotopes (^{20}Ne, ^{21}Ne, ^{22}Ne, with ^{21}Ne present only in trace abundance $\approx 0.27\%$), a correct spectrum of a natural sample must show three peaks, with the 21 peak very short. Sample A is missing the trace isotope. **(B)**.

Bài tập luyện tập

An unknown element X gives a mass spectrum with three peaks: $m/z = 24$ (23.985 amu, 78.99%), $m/z = 25$ (24.986 amu, 10.00%), $m/z = 26$ (25.983 amu, 11.01%). Calculate the average atomic mass and identify element X.

Lời giải chi tiết

$$\bar{m} = (0.7899)(23.985) + (0.1000)(24.986) + (0.1101)(25.983)$$

$$= 18.946 + 2.499 + 2.861 = 24.31 \text{ amu}.$$

This matches the standard atomic weight of magnesium (24.31 g/mol, more precisely 24.305), so element X is **magnesium** (Mg) — the three peaks correspond exactly to its natural isotopes ^{24}Mg, ^{25}Mg, and ^{26}Mg.

Bài tập luyện tập

A chemist needs exactly 2.50×10^{22} formula units of iron(III) oxide, Fe_2O_3, for a synthesis. (a) What mass in grams should be measured out? (b) How many oxygen atoms does this sample contain?

Lời giải chi tiết

$M(Fe_2O_3) = 2(55.85) + 3(16.00) = 111.70 + 48.00 = 159.70$ g/mol.

(a) $n = \dfrac{2.50 \times 10^{22}}{6.022 \times 10^{23}} = 0.04151$ mol, so

$$m = 0.04151 \times 159.70 = 6.63 \text{ g}.$$

(b) Each formula unit contains 3 oxygen atoms, so the number of oxygen atoms is found directly from the given particle count, without needing the molar mass:

$$N(O) = 3 \times (2.50 \times 10^{22}) = 7.50 \times 10^{22} \text{ atoms}.$$

Bài tập luyện tập

Lithium has two naturally occurring isotopes: ^{6}Li (mass 6.015 amu, abundance 7.59%) and ^{7}Li (mass 7.016 amu, abundance 92.41%). What is the average atomic mass of lithium?

(A) 6.02 amu

(B) 6.50 amu

(C) 6.94 amu

(D) 7.02 amu

Lời giải chi tiết

$$\bar{m} = (0.0759)(6.015) + (0.9241)(7.016) = 0.4565 + 6.4835 = 6.94 \text{ amu}.$$

This matches the standard atomic weight of lithium used throughout this book. **(C)**.

Bài tập luyện tập

Find the percent composition by mass of ammonium nitrate, NH_4NO_3 (a common fertilizer), and verify that the percentages sum to 100%.

Lời giải chi tiết

The formula contains 2 N atoms (one in NH_4^+, one in NO_3^-), 4 H atoms, and 3 O atoms:

$$M = 2(14.01) + 4(1.008) + 3(16.00) = 28.02 + 4.032 + 48.00 = 80.05 \text{ g/mol}.$$

$$\%N = \frac{28.02}{80.05} \times 100 = 35.00\%, \qquad \%H = \frac{4.032}{80.05} \times 100 = 5.04\%, \qquad \%O = \frac{48.00}{80.05} \times 100 = 59.96\%.$$

Check: $35.00 + 5.04 + 59.96 = 100.00\%$. ✓

Bài tập luyện tập

A phosphorus oxide is found by combustion analysis to be 43.64% P and 56.36% O by mass. What is its empirical formula?

(A) PO
(B) P_2O_3
(C) P_2O_5
(D) P_2O_7

Lời giải chi tiết

Assume 100 g of sample:

$$n(\text{P}) = \frac{43.64}{30.97} = 1.409 \text{ mol}, \qquad n(\text{O}) = \frac{56.36}{16.00} = 3.523 \text{ mol}.$$

Divide by the smaller value (1.409):

$$\text{P} : 1.000, \qquad \text{O} : 2.500 \ (\approx \tfrac{5}{2}).$$

Multiply both by 2 to clear the fraction: P : 2, O : 5, giving empirical formula P_2O_5.
(C).

Bài tập luyện tập

A gaseous hydrocarbon used in lighters is 82.66% C and 17.34% H by mass, with a molar mass of 58.12 g/mol. Determine its molecular formula.

Lời giải chi tiết

Assume 100 g of sample:

$$n(\text{C}) = \frac{82.66}{12.01} = 6.883 \text{ mol}, \qquad n(\text{H}) = \frac{17.34}{1.008} = 17.20 \text{ mol}.$$

Divide by the smaller value (6.883):

$$\text{C} : 1.000, \qquad \text{H} : 2.500 \ (\approx \tfrac{5}{2}).$$

Multiply by 2: C : 2, H : 5, empirical formula C_2H_5, with empirical formula mass

$$M_{\text{empirical}} = 2(12.01) + 5(1.008) = 24.02 + 5.04 = 29.06 \text{ g/mol}.$$

$$n = \frac{58.12}{29.06} = 2.00 \ \Rightarrow \ \text{molecular formula} = C_2H_5 \times 2 = C_4H_{10}.$$

(This is butane.)

Bài tập luyện tập

Copper(II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, is a common blue crystalline hydrate. What percent of its mass is water?

(A) 18.0%
(B) 28.9%
(C) 36.1%
(D) 45.2%

Lời giải chi tiết

$M(\text{CuSO}_4) = 63.55+32.07+4(16.00) = 159.62$ g/mol, $M(\text{H}_2\text{O}) = 2(1.008)+16.00 = 18.02$ g/mol.

$$M(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 159.62 + 5(18.02) = 159.62 + 90.10 = 249.72 \text{ g/mol}.$$

$$\%\text{H}_2\text{O} = \frac{90.10}{249.72} \times 100 = 36.1\%.$$

(C).

Bài tập luyện tập

A 5.00 g mixture of NaCl and NaBr is dissolved in water and treated with excess silver nitrate solution, precipitating both AgCl and AgBr. The combined, dried precipitate has a mass of 10.38 g. Find the percent NaCl by mass in the original mixture.

Lời giải chi tiết

Let x = mass of NaCl (g), so $(5.00 - x)$ = mass of NaBr. Each gram of NaCl ($M = 58.44$) yields $\frac{143.32}{58.44} = 2.452$ g of AgCl ($M = 143.32$); each gram of NaBr ($M = 102.89$) yields $\frac{187.77}{102.89} = 1.825$ g of AgBr ($M = 187.77$). The total precipitate mass gives:

$$2.452x + 1.825(5.00 - x) = 10.38.$$

$$2.452x + 9.125 - 1.825x = 10.38 \;\Rightarrow\; 0.627x = 1.255 \;\Rightarrow\; x = 2.00 \text{ g}.$$

$$\%\text{NaCl} = \frac{2.00}{5.00} \times 100 = 40.0\%.$$

Bài tập luyện tập

A 25.0 g sample of brass (an alloy containing only copper and zinc) is dissolved in excess hydrochloric acid. Only the zinc reacts, via $\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$; copper does not react with HCl. The reaction produces 0.185 mol of H_2 gas. What is the percent zinc by mass in the brass sample?

(A) 32.6%

(B) 48.4%

(C) 65.4%

(D) 74.1%

Lời giải chi tiết

By the $1{:}1$ stoichiometry of the reaction, $n(\text{Zn}) = n(\text{H}_2) = 0.185$ mol.

$$m(\text{Zn}) = 0.185 \times 65.38 = 12.10 \text{ g}.$$

$$\%\text{Zn} = \frac{12.10}{25.0} \times 100 = 48.4\%.$$

(B).

Bài tập luyện tập

A $10.00\,\text{g}$ sample of impure limestone is heated strongly until its mass stops changing. Assume the only mass loss comes from decomposition of the $CaCO_3$ component, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, and that the impurity does not decompose. The sample loses $3.52\,\text{g}$. Find the percent $CaCO_3$ by mass in the original impure sample.

Lời giải chi tiết

The mass lost is entirely CO_2 gas escaping:

$$n(CO_2) = \frac{3.52}{44.01} = 0.0800 \text{ mol}.$$

By the $1{:}1$ stoichiometry, $n(CaCO_3) = n(CO_2) = 0.0800$ mol. With $M(CaCO_3) = 40.08 + 12.01 + 3(16.00) = 100.09$ g/mol:

$$m(CaCO_3) = 0.0800 \times 100.09 = 8.01\ \text{g} \ \Rightarrow\ \%CaCO_3 = \frac{8.01}{10.00} \times 100 = 80.1\%.$$

Bài tập luyện tập

Write the full ground-state electron configuration of neutral chromium (Cr, $Z = 24$) and of the Cr^{3+} ion. Explain the order in which electrons are removed to form the ion.

Lời giải chi tiết

Chromium is one of the Aufbau exceptions: instead of $[Ar]4s^2 3d^4$, the extra stability of a half-filled $3d^5$ subshell favors

$$\text{Cr}: \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1\,3d^5 = [Ar]4s^1 3d^5.$$

To form Cr^{3+}, three electrons are removed. As with all transition metals, the highest-n subshell empties first: the single $4s^1$ electron is removed first, then two electrons from $3d^5$:

$$Cr^{3+}: \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3 = [Ar]3d^3.$$

Bài tập luyện tập

Which of the following is the correct ground-state electron configuration of the sulfide ion, S^{2-} (S, $Z = 16$)?

(A) $1s^2 2s^2 2p^6 3s^2 3p^4$

(B) $1s^2 2s^2 2p^6 3s^2 3p^6$

(C) $1s^2 2s^2 2p^6 3s^2 3p^2$

(D) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Lời giải chi tiết

Neutral sulfur (16 electrons) is $1s^2 2s^2 2p^6 3s^2 3p^4$. Forming S^{2-} adds 2 electrons to reach 18 electrons total, filling the $3p$ subshell completely:

$$S^{2-}: \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6.$$

This is isoelectronic with argon. **(B)**.

Bài tập luyện tập

How many unpaired electrons are present in the ground-state Fe^{2+} ion (Fe, $Z = 26$)?

(A) 0
(B) 2
(C) 4
(D) 6

Lời giải chi tiết

Neutral iron is $[Ar]4s^2 3d^6$. Forming Fe^{2+} removes both $4s$ electrons first (transition-metal cations always lose ns before $(n-1)d$):

$$Fe^{2+}: \quad [Ar]3d^6.$$

By Hund's rule, the 6 electrons fill the 5 degenerate $3d$ orbitals singly first (giving 5 singly occupied orbitals), and only the 6th electron pairs up in one of those orbitals, leaving 4 orbitals singly occupied and 1 orbital doubly occupied. So Fe^{2+} has 4 unpaired electrons. **(C)**.

Bài tập luyện tập

Which of the following correctly represents the ground-state electron configuration of copper (Cu, $Z = 29$)?

(A) $[Ar]4s^2 3d^9$
(B) $[Ar]4s^1 3d^{10}$
(C) $[Ar]4s^2 3d^{10} 4p^{-1}$
(D) $[Ar]3d^{11}$

Lời giải chi tiết

Choice (A) is the naive Aufbau prediction, but copper is an exception: a completely filled $3d^{10}$ subshell is extra stable, so one $4s$ electron shifts into $3d$, giving $[Ar]4s^1 3d^{10}$. Choice (C) is not physically meaningful (negative orbital occupancy), and choice (D) exceeds the 10-electron capacity of the $3d$ subshell. **(B)**.

Bài tập luyện tập

An unknown element's PES spectrum shows five peaks. From highest to lowest binding energy, the approximate binding energies (MJ/mol) and relative heights are: 189 (2), 17.6 (2), 12.6 (6), 2.15 (2), 1.06 (3). Identify the element.

Lời giải chi tiết

Five peaks in decreasing binding energy correspond to the subshells $1s, 2s, 2p, 3s, 3p$. Assigning the given heights:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3.$$

Total electrons $= 2+2+6+2+3 = 15$, so $Z = 15$: the element is **phosphorus** (P), configuration $[Ne]3s^2 3p^3$.

Bài tập luyện tập

In the PES spectrum of a ground-state oxygen atom, which subshell's peak appears at the highest binding energy?

(A) $1s$

(B) $2s$

(C) $2p$

(D) All three peaks appear at the same binding energy

Lời giải chi tiết

Binding energy decreases as n increases and, within the same shell, as l increases, so $1s > 2s > 2p$ always. The $1s$ electrons are closest to the nucleus and least shielded, so they are held most tightly. **(A)**.

Bài tập luyện tập

Compare the PES spectrum of a ground-state neutral sodium atom to that of a ground-state Na^+ ion. How many peaks does each show, and how do the binding energies of the remaining peaks compare?

Lời giải chi tiết

Neutral Na ($1s^2 2s^2 2p^6 3s^1$) shows **four** peaks ($1s, 2s, 2p, 3s$) with height ratio $2 : 2 : 6 : 1$. Removing the single $3s$ electron to form Na^+ (isoelectronic with neon, $1s^2 2s^2 2p^6$) eliminates the $3s$ peak entirely, leaving **three** peaks ($1s, 2s, 2p$) with height ratio $2 : 2 : 6$. Furthermore, the remaining three peaks in Na^+ appear at *higher* binding energy than the corresponding peaks in neutral Na: the nuclear charge is unchanged, but with one fewer electron the remaining electrons feel a greater effective nuclear charge per electron (less electron–electron repulsion diluting the pull), so every remaining electron is held more tightly — consistent with cations always being smaller and harder to ionize further than the parent atom.

Bài tập luyện tập

An unknown element's PES spectrum shows five peaks with relative heights, from highest to lowest binding energy, of $2 : 2 : 6 : 2 : 4$. Identify the element.

(A) Silicon

(B) Phosphorus

(C) Sulfur

(D) Chlorine

Lời giải chi tiết

Five peaks $\Rightarrow$ subshells $1s, 2s, 2p, 3s, 3p$. Heights give configuration $1s^2 2s^2 2p^6 3s^2 3p^4$, total electrons $= 2 + 2 + 6 + 2 + 4 = 16$, so $Z = 16$: **sulfur** (S), $[Ne]3s^2 3p^4$. **(C)**.

Bài tập luyện tập

Rank potassium (K), calcium (Ca), sodium (Na), and magnesium (Mg) in order of *decreasing* atomic radius.

(A) K > Ca > Na > Mg

(B) Ca > K > Mg > Na

(C) Na > Mg > K > Ca

(D) K > Na > Ca > Mg

Lời giải chi tiết

K and Ca are in Period 4; Na and Mg are in Period 3, one shell smaller. Within Period 4, K (Group 1) has a smaller Z_{eff} than Ca (Group 2) at the same shell, so K $>$ Ca; likewise within Period 3, Na $>$ Mg. Since the whole $n = 4$ shell sits farther from the nucleus than $n = 3$, both Period-4 elements are larger than both Period-3 elements. Using approximate empirical radii K ≈ 227 pm, Ca ≈ 197 pm, Na ≈ 186 pm, Mg ≈ 160 pm:

$$\text{K} > \text{Ca} > \text{Na} > \text{Mg}.$$

(A).

Bài tập luyện tập

An unknown main-group element Q has successive ionization energies (kJ/mol): $\text{IE}_1 = 577$, $\text{IE}_2 = 1817$, $\text{IE}_3 = 2745$, $\text{IE}_4 = 11577$. How many valence electrons does Q have, and to which group does it belong?

Lời giải chi tiết

IE rises modestly from IE_1 through IE_3 (all removed from the valence shell), then jumps by more than $4\times$ from IE_3 to IE_4 ($11577/2745 \approx 4.2$). This large jump marks the point where the valence electrons are exhausted and the next electron must be pulled from the full, lower-energy core shell. Since the jump occurs *after* the third ionization, Q has 3 valence electrons and belongs to **Group 13** — these are in fact the ionization energies of aluminum.

Bài tập luyện tập

A valence electron in ion A experiences an effective nuclear charge of $+2e$ at a distance of 150 pm from the nucleus. A valence electron in ion B experiences an effective nuclear charge of $+4e$ at a distance of 100 pm. What is the ratio F_B/F_A of the Coulombic attractive forces, and which ion would you expect to have the higher ionization energy?

(A) 1.5; ion A

(B) 2.25; ion A

(C) 4.5; ion B

(D) 9.0; ion B

Lời giải chi tiết

Since $F = kQ_1Q_2/r^2$ and the electron charge is the same $-e$ in both cases,

$$\frac{F_B}{F_A} = \frac{Z_{\text{eff},B}/r_B^2}{Z_{\text{eff},A}/r_A^2} = \frac{4/(100)^2}{2/(150)^2} = \frac{4 \times 150^2}{2 \times 100^2} = \frac{4 \times 22500}{2 \times 10000} = \frac{90000}{20000} = 4.5.$$

Ion B's electron is held $4.5\times$ more strongly, so ion B has the higher ionization energy. **(C)**.

Bài tập luyện tập

Explain why the first ionization energy of phosphorus ($\text{IE}_1 \approx 1012$ kJ/mol, $[\text{Ne}]3s^2 3p^3$) is *greater* than that of sulfur ($\text{IE}_1 \approx 1000$ kJ/mol, $[\text{Ne}]3s^2 3p^4$), even though sulfur has one more proton.

Lời giải chi tiết

Phosphorus has a half-filled $3p^3$ subshell, with one electron in each of the three $3p$ orbitals (Hund's rule, no pairing) — a symmetric, minimum-repulsion arrangement that is extra stable and therefore harder to ionize. Sulfur's fourth $3p$ electron must pair up in an already-occupied orbital, and the resulting extra electron–electron repulsion in that orbital makes the paired electron easier to remove than expected from nuclear charge alone. This repulsion effect outweighs the modest increase in Z_{eff} from the additional proton, so $\text{IE}_1(\text{P}) > \text{IE}_1(\text{S})$ — the same Group 15/16 pattern seen earlier with nitrogen and oxygen.

Bài tập luyện tập

Rank the following isoelectronic species (all 10 electrons, neon configuration) from largest to smallest radius: Na^+, O^{2-}, Mg^{2+}, N^{3-}, F^-.

Lời giải chi tiết

All five species have the same 10 electrons and the same shielding pattern, so radius depends only on nuclear charge Z: $\text{N}\,(Z=7) < \text{O}\,(Z=8) < \text{F}\,(Z=9) < \text{Na}\,(Z=11) < \text{Mg}\,(Z=12)$. More protons pull the same 10-electron cloud in tighter, so ranking largest to smallest radius is

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

Bài tập luyện tập

Predict the empirical formula formed between: (a) magnesium (Mg^{2+}) and nitride (N^{3-}); (b) potassium (K^+) and phosphide (P^{3-}); (c) chromium(III) (Cr^{3+}) and oxide (O^{2-}).

Lời giải chi tiết

(a) Criss-cross: Mg gets subscript 3, N gets subscript 2: Mg_3N_2. Check: $3(+2)+2(-3)=0$. ✓

(b) K gets subscript 3 (from P's charge), P gets subscript 1 (omitted): K_3P. Check: $3(+1)+1(-3)=0$. ✓

(c) Cr gets subscript 2, O gets subscript 3: Cr_2O_3. Check: $2(+3)+3(-2)=0$. ✓

Bài tập luyện tập

Rank NaCl, MgO, CaO, and KBr in order of *increasing* lattice energy magnitude.

(A) KBr < NaCl < CaO < MgO

(B) NaCl < KBr < MgO < CaO

(C) MgO < CaO < NaCl < KBr

(D) KBr < NaCl < MgO < CaO

Lời giải chi tiết

NaCl and KBr both have charge product $|Q_1Q_2|=1$; between them, K^+ and Br^- are both larger than Na^+ and Cl^-, giving a larger $r_+ + r_-$ and therefore a *smaller*-magnitude lattice energy, so KBr < NaCl. MgO and CaO both have charge product $|Q_1Q_2|=4$, four times larger than the $1{:}1$ salts, which dominates the Coulombic ratio and makes both far larger in magnitude than NaCl or KBr; between them, Mg^{2+} has a smaller radius than Ca^{2+}, giving a smaller $r_+ + r_-$ and therefore a *larger*-magnitude lattice energy, so CaO < MgO. Combining both comparisons:

$$\text{KBr} < \text{NaCl} < \text{CaO} < \text{MgO}.$$

This matches approximate literature values (kJ/mol): KBr ≈ 671, NaCl ≈ 787, CaO ≈ 3414, MgO ≈ 3795. **(A)**.

Bài tập luyện tập

Ion X^{2+} is isoelectronic with argon. (a) Identify element X. (b) Write the empirical formula of the ionic compound formed between X^{2+} and nitride, N^{3-}. (c) Would you expect the lattice energy magnitude of this compound to be greater or less than that of NaCl? Explain.

Lời giải chi tiết

(a) Argon has 18 electrons. X^{2+} has 18 electrons, so neutral X has $18 + 2 = 20$ electrons, meaning $Z = 20$: X is **calcium** (Ca).

(b) Criss-cross: Ca gets subscript 3, N gets subscript 2: Ca_3N_2. Check: $3(+2) + 2(-3) = 0$. ✓

(c) Greater. NaCl has charge product $|Q_1Q_2| = 1(1) = 1$, while Ca_3N_2's ions have charge product $|Q_1Q_2| = 2(3) = 6$. Even though Ca^{2+} and N^{3-} are somewhat larger than Na^+ and Cl^-, the six-fold larger charge product dominates the Coulombic ratio $|Q_1Q_2|/(r_+ + r_-)$, so Ca_3N_2 has a substantially larger lattice energy magnitude than NaCl.

Molecular and Ionic Compound Structure and Properties

Mục tiêu Unit: Sau khi học xong Unit này, học sinh có thể: (1) phân loại liên kết ion, cộng hoá trị, kim loại dựa trên hiệu độ âm điện ΔEN; (2) đọc và giải thích đường cong thế năng theo khoảng cách liên hạt nhân, liên hệ bậc liên kết với độ dài và năng lượng liên kết; (3) mô tả cấu trúc tinh thể ion, số phối trí, và dự đoán xu hướng năng lượng mạng tinh thể theo điện tích và bán kính ion; (4) giải thích mô hình biển electron của kim loại và tính chất dẫn điện, dẻo, dát mỏng; phân biệt hợp kim thay thế và hợp kim xen kẽ; (5) vẽ công thức Lewis đầy đủ, kể cả các trường hợp ngoại lệ quy tắc bát tử (mở rộng, thiếu, electron lẻ); (6) tính điện tích hình thức để chọn cấu trúc cộng hưởng tốt nhất và xác định bậc liên kết trung bình; (7) áp dụng thuyết VSEPR để xác định hình học electron, hình học phân tử, lai hoá orbital, và dự đoán độ phân cực phân tử từ hình học và mô-men lưỡng cực liên kết.

2.1 Types of chemical bonds

A **chemical bond** is the net attractive force that holds two or more atoms together in a stable arrangement lower in potential energy than the separated atoms. All chemical bonding arises from the same underlying electrostatics — attraction between nuclei and shared or transferred electrons — but three limiting models are useful for classifying observed behavior: **ionic**, **covalent**, and **metallic** bonding.

Three bonding models

- **Ionic bonding**: electrons are transferred (not shared) from a low-electronegativity atom (typically a metal) to a high-electronegativity atom (typically a nonmetal), producing a cation and an anion that attract each other electrostatically. The result is an extended three-dimensional lattice of alternating ions, not discrete molecules.
- **Covalent bonding**: electrons are shared between two atoms, typically both nonmetals, with the shared electron density concentrated in the region between the two nuclei. Covalent bonding produces discrete molecules (or, in network solids such as diamond and SiO_2, an extended covalent lattice).
- **Metallic bonding**: valence electrons are delocalized over an entire lattice of metal cations, forming a shared "sea" of mobile electrons that binds the lattice together (Section 2.4).

VN **GIẢI THÍCH TIẾNG VIỆT**

Ba mô hình liên kết — ion, cộng hoá trị, kim loại — thực chất đều là lực hút tĩnh điện giữa hạt nhân và electron, chỉ khác nhau ở việc electron được **chuyển hẳn** (ion: kim loại nhường electron cho phi kim), **dùng chung** giữa hai nguyên tử cụ thể (cộng hoá trị), hay **dùng chung cho cả mạng tinh thể** (kim loại: electron "bơi tự do" quanh các cation kim loại).

2.1.1 The electronegativity-difference continuum

Real bonds rarely fit a pure ionic or pure covalent extreme; instead, bond character forms a continuum governed by the **electronegativity difference**, $\Delta\text{EN} = |\text{EN}_A - \text{EN}_B|$, between the two bonded atoms (Pauling scale). A large ΔEN means one atom pulls the shared electron density strongly toward itself, approaching complete electron transfer (ionic); a small or zero ΔEN means the electron density is shared roughly evenly (covalent).

Approx. ΔEN	Bond classification	Example
0	Nonpolar covalent (pure covalent)	Cl $-$ Cl ($\Delta\text{EN} = 0$)
0 to ≈ 0.4	Nonpolar covalent (essentially)	C $-$ H ($\Delta\text{EN} \approx 0.35$)
≈ 0.4 to ≈ 1.7	Polar covalent	H $-$ Cl ($\Delta\text{EN} \approx 0.96$)
$\gtrsim 1.7$	Ionic	Na $-$ Cl ($\Delta\text{EN} \approx 2.23$)

Classifying bond type from electronegativity difference

Using Pauling electronegativities (EN: H $= 2.20$, C $= 2.55$, N $= 3.04$, O $= 3.44$, F $= 3.98$, Na $= 0.93$, Cl $= 3.16$, Ca $= 1.00$), classify the bonds in (a) CaO, (b) N_2, (c) HF, (d) CO.

(a) CaO: $\Delta\text{EN} = |3.44 - 1.00| = 2.44$ — large, **ionic**.
(b) N_2: $\Delta\text{EN} = 0$ (identical atoms) — **nonpolar covalent**.
(c) HF: $\Delta\text{EN} = |3.98 - 2.20| = 1.78$ — right at the ionic/polar-covalent border; HF is conventionally treated as a **highly polar covalent** molecule (it forms discrete molecules, not an ionic lattice, and is a molecular gas/liquid, not a high-melting solid).
(d) CO: $\Delta\text{EN} = |3.44 - 2.55| = 0.89$ — **polar covalent**.

VN **GIẢI THÍCH TIẾNG VIỆT**

ΔEN chỉ là **ước lượng xu hướng**, không phải ranh giới tuyệt đối. Quy tắc thực dụng: ΔEN nhỏ (dưới ≈ 0.4) $\rightarrow$ cộng hoá trị không phân cực; ΔEN trung bình (0.4–1.7) $\rightarrow$ cộng hoá trị phân cực (electron lệch về nguyên tử âm điện hơn nhưng vẫn dùng chung); ΔEN lớn (trên ≈ 1.7) $\rightarrow$ ion (electron coi như chuyển hẳn). Trường hợp biên như HF cần xét thêm tính chất vật lý thực tế (nhiệt độ sôi, có tạo mạng tinh thể ion hay không) chứ không chỉ dựa vào con số ΔEN.

2.1.2 Polar vs. nonpolar covalent bonds

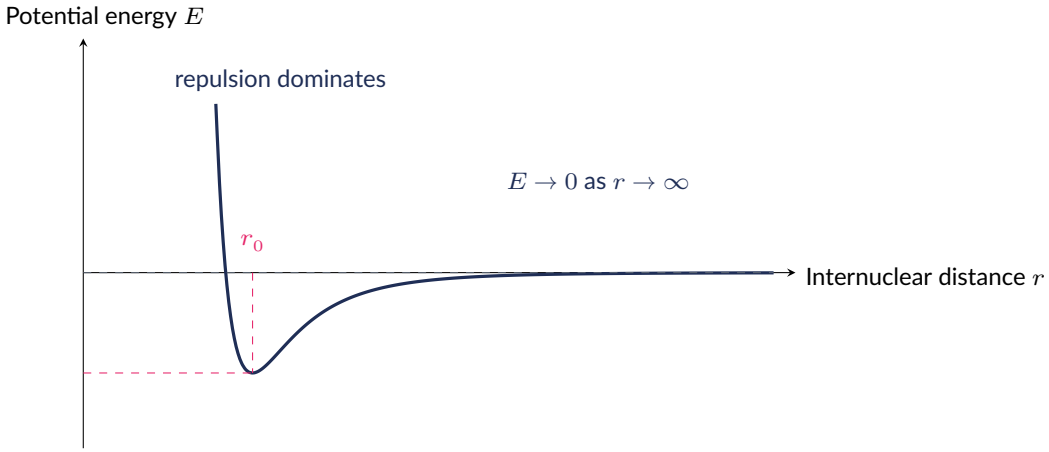
Within a single covalent bond, unequal sharing of electron density creates a **bond dipole**: the more electronegative atom carries a partial negative charge δ^-, and the less electronegative atom carries a partial positive charge δ^+. A bond is **nonpolar covalent** when $\Delta\text{EN} \approx 0$ (identical or near-identical atoms, e.g. H $-$ H, Cl $-$ Cl, C $-$ C) and **polar covalent** when ΔEN is moderate and nonzero. The direction of a bond dipole is conventionally drawn as an arrow pointing from δ^+ toward δ^-, crossed at the tail. Note that a molecule with polar *bonds* is not necessarily a polar *molecule* overall — molecular polarity also depends on geometry (Section 2.7).

(!) Lỗi thường gặp: Students often equate "polar bond" with "polar molecule." A molecule can contain highly polar bonds yet be nonpolar overall if the bond dipoles are arranged symmetrically and cancel by vector addition (e.g. CO_2, CCl_4, BF_3). Bond polarity is a property of one bond; molecular polarity requires summing *all* bond dipole vectors according to the molecular geometry.

2.2 Intramolecular force and potential energy

2.2.1 The bond-formation potential energy curve

When two isolated atoms are infinitely far apart, they exert no force on each other and the system's potential energy is defined as zero. As the atoms approach, two competing effects appear: (1) attraction between each nucleus and the other atom's electrons (and, in a covalent bond, the buildup of shared electron density between the nuclei) lowers the potential energy; (2) at very short range, nucleus–nucleus repulsion and electron–electron repulsion sharply raise the potential energy. The balance of these two effects produces a potential-energy curve with a single minimum.



Potential energy vs. internuclear distance for bond formation. The curve minimum defines the **bond length** r_0 (equilibrium internuclear distance) and the **well depth** D_e defines the **bond energy** (energy required to separate the bonded atoms back to $r \to \infty$).

Reading the curve

- At large r (far right), $E \to 0$: no interaction, atoms behave as if independent.
- As r decreases, E drops (attraction dominates) until it reaches a **minimum** — this is the most stable arrangement, the point of maximum net attraction before repulsion takes over.
- The internuclear distance at the minimum is the **bond length** (r_0).
- The depth of the well, measured from $E = 0$ down to the minimum, is the **bond energy** (also called bond dissociation energy) — the energy that must be *added* to break the bond and separate the atoms to $r = \infty$.
- At r smaller than r_0 (left of the minimum), E rises steeply: nuclear and electron-cloud repulsion dominate at very short range, so the atoms strongly resist further approach.

GIẢI THÍCH TIẾNG VIỆT VN

Đường cong thế năng theo khoảng cách liên hạt nhân mô tả quá trình hai nguyên tử tiến lại gần nhau: khi còn xa, thế năng gần 0 (không tương tác); khi tiến gần, lực hút chiếm ưu thế, thế năng giảm dần tới điểm cực tiểu — đó chính là **độ dài liên kết** r_0 (khoảng cách bền nhất); độ sâu của "hố thế năng" đo từ 0 xuống đáy chính là **năng lượng liên kết** (năng lượng cần để phá vỡ liên kết). Nếu ép hai nguyên tử lại gần hơn r_0, lực đẩy giữa hai hạt nhân và giữa các đám mây electron sẽ áp đảo, khiến thế năng tăng vọt.

2.2.2 Bond order, bond length, and bond energy

Bond order is the number of shared electron pairs between two bonded atoms: 1 for a single bond, 2 for a double bond, 3 for a triple bond (and non-integer values are possible in resonance systems,

Section 2.6). Increasing bond order packs more electron density between the same two nuclei, pulling them into closer, more strongly held contact.

Higher bond order ⇒ shorter bond length ⇒ higher bond energy (stronger bond). This trend holds when comparing bonds between the *same pair of elements* (e.g. C–C vs. C=C vs. C≡C), not necessarily across different element pairs.

Bond	Bond order	Bond length (pm)	Bond energy (kJ/mol)
C – C	1	154	347
C = C	2	134	614
C ≡ C	3	120	839
C – O	1	143	358
C = O	2	123	799
N – N	1	145	163
N = N	2	125	418
N ≡ N	3	110	945

Ranking bond length and energy from bond order

Without consulting a data table, rank the N – O bonds in NO^+ (bond order 3), NO (bond order 2.5), and NO_2^- (bond order 1.5, averaged over two resonance structures) from shortest to longest and from strongest to weakest.

Higher bond order means more shared electron density holding the nuclei together, hence a shorter, stronger bond. Ranking bond order: NO^+ (3) > NO (2.5) > NO_2^- (1.5).
Shortest to longest bond: $NO^+ < NO < NO_2^-$.
Strongest to weakest bond: $NO^+ > NO > NO_2^-$ (same order, since shorter bonds with higher bond order are also stronger).

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Bậc liên kết càng cao (đơn → đôi → ba) nghĩa là càng nhiều cặp electron dùng chung kéo hai hạt nhân lại gần nhau hơn và giữ chặt hơn. Vì vậy: **bậc liên kết tăng ⇒ độ dài liên kết giảm ⇒ năng lượng liên kết tăng**. Quy tắc này áp dụng khi so sánh cùng một cặp nguyên tố (ví dụ C–C, C=C, C≡C), không nhất thiết đúng khi so sánh các cặp nguyên tố khác nhau.

2.3 Structure of ionic solids

An ionic compound does not exist as discrete molecules; instead, cations and anions pack together in a repeating three-dimensional **crystal lattice** that maximizes electrostatic attraction between oppositely charged ions while minimizing repulsion between like-charged ions. Each ion is surrounded by a fixed number of oppositely charged nearest neighbors, called its **coordination number**, which depends on the relative sizes of the cation and anion.

Schematic 2-D slice of an ionic lattice (e.g. NaCl-type): cations and anions alternate on a regular grid so that every ion's nearest neighbors carry the opposite charge, maximizing net Coulombic attraction throughout the crystal.

Coordination number

The **coordination number** of an ion is the number of oppositely charged nearest-neighbor ions immediately surrounding it in the lattice. It is set primarily by the **radius ratio** of cation to anion: when the cation and anion are similar in size, more anions can pack around each cation before they touch each other, giving a higher coordination number.

- In the NaCl-type (rock-salt) lattice, each Na^+ is surrounded by 6 Cl^- ions and each Cl^- by 6 Na^+ ions — coordination number $6{:}6$ (octahedral arrangement).
- In the CsCl-type lattice, the larger Cs^+ cation permits 8 nearest-neighbor Cl^- ions around it (and vice versa) — coordination number $8{:}8$ (cubic arrangement), because the larger cation-to-anion radius ratio in CsCl allows more anions to fit around each cation without the anions crowding each other.

The three-dimensional lattice (of which the 2-D grid above is one slice) repeats this local coordination environment throughout the entire crystal, which is why ionic solids are best described by a lattice *formula unit ratio* rather than a discrete molecule.

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Số phối trí (coordination number) là số ion trái dấu bao quanh gần nhất một ion trong mạng tinh thể, phụ thuộc chủ yếu vào **tỉ lệ bán kính** cation/anion. Cation và anion kích thước gần bằng nhau cho phép nhiều anion xếp quanh cation hơn trước khi các anion chạm nhau. Mạng NaCl có số phối trí $6{:}6$ (mỗi ion có 6 ion trái dấu bao quanh); mạng CsCl, do Cs^+ lớn hơn nhiều, có số phối trí $8{:}8$.

2.3.1 Lattice energy

Lattice energy ($\Delta H_{\text{lattice}}$, or U) is the energy released when gaseous cations and anions come together to form one mole of a solid ionic lattice (by convention, often reported as the energy required to do the reverse — separate the solid into gaseous ions — making it a large positive number; either sign convention describes the same underlying stability). Lattice energy is well modeled by **Coulomb's law**, since the dominant interaction is simple electrostatic attraction between point charges:

$$E \propto \frac{Q_1 Q_2}{r}$$

where Q_1, Q_2 are the magnitudes of the ionic charges and r is the distance between ion centers (sum of ionic radii).

Lattice energy trends

- **Charge dominates**: lattice energy increases sharply as ionic charge magnitude increases, because Coulomb's law depends on the *product* $Q_1 Q_2$. Doubling either ion's charge roughly doubles the lattice energy; a $2+/2-$ pair (e.g. MgO) has vastly higher lattice energy than a $1+/1-$ pair (e.g. NaCl) even at similar ionic radii.
- **Radius matters inversely**: lattice energy increases as the sum of ionic radii r decreases (ions pack closer, so the $1/r$ term grows). Smaller ions of the same charge give higher lattice energy.
- Charge effects are typically far larger in magnitude than radius effects, so charge is the dominant factor when ranking lattice energies of compounds with different charge combinations.

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Năng lượng mạng tinh thể tuân theo định luật Coulomb: $E \propto \frac{Q_1 Q_2}{r}$. Hai quy tắc cần nhớ: (1) **điện tích ion càng lớn** thì năng lượng mạng càng cao — vì đây là tích $Q_1 \times Q_2$, ảnh hưởng rất mạnh (so sánh MgO ($2+/2-$) với NaCl ($1+/1-$) thấy ngay chênh lệch lớn); (2) **bán kính ion càng nhỏ** (ion áp sát nhau hơn) thì năng lượng mạng càng cao. Khi so sánh nhiều hợp chất, ưu tiên xét điện tích trước vì ảnh hưởng của điện tích thường lớn hơn nhiều so với bán kính.

Ranking lattice energies

Rank NaF, MgO, NaCl, and CaO in order of *increasing* lattice energy.

Step 1 — identify charges. NaF and NaCl are $1+/1-$ pairs; MgO and CaO are $2+/2-$ pairs. Since $Q_1 Q_2$ dominates, both $2+/2-$ compounds will have substantially higher lattice energy than either $1+/1-$ compound.
Step 2 — rank within each charge group by radius. Between NaF and NaCl: F^- (radius ≈ 133 pm) is smaller than Cl^- (radius ≈ 181 pm), so r is smaller in NaF, giving NaF the higher lattice energy of the two. Between MgO and CaO: Mg^{2+} (radius ≈ 72 pm) is smaller than Ca^{2+} (radius ≈ 100 pm), so MgO has the smaller r and higher lattice energy.
Step 3 — combine. Increasing lattice energy: NaCl $<$ NaF $<$ CaO $<$ MgO.

2.3.2 Melting point trends in ionic solids

Because ionic bonding is strong and non-directional throughout the lattice, ionic solids generally have **high melting points**, and melting point trends parallel lattice-energy trends: compounds with higher lattice energy require more thermal energy to disrupt the lattice and require a higher temperature to melt. MgO (lattice energy very high due to $2+/2-$ charges and small ionic radii) melts at 2852°C, whereas NaCl ($1+/1-$) melts at only 801°C.

Ranking melting points

Based on lattice energy reasoning, which compound should have the higher melting point: KBr or Al_2O_3?

(A) KBr, because K^+ is a larger cation

(B) Al_2O_3, because it involves $3+/2-$ charges, giving a much larger $Q_1 Q_2$ product than the $1+/1-$ pair in KBr

(C) They are equal, since both are ionic solids

(D) KBr, because Br is a larger anion so the lattice is denser

Lời giải chi tiết

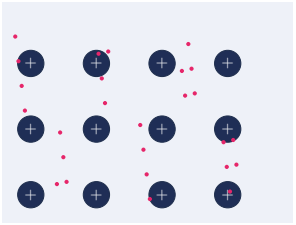
(B). KBr is a $1+/1-$ ionic compound; Al_2O_3 contains Al^{3+} and O^{2-} ions, so $Q_1 Q_2 = 3 \times 2 = 6$ compared to $Q_1 Q_2 = 1 \times 1 = 1$ for KBr. Since lattice energy $\propto Q_1 Q_2 / r$ and the charge term dominates over the modest radius differences here, Al_2O_3 has a far higher lattice energy and correspondingly a much higher melting point (Al_2O_3 melts near 2072°C; KBr melts near 734°C).

2.4 Structure of metals and alloys

2.4.1 The electron-sea model

In a metallic solid, each metal atom's valence electrons are not localized to a single bond or a single atom; instead they are **delocalized** over the entire lattice, forming a mobile "sea" of electrons that flows freely among a fixed lattice of positively charged metal cations (metal nuclei plus core

electrons). The metallic bond is the electrostatic attraction between the stationary cations and this shared, mobile electron sea.



Electron-sea model: fixed metal cations (navy, labeled +) occupy lattice sites; delocalized valence electrons (pink dots) move freely throughout the entire structure, binding the lattice non-directionally.

Metallic properties explained by the electron sea

- **Electrical conductivity**: the delocalized electrons are free to drift in response to an applied electric field, carrying current with little resistance — this works in the solid *and* molten state, since the mobile electrons do not depend on a rigid crystal shape.
- **Thermal conductivity**: the same mobile electrons rapidly transport kinetic energy (heat) throughout the lattice by colliding and transferring energy.
- **Malleability and ductility**: because the electron sea is non-directional (unlike a covalent or ionic bond tied to a specific pair/arrangement of ions), layers of metal cations can slide past one another under stress without breaking any specific, oriented bond — the mobile sea simply re-forms around the cations in their new positions. This is why metals can be hammered into sheets (malleable) or drawn into wires (ductile) rather than shattering, unlike ionic solids (see pitfall below).
- **Metallic luster**: the mobile electrons readily absorb and re-emit photons across a broad range of visible wavelengths, giving metals their characteristic shine.

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Mô hình "biển electron" hình dung kim loại là mạng các cation (ion dương) cố định, "ngâm" trong một "biển" electron hoá trị di chuyển tự do khắp toàn bộ khối kim loại. Vì electron không dính cố định vào một liên kết cụ thể, các lớp cation có thể trượt lên nhau mà biển electron vẫn bao quanh và giữ chúng lại — đây là lý do kim loại **dẻo** (kéo thành dây) và **dát mỏng** (dập thành lá) được, khác hẳn tinh thể ion sẽ vỡ vụn khi bị lệch lớp (vì lớp ion cùng dấu áp sát nhau sẽ đẩy nhau mạnh).

(!) Lỗi thường gặp: Do not confuse the malleability of metals with the brittleness of ionic solids. In an ionic lattice, shifting one layer relative to another brings like-charged ions into direct contact, causing strong repulsion that shatters the crystal. In a metal, the nondirectional electron sea re-accommodates any new cation arrangement, so metals deform smoothly instead of fracturing.

2.4.2 Alloys: substitutional and interstitial

An **alloy** is a mixture (solid solution) of a metal with one or more other elements, engineered to modify the properties of the pure metal.

Two alloy types

- **Substitutional alloy**: solute atoms of similar atomic radius to the host metal *replace* host atoms at regular lattice sites. Example: **brass** (Cu with Zn substituted into the copper lattice; Cu radius ≈ 128 pm, Zn radius ≈ 134 pm — comparable sizes allow substitution).
- **Interstitial alloy**: small solute atoms fit into the *gaps (interstices)* between the larger host metal atoms, without replacing them. Example: **steel** (Fe lattice with small C atoms occupying interstitial sites; C radius ≈ 77 pm is much smaller than Fe radius ≈ 126 pm).

Both alloy types typically make the pure metal **harder and less malleable** than the pure element, because the intruding atoms (substitutional or interstitial) disrupt the uniform, orderly layers of the pure metal lattice, making it harder for planes of atoms to slide past one another. Steel (Fe + interstitial C) is markedly harder and stronger than pure iron; brass (Cu + substitutional Zn) is harder than pure copper.

Predicting alloy type from atomic radii

Sterling silver is an alloy of silver (Ag, atomic radius ≈ 144 pm) with a small amount of copper (Cu, atomic radius ≈ 128 pm). Predict whether this is a substitutional or interstitial alloy, and predict how its hardness compares to pure silver.

The atomic radii of Ag (144 pm) and Cu (128 pm) are reasonably comparable in size (within about 10–15%), so Cu atoms can replace Ag atoms at regular lattice sites — this is a **substitutional alloy**. Because the Cu atoms are a different size than Ag and disrupt the uniform stacking of the pure silver lattice, sterling silver is **harder and more durable** than pure silver, which is why silver used in jewelry and tableware is usually alloyed rather than pure (99.9% "fine" silver is very soft).

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Hợp kim thay thế (substitutional): nguyên tử lạ có kích thước gần bằng nguyên tử kim loại chủ nên **thay thế trực tiếp** vào vị trí nút mạng (ví dụ: đồng thau brass = Cu thay bằng Zn, kích thước hai nguyên tử gần bằng nhau). Hợp kim xen kẽ (interstitial): nguyên tử lạ rất nhỏ nên **chui vào khe hở** giữa các nguyên tử kim loại chủ mà không thay thế (ví dụ: thép = Fe với C nhỏ xen vào khe). Cả hai loại đều làm mạng tinh thể kém đều đặn hơn, khiến các lớp nguyên tử khó trượt lên nhau → hợp kim thường **cứng hơn** kim loại nguyên chất.

2.5 Lewis diagrams

A **Lewis structure** (Lewis dot diagram) represents the bonding and lone-pair electrons in a molecule or polyatomic ion, showing every valence electron as either a bonding pair (a line, or two dots, between two atom symbols) or a lone pair (two dots on one atom).

Systematic method for drawing Lewis structures

1. **Count total valence electrons**: sum the group-number valence electrons of every atom in the formula. For a polyatomic *anion*, add one electron per unit of negative charge; for a polyatomic *cation*, subtract one electron per unit of positive charge.
2. **Choose a skeleton structure**: the least electronegative atom (other than H, which is always terminal) is usually the central atom, since it can form the most bonds; more electronegative atoms surround it as terminal atoms. Connect each terminal atom to the central atom with

a single bond (using 2 electrons per bond).

3. **Distribute remaining electrons as lone pairs**, starting with the terminal (outer) atoms, giving each an octet (8 electrons total, bonding + lone pair), then placing any leftover electrons on the central atom.
4. **Check the central atom's octet.** If the central atom has fewer than 8 electrons, convert one or more terminal-atom lone pairs into additional bonding pairs (double or triple bonds) with the central atom until it, too, has an octet (subject to the recognized exceptions below).
5. **Verify**: total electrons shown (bonding pairs $\times 2$ + lone pairs $\times 2$) must equal the count from step 1.

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Quy trình vẽ công thức Lewis: (1) đếm tổng electron hoá trị (cộng số nhóm của mỗi nguyên tử; ion âm thì cộng thêm electron theo điện tích, ion dương thì trừ bớt); (2) chọn nguyên tử trung tâm — thường là nguyên tử **kém âm điện nhất** (trừ H luôn ở ngoài); (3) nối các nguyên tử ngoài với trung tâm bằng liên kết đơn; (4) phân bố electron còn lại làm cặp electron riêng, ưu tiên cho nguyên tử ngoài đủ bát tử trước, dư thì đặt vào trung tâm; (5) nếu nguyên tử trung tâm chưa đủ 8 electron, chuyển cặp riêng của nguyên tử ngoài thành liên kết đôi/ba với trung tâm.

Lewis structure of a simple molecule: CO_2

Draw the Lewis structure of carbon dioxide, CO_2.

Step 1: Valence electrons $= 4(\text{C}) + 2 \times 6(\text{O}) = 4 + 12 = 16$.
Step 2: C is less electronegative than O, so C is central: O − C − O skeleton uses 2 bonds $= 4$ electrons, leaving 12.
Step 3: Give each O three lone pairs (6 electrons each, 12 total) — all 16 electrons used, but count electrons on C: C has only 4 bonding electrons (from the two single bonds), an incomplete octet.
Step 4: Convert one lone pair from each O into a second bond to C: each C–O single bond becomes a C=O double bond. Now C has 4 bonding pairs $= 8$ electrons (octet, satisfied by two double bonds), and each O has 2 lone pairs + one double bond $= 4 + 4 = 8$ electrons (octet).
Result: O = C = O, linear skeleton, each O bearing two lone pairs, C with no lone pairs. Total electrons: 2 double bonds (8 e$^-$) + 4 lone pairs on O (8 e$^-$) $= 16$ e$^-$ ✓.

2.5.1 The octet rule and its exceptions

The **octet rule** states that main-group atoms tend to gain, lose, or share electrons to achieve 8 valence electrons (a noble-gas configuration), which is a particularly stable arrangement. Most Lewis structures for period-2 nonmetals (C, N, O, F) obey the octet rule strictly, but three recognized categories of exceptions occur.

Octet rule exceptions

- **Expanded octet**: central atoms from period 3 or below (accessible d orbitals or simply large enough atomic/ionic radius) can accommodate more than 8 electrons. Examples: SF_6 (S has 12 electrons, 6 bonding pairs, no lone pairs), PCl_5 (P has 10 electrons, 5 bonding pairs). Expanded octets are *never* seen for period-2 elements (C, N, O, F) — they lack the orbital capacity/size for more than 8 electrons around them.

- **Incomplete octet**: some central atoms are stable with fewer than 8 electrons, most commonly Be (group 2, often only 4 electrons, e.g. $BeCl_2$ with 2 bonding pairs and no lone pairs) and B (group 13, often only 6 electrons, e.g. BF_3 with 3 bonding pairs and no lone pairs on B).
- **Odd-electron species (free radicals)**: molecules with an odd total number of valence electrons cannot possibly pair every electron into a lone pair or bonding pair — one electron is necessarily unpaired. Examples: NO ($5+6=11$ valence electrons, odd), NO_2 ($5+2\times6=17$ valence electrons, odd).

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Quy tắc bát tử (octet) là xu hướng chung nhưng có ba nhóm ngoại lệ cần nhớ: (1) **bát tử mở rộng** — nguyên tử trung tâm chu kỳ 3 trở xuống (như S, P, Cl, Xe) có thể chứa nhiều hơn 8 electron, ví dụ SF_6 (12 electron quanh S), PCl_5 (10 electron quanh P); ngoại lệ này **không bao giờ** xảy ra với nguyên tố chu kỳ 2 (C, N, O, F); (2) **thiếu bát tử** — Be và B thường bền với ít hơn 8 electron, ví dụ $BeCl_2$ (4 electron), BF_3 (6 electron); (3) **electron lẻ (gốc tự do)** — phân tử có tổng số electron hoá trị lẻ (như NO, NO_2) chắc chắn có một electron không thể ghép cặp.

Expanded octet: SF_6

Draw the Lewis structure of sulfur hexafluoride, SF_6, and identify why it requires an expanded octet.

Valence electrons $= 6(\text{S}) + 6\times7(\text{F}) = 6+42 = 48$. Six S–F single bonds use 12 electrons, leaving 36 electrons ($=18$ lone pairs) for the six F atoms — exactly 3 lone pairs (an octet, $6+2=8$) on each F. Total on S: 6 bonding pairs $=12$ electrons around the central S atom — an expanded octet, possible because S is a period-3 element with sufficient orbital capacity (and larger atomic radius) to accommodate 6 bonding domains, unlike a period-2 element such as O or N.

Incomplete octet: BF_3

Draw the Lewis structure of boron trifluoride, BF_3.

Valence electrons $= 3(\text{B}) + 3\times7(\text{F}) = 3+21 = 24$. Three B–F single bonds use 6 electrons, leaving 18 electrons (9 lone pairs) distributed as 3 lone pairs on each F (each F: $6+2=8$, octet satisfied). Boron ends up with only 3 bonding pairs $=6$ electrons — an incomplete octet. Although a resonance structure with one B=F double bond could technically give B a full octet, formal-charge analysis (Section 2.6) shows this is *not* favored: it would place a negative formal charge on B and a positive formal charge on the highly electronegative F, which is chemically unreasonable. BF_3 is best represented with an incomplete octet on B.

Odd-electron species: NO

Draw a reasonable Lewis structure for nitric oxide, NO.

Valence electrons $= 5(\text{N})+6(\text{O}) = 11$, an odd number. Placing a N=O double bond (4 bonding electrons) leaves 7 electrons to distribute: give O two lone pairs (4 electrons, total on O $=4+4=8$, octet) and N one lone pair plus one unpaired (single) electron ($2+1=3$ nonbonding electrons on N, total on N $=4+3=7$, one short of an octet). The unpaired electron makes NO a stable free radical — it cannot satisfy the octet rule on both atoms simultaneously because 11 is odd and cannot be split into whole pairs.

2.6 Resonance and formal charge

2.6.1 Formal charge

When more than one Lewis structure can be drawn for the same skeleton (same atom connectivity), **formal charge** (FC) is used to evaluate which structure is the most reasonable (lowest-energy) representation. Formal charge is the hypothetical charge an atom would carry if every bonding pair were split *equally* between the two bonded atoms (i.e. ignoring real electronegativity differences):

$$\text{FC} = (\text{valence electrons of free atom}) - (\text{nonbonding electrons}) - \frac{1}{2}(\text{bonding electrons}).$$

Rules for choosing the best Lewis structure using formal charge

1. The sum of all formal charges in a structure must equal the overall charge on the species (neutral molecule: sum $= 0$; ion: sum $=$ the ion's charge).
2. The best structure minimizes the magnitude of formal charges on all atoms (formal charges as close to zero as possible).
3. When formal charges cannot all be zero, negative formal charge should reside on the *more electronegative* atom (consistent with that atom's greater electron-attracting ability).
4. Structures with large formal charges (e.g. ± 2 or more) on adjacent atoms, or with like charges on adjacent atoms, are disfavored.

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Điện tích hình thức (formal charge) là điện tích **giả định** nếu ta chia đều mỗi cặp electron liên kết cho hai nguyên tử (bỏ qua độ âm điện thực tế), dùng để **so sánh** và chọn công thức Lewis hợp lý nhất khi có nhiều cách vẽ. Công thức: FC $=$ (electron hoá trị của nguyên tử tự do) $-$ (electron không liên kết) $-$ $\frac{1}{2}$(electron liên kết). Cấu trúc tốt nhất là cấu trúc có điện tích hình thức gần 0 nhất, và nếu buộc phải có điện tích âm thì nên đặt ở nguyên tử **âm điện hơn**.

Formal charge calculation: NO_3^-

Calculate the formal charge on every atom in one Lewis structure of the nitrate ion, NO_3^-, drawn with one N=O double bond and two N–O single bonds (one O carrying the negative charge as a single-bonded, three-lone-pair oxygen).

Total valence electrons: $5(\text{N}) + 3 \times 6(\text{O}) + 1(\text{extra for charge}) = 5 + 18 + 1 = 24$.
Skeleton: N central, bonded to three O atoms: one N=O double bond, two N–O single bonds. Double-bonded O gets 2 lone pairs; each single-bonded O gets 3 lone pairs. Electron count check: 1 double bond (4 e$^-$) $+2$ single bonds (4 e$^-$) $+2$ lone pairs on double-bonded O (4 e$^-$) $+2 \times 3$ lone pairs on single-bonded O's (12 e$^-$) $= 4 + 4 + 4 + 12 = 24$ ✓.

FC on N (4 bonding pairs total around N: forms 1 double + 2 single bonds $= 4$ bonding pairs, 8 bonding electrons; 0 lone pairs): FC $= 5 - 0 - \frac{1}{2}(8) = 5 - 4 = +1$.
FC on double-bonded O (2 lone pairs $= 4$ nonbonding e$^-$; 1 double bond $= 4$ bonding e$^-$): FC $= 6 - 4 - \frac{1}{2}(4) = 6 - 4 - 2 = 0$.
FC on each single-bonded O (3 lone pairs $= 6$ nonbonding e$^-$; 1 single bond $= 2$ bonding e$^-$): FC $= 6 - 6 - \frac{1}{2}(2) = 6 - 6 - 1 = -1$ (each of the two single-bonded O atoms).
Check: sum of formal charges $= (+1) + 0 + (-1) + (-1) = -1$, matching the ion's overall $1-$ charge ✓.

2.6.2 Resonance structures and the resonance hybrid

When a molecule or ion can be represented by two or more valid Lewis structures that differ *only* in the placement of electrons (never in the position of atoms), these structures are called **resonance structures**, connected by a double-headed resonance arrow ($\leftrightarrow$). No single resonance structure is the "real" molecule; the true structure is a **resonance hybrid**, an average of all contributing structures, with bonding and electron density intermediate between them.

$$\mathrm{O{=}N(-O^-)-O^-} \;\longleftrightarrow\; \mathrm{{}^-O-N(=O)-O^-} \;\longleftrightarrow\; \mathrm{{}^-O-N(-O^-){=}O}$$

Three equivalent resonance structures of NO_3^-: the double bond location shifts among the three oxygens, but each individual structure has the same connectivity and the same formal-charge pattern ($+1$ on N, 0 on the doubly-bonded O, -1 on each singly-bonded O).

Structure	FC on N	FC on double-bond O	FC on each single-bond O
Structure I (N=O_1)	$+1$	0 (O_1)	$-1, -1$ (O_2, O_3)
Structure II (N=O_2)	$+1$	0 (O_2)	$-1, -1$ (O_1, O_3)
Structure III (N=O_3)	$+1$	0 (O_3)	$-1, -1$ (O_1, O_2)

All three structures are equally valid contributors (equivalent formal-charge patterns), so the true bonding is an equal-weighted average — the resonance hybrid.

Bond order from resonance is the average bond order across all equivalent resonance structures: bond order $= \dfrac{\text{total N–O bonds (counting double bonds as 2)}}{\text{number of N–O linkages}}$. For NO_3^-: each of the three resonance structures has one N=O (bond order 2) and two N–O (bond order 1 each), so the total bond order summed over the three linkages is $2+1+1=4$ in any one structure; averaged appropriately across the three equivalent resonance forms, each N–O linkage has average bond order $\dfrac{2+1+1}{3} = 1.33$. Experimentally, all three N–O bonds in NO_3^- are observed to have *identical* length (124 pm, intermediate between a typical N–O single bond ≈ 140 pm and N=O double bond ≈ 120 pm), confirming the resonance hybrid model rather than any single resonance structure.

VN **GIẢI THÍCH TIẾNG VIỆT**

Cộng hưởng (resonance) xảy ra khi một phân tử/ion có thể vẽ được nhiều công thức Lewis hợp lệ, chỉ khác nhau ở **vị trí electron** (vị trí nguyên tử giữ nguyên). Không có công thức nào là "thật" — cấu trúc thật là **dạng lai cộng hưởng** (resonance hybrid), trung bình của tất cả các công thức. Với NO_3^-, cả ba liên kết N–O đều dài bằng nhau trên thực tế (124 pm, nằm giữa liên kết đơn và đôi), chứng minh cấu trúc thật là trung bình của 3 công thức cộng hưởng, với bậc liên kết trung bình $= 1.33$ cho mỗi liên kết N–O.

Bond order and formal charge in SO_4^{2-}

Draw the best Lewis structure for the sulfate ion, SO_4^{2-}, using an expanded octet on S, and find the average S–O bond order.

Valence electrons: $6(\mathrm{S}) + 4\times 6(\mathrm{O}) + 2(\text{charge}) = 6+24+2 = 32$.
Best structure: S is central, bonded to 4 O atoms. To minimize formal charges, place *two* S=O double bonds and *two* S–O single bonds (rather than all single bonds).
FC on S (expanded octet, 6 bonding pairs $= 12$ bonding e^-, 0 lone pairs): $6-0-\frac{1}{2}(12) = 6-6 = 0$.
FC on double-bonded O (2 lone pairs, 1 double bond): $6-4-\frac{1}{2}(4) = 0$.

FC on single-bonded O (3 lone pairs, 1 single bond): $6 - 6 - \frac{1}{2}(2) = -1$ (two such O atoms). Sum of formal charges: $0 + 0 + 0 + (-1) + (-1) = -2$, matching the ion charge ✓. (By symmetry, resonance distributes the two double bonds equally among all four O atoms across four equivalent resonance structures.)
Average S–O bond order: each resonance structure has 2 double bonds (order 2) and 2 single bonds (order 1) among 4 S–O linkages: $\frac{2(2) + 2(1)}{4} = \frac{6}{4} = 1.5$.

(!) Lỗi thường gặp: A common sign error: when computing formal charge, students forget that *only half* the bonding electrons count toward each atom (bonding electrons are shared, so each bonded atom "owns" half). Forgetting the $\frac{1}{2}$ factor, or counting all bonding electrons as belonging to one atom, produces formal charges that are far too large and do not sum to the correct overall charge. Always finish by checking that the sum of all formal charges equals the net charge of the species.

Choosing the best resonance structure by formal charge: ClO_3^-

Compare two candidate Lewis structures for chlorate, ClO_3^-: Structure A has all three Cl–O bonds as single bonds (with Cl bearing one lone pair). Structure B has one Cl=O double bond and two Cl–O single bonds (with Cl bearing no lone pairs, using an expanded octet). Which is favored?

Valence electrons: $7(\text{Cl}) + 3 \times 6(\text{O}) + 1 = 7 + 18 + 1 = 26$.
Structure A (all single bonds; Cl has 3 bonding pairs $+1$ lone pair $= 8$ electrons around Cl): FC on Cl $= 7 - 2 - \frac{1}{2}(6) = 7 - 2 - 3 = +2$. Each O (single bond, 3 lone pairs): FC $= 6 - 6 - \frac{1}{2}(2) = -1$. Sum: $+2 + 3(-1) = -1$ ✓, but Cl carries a large $+2$ formal charge.
Structure B (one Cl=O double bond, two Cl–O single bonds, no lone pairs on Cl, expanded octet with 4 bonding pairs $= 8$ electrons around Cl): FC on Cl $= 7 - 0 - \frac{1}{2}(8) = 7 - 4 = +1$. FC on double-bonded O: $6 - 4 - \frac{1}{2}(4) = 0$. FC on each single-bonded O: $6 - 6 - \frac{1}{2}(2) = -1$ (two such O). Sum: $+1 + 0 + (-1) + (-1) = -1$ ✓.
Conclusion: Structure B is favored — it minimizes the magnitude of formal charges (largest magnitude $+1$, vs. $+2$ in Structure A). Chlorine, a period-3 element, can support the expanded octet needed to lower its formal charge. (In reality resonance distributes the double-bond character among all three O atoms, giving an average Cl–O bond order of $\frac{2+1+1}{3} = 1.33$, analogous to NO_3^-.)

2.7 VSEPR and bond hybridization

Valence Shell Electron Pair Repulsion (VSEPR) theory predicts molecular shape from the principle that electron domains (regions of electron density: bonding pairs, whether single/double/triple, and lone pairs) around a central atom arrange themselves in three-dimensional space to be as far apart as possible, minimizing electron–electron repulsion.

2.7.1 Electron-domain geometry vs. molecular geometry

The **electron-domain geometry** is the arrangement of *all* electron domains (bonding + lone pairs) around the central atom. The **molecular geometry** (also called molecular shape) describes only the positions of the *atoms* (bonded nuclei), ignoring lone pairs even though lone pairs still occupy space and push bonding pairs away, compressing bond angles below the ideal electron-domain values. Lone pairs occupy more space than bonding pairs (they are held by only one nucleus rather than

shared between two), so each lone pair compresses adjacent bond angles slightly more than a bonding pair would.

(!) Lỗi thường gặp: The single most common VSEPR error is reporting the *electron-domain* geometry when asked for the *molecular* geometry (or vice versa) once lone pairs are present. For NH_3 (3 bonding pairs $+1$ lone pair), the electron-domain geometry is tetrahedral, but the molecular geometry — describing only the 4 atoms — is **trigonal pyramidal**. Always identify how many domains are lone pairs before naming the final molecular shape.

Counting electron domains: SO_2

Determine the number of electron domains around the central S atom in SO_2, and its electron-domain and molecular geometries.

Valence electrons on S (before bonding) $= 6$. Drawing the Lewis structure (18 total valence electrons: $6 + 2(6) = 18$), the best resonance structure places one S=O double bond and one S–O single bond, with one lone pair remaining on S. Counting domains around S: the double bond counts as *one* electron domain (multiple bonds count once, regardless of bond order), the single bond is a second domain, and the lone pair is a third domain — **3 electron domains total** (2 bonding $+1$ lone pair).
Electron-domain geometry: trigonal planar (3 domains).
Molecular geometry: with one domain being a lone pair, the 3 atoms (S and 2 O) trace out a **bent** (angular) shape, bond angle slightly less than 120°C due to lone-pair compression (actual $\approx 119^\circ$C).

VN **GIẢI THÍCH TIẾNG VIỆT**
Cần phân biệt rõ **hình học electron** (electron-domain geometry — tính luôn cả cặp electron riêng) và **hình học phân tử** (molecular geometry — chỉ tính vị trí các nguyên tử, bỏ qua cặp riêng dù nó vẫn chiếm không gian và đẩy các cặp liên kết lại gần nhau hơn). Ví dụ NH_3 có hình học electron là tứ diện (4 miền: 3 liên kết N–H + 1 cặp riêng), nhưng hình học phân tử (chỉ nhìn N và 3 H) là **chóp tam giác** (trigonal pyramidal). Lỗi thường gặp nhất của học sinh là nhầm lẫn hai khái niệm này.

2.7.2 VSEPR geometry reference table

Dom.	L.p.	Angle	Electron-domain geom.	Molecular geom.	Example / hyb.
2	0	180°C	Linear	Linear	$BeCl_2$ / sp
3	0	120°C	Trigonal planar	Trigonal planar	BF_3 / sp^2
3	1	$< 120^\circ$C	Trigonal planar	Bent	SO_2 / sp^2
4	0	109.5°C	Tetrahedral	Tetrahedral	CH_4 / sp^3
4	1	$< 109.5^\circ$C	Tetrahedral	Trigonal pyramidal	NH_3 / sp^3
4	2	$< 109.5^\circ$C	Tetrahedral	Bent	H_2O / sp^3
5	0	$120/90^\circ$C	Trig. bipyramidal	Trig. bipyramidal	PCl_5 / sp^3d
5	1	$\approx 120/90^\circ$C	Trig. bipyramidal	Seesaw	SF_4 / sp^3d
5	2	$\approx 90^\circ$C	Trig. bipyramidal	T-shaped	ClF_3 / sp^3d
5	3	180°C	Trig. bipyramidal	Linear	XeF_2 / sp^3d
6	0	90°C	Octahedral	Octahedral	SF_6 / sp^3d^2
6	1	$< 90^\circ$C	Octahedral	Square pyramidal	BrF_5 / sp^3d^2
6	2	90°C	Octahedral	Square planar	XeF_4 / sp^3d^2

Why lone pairs occupy trigonal bipyramidal equatorial positions preferentially

In a trigonal bipyramidal electron-domain geometry (5 domains), lone pairs always occupy **equatorial** positions rather than axial ones. Equatorial positions have only two $90°$C neighbors (the two axial positions), while axial positions have three $90°$C neighbors (the three equatorial positions). Since lone pairs are bulkier and repulsion is strongest at $90°$C, placing a lone pair equatorially minimizes the number of close, high-repulsion $90°$C interactions. This is why SF_4 (seesaw), ClF_3 (T-shaped), and XeF_2 (linear, both lone pairs equatorial, $180°$C apart) all place their lone pair(s) equatorially.

VN **GIẢI THÍCH TIẾNG VIỆT**

Trong hình học lưỡng chóp tam giác (5 miền electron), cặp electron riêng luôn ưu tiên nằm ở vị trí **xích đạo (equatorial)** thay vì trục (axial), vì vị trí xích đạo chỉ có 2 hàng xóm ở góc $90°$C (hai vị trí trục), trong khi vị trí trục có tới 3 hàng xóm ở góc $90°$C (ba vị trí xích đạo). Cặp riêng cồng kềnh hơn liên kết nên đặt ở xích đạo giúp giảm thiểu lực đẩy ở góc hẹp $90°$C.

2.7.3 Hybridization

Hybridization describes how an atom's atomic orbitals mathematically combine (mix) to form a new set of equivalent hybrid orbitals matching the number and geometry of its electron domains. The number of hybrid orbitals always equals the number of electron domains (bonding domains + lone pairs) around that atom.

Electron domains	Hybridization	Orbitals mixed
2	sp	1 s + 1 p
3	sp^2	1 s + 2 p
4	sp^3	1 s + 3 p
5	sp^3d	1 s + 3 p + 1 d
6	sp^3d^2	1 s + 3 p + 2 d

Hybridization is determined purely by **electron-domain count**, not molecular geometry. An atom with 4 electron domains is sp^3-hybridized whether those domains are 4 bonds (CH_4), 3 bonds $+1$ lone pair (NH_3), or 2 bonds $+2$ lone pairs (H_2O) — all three are sp^3.

2.7.4 Sigma and pi bonds

Every single covalent bond consists of exactly one **sigma (σ) bond**, formed by the head-on, end-to-end overlap of two orbitals (hybrid–hybrid, hybrid–s, or s–s) along the internuclear axis, giving electron density concentrated directly between the two nuclei with cylindrical symmetry about the bond axis. A double bond consists of one σ bond plus one **pi (π) bond**; a triple bond consists of one σ bond plus two π bonds. A π bond forms from the **sideways** overlap of unhybridized, parallel p orbitals (one on each atom) above and below (or in front of and behind) the internuclear axis, concentrating electron density off the bond axis in two lobes.

Single bond $= 1\,\sigma$. **Double bond** $= 1\,\sigma + 1\,\pi$. **Triple bond** $= 1\,\sigma + 2\,\pi$. An atom involved in a double bond has one p orbital left unhybridized (for the π bond) and is sp^2 hybridized (using 3 hybrid orbitals for σ bonds/lone pairs). An atom in a triple bond has two unhybridized p orbitals (for two π bonds) and is sp hybridized.

σ and π bond count: acetylene C_2H_2

Ethyne (acetylene), $H-C\equiv C-H$, is a linear molecule with a carbon–carbon triple bond. Count the total number of σ and π bonds, and state the hybridization of each carbon.

Each C is bonded to 1 H and 1 other C via a triple bond — that is 2 electron domains per carbon (the triple bond counts as one domain, the C–H bond is the second), so each carbon is sp **hybridized**, linear electron-domain geometry ($180°$C), leaving 2 unhybridized p orbitals per carbon for π bonding.
Bond inventory: 2 C–H bonds ($1\,\sigma$ each $= 2\,\sigma$) + the C≡C triple bond ($1\,\sigma + 2\,\pi$). **Total:** $3\,\sigma$ bonds and $2\,\pi$ bonds.

2.7.5 Molecular polarity from geometry and bond dipoles

A molecule is **polar** if it has a net, nonzero dipole moment — the vector sum of all individual bond dipoles does not cancel to zero. This requires *both*: (1) at least one polar bond (nonzero ΔEN), and (2) a molecular geometry that does not allow those bond dipoles to cancel by symmetry.

Predicting polarity

1. Draw the correct Lewis structure and determine the molecular geometry (VSEPR).
2. Identify whether each bond is polar (nonzero ΔEN) or nonpolar.
3. If all bonds to the central atom are identical (same terminal atom, same bond type) and arranged symmetrically (linear, trigonal planar, tetrahedral, square planar, octahedral, trigonal bipyramidal — all with no lone pairs on the central atom and all identical terminal atoms), the bond dipoles cancel by symmetry and the molecule is **nonpolar**, even though individual bonds are polar.
4. If terminal atoms differ, or a lone pair on the central atom breaks the symmetry (as in bent, trigonal pyramidal, seesaw, T-shaped shapes), the dipoles do not fully cancel and the molecule is **polar**.

VN **GIẢI THÍCH TIẾNG VIỆT**

Một phân tử **phân cực** cần đồng thời hai điều kiện: (1) có ít nhất một liên kết phân cực (ΔEN $\neq 0$), và (2) hình học phân tử **không đối xứng** đủ để triệt tiêu hết các véc-tơ mô-men lưỡng cực liên kết. Nếu nguyên tử trung tâm không có cặp electron riêng và tất cả nguyên tử ngoài giống hệt nhau, sắp xếp đối xứng (thẳng, tam giác phẳng, tứ diện, vuông phẳng, bát diện, lưỡng chóp tam giác) thì các mô-men lưỡng cực liên kết sẽ triệt tiêu lẫn nhau → phân tử **không phân cực** dù từng liên kết đều phân cực. Ngược lại, nếu có cặp electron riêng ở trung tâm (phá vỡ đối xứng) hoặc các nguyên tử ngoài khác nhau, phân tử sẽ **phân cực**.

Full VSEPR analysis: XeF_4

Determine the Lewis structure, electron-domain geometry, molecular geometry, hybridization, and polarity of XeF_4.

Valence electrons: $8(\text{Xe}) + 4\times 7(\text{F}) = 8 + 28 = 36$. Xe is central, bonded to 4 F by single bonds (8 electrons), each F gets 3 lone pairs (24 electrons, octet complete on each F); remaining electrons on Xe: $36 - 8 - 24 = 4$, i.e. 2 lone pairs on Xe.
Electron domains on Xe: 4 bonding $+2$ lone pairs $= 6$ domains.
Electron-domain geometry: octahedral. **Hybridization:** sp^3d^2.
Molecular geometry: with 2 lone pairs placed on opposite (trans/axial) sides to minimize re-

pulsion, the 4 F atoms occupy the remaining 4 positions in one plane — **square planar**, bond angles $90°$C.
Polarity: all 4 terminal atoms are identical (F) and arranged with perfect square-planar symmetry around Xe, so the 4 polar Xe–F bond dipoles cancel exactly by symmetry (opposite bonds point in exactly opposite directions). XeF_4 **is nonpolar**, despite having polar individual bonds.

Full VSEPR analysis: H_2O

Determine the Lewis structure, electron-domain geometry, molecular geometry, hybridization, and polarity of H_2O.

Valence electrons: $6(\text{O})+2(1)(\text{H}) = 8$. O is central, bonded to 2 H by single bonds (4 electrons); remaining 4 electrons form 2 lone pairs on O.
Electron domains on O: 2 bonding $+2$ lone pairs $= 4$ domains.
Electron-domain geometry: tetrahedral. **Hybridization:** sp^3.
Molecular geometry: bent, with bond angle compressed below the ideal $109.5°$C by the two lone pairs (actual $\approx 104.5°$C).
Polarity: the two O–H bond dipoles point toward O (O more electronegative) and, because the molecule is bent (not linear), these two dipole vectors do *not* cancel — they add to a net dipole pointing from the midpoint of the two H atoms toward O. H_2O **is polar.**

Full VSEPR analysis: PCl_5

Determine the electron-domain geometry, molecular geometry, hybridization, and polarity of PCl_5.

Valence electrons: $5(\text{P}) + 5 \times 7(\text{Cl}) = 5 + 35 = 40$. P is central, bonded to 5 Cl by single bonds (10 electrons); each Cl gets 3 lone pairs (30 electrons total), using all 40 electrons; no lone pairs remain on P.
Electron domains on P: 5 bonding, 0 lone pairs.
Electron-domain geometry $=$ molecular geometry: trigonal bipyramidal (3 equatorial Cl at $120°$C to each other, 2 axial Cl at $90°$C to the equatorial plane and $180°$C to each other). **Hybridization:** sp^3d.
Polarity: all 5 terminal atoms are identical Cl, and the trigonal bipyramidal arrangement is symmetric (the three equatorial dipoles cancel among themselves by $120°$C symmetry in their plane, and the two axial dipoles point in exactly opposite directions and cancel each other). PCl_5 **is nonpolar.**

Full VSEPR analysis: CH_2Cl_2

Determine the molecular geometry, hybridization, and polarity of dichloromethane, CH_2Cl_2.

C is central, bonded to 2 H and 2 Cl atoms by single bonds (4 bonding domains, 0 lone pairs on C, since C forms exactly 4 bonds to satisfy its octet with no electrons left over).
Electron-domain geometry $=$ molecular geometry: tetrahedral. **Hybridization:** sp^3.
Polarity: although the electron-domain and molecular geometries are the same symmetric tetrahedron as CH_4 or CCl_4, here the 4 terminal atoms are *not* all identical — 2 are H and 2 are Cl. The C–Cl bond dipoles (Cl more electronegative than C) and C–H bond dipoles (C more electronegative than H, so these point the opposite way relative to C) do not cancel, because the molecule lacks the required symmetry (a tetrahedron with all-identical substituents is re-

quired for cancellation). CH_2Cl_2 **is polar**, even though its shape is "just" tetrahedral.

(!) Lỗi thường gặp: Do not assume that any molecule with a symmetric-*sounding* geometry name (tetrahedral, trigonal planar, etc.) is automatically nonpolar. Symmetry cancellation of bond dipoles requires *identical* terminal atoms/groups arranged symmetrically around a central atom with no lone pairs breaking the symmetry. CH_2Cl_2 and $CHCl_3$ are both tetrahedral yet polar, because their terminal atoms are not all the same.

2.8 Comparing types of solids

The four broad categories of solids — ionic, molecular, covalent-network (atomic), and metallic — differ dramatically in physical properties because of the different nature of the particles and forces holding them together.

Solid type	Particles	Forces	Melting pt.	Example (m.p.)
Ionic	Cations, anions	Electrostatic (Coulombic)	High	NaCl (801°C)
Molecular	Molecules	IMFs (LDF, dipole, H-bond)	Low	H_2O (0°C), I_2 (114°C)
Covalent-network	Atoms	Covalent bonds throughout	Very high	SiO_2 (1713°C), diamond (3550°C)
Metallic	Cations + e^- sea	Metallic bonding	Varies (mod.–high)	Fe (1538°C), Hg (-39°C)

VN **GIẢI THÍCH TIẾNG VIỆT**

Bốn loại tinh thể rắn có tính chất rất khác nhau vì bản chất hạt và lực liên kết khác nhau: **tinh thể ion** (lực Coulomb giữa các ion, nhiệt độ nóng chảy cao); **tinh thể phân tử** (chỉ có lực liên phân tử yếu như LDF, lưỡng cực, liên kết hydro giữ các phân tử lại, nên nhiệt độ nóng chảy thấp); **tinh thể cộng hoá trị mạng lưới** (toàn bộ tinh thể là một mạng liên kết cộng hoá trị liên tục, ví dụ kim cương, thạch anh SiO_2, nhiệt độ nóng chảy cực cao); **tinh thể kim loại** (biển electron, nhiệt độ nóng chảy dao động tuỳ kim loại).

2.9 Practice problems

Bài tập luyện tập

Which of the following bonds is most polar, based on Pauling electronegativities (H $= 2.20$, C $= 2.55$, N $= 3.04$, O $= 3.44$, F $= 3.98$, Cl $= 3.16$)?

(A) C – H
(B) N – H
(C) O – H
(D) H – F

Lời giải chi tiết

ΔEN values: C–H $= 0.35$; N–H $= 0.84$; O–H $= 1.24$; H–F $= 1.78$. The largest ΔEN, and therefore the most polar bond, is **(D)** H–F.

Bài tập luyện tập

On a potential-energy vs. internuclear-distance curve for bond formation, what does the internuclear distance at the minimum of the curve represent?

(A) The bond energy
(B) The bond length
(C) The ionization energy
(D) The point where repulsion first appears

Lời giải chi tiết

(B). The minimum of the potential-energy curve is the most stable (lowest-energy) internuclear separation, defined as the bond length r_0. The *depth* of the well (not the x-coordinate) represents the bond energy.

Bài tập luyện tập

Rank the following in order of increasing bond length: C $\equiv$ C, C $-$ C, C $=$ C.

Lời giải chi tiết

Higher bond order means shorter bond length (more shared electron density pulls the nuclei closer). Bond order: triple (3) > double (2) > single (1). Increasing bond length is therefore the reverse: C $\equiv$ C < C $=$ C < C $-$ C.

Bài tập luyện tập

Which pair of ionic compounds would you expect to have the higher lattice energy, and why: LiF or CsI?

Lời giải chi tiết

Both are $1+/1-$ compounds, so the charge product $Q_1Q_2 = 1$ is identical for both — the comparison comes down to ionic radius. Li^+ ($\approx$ 76 pm) and F^- ($\approx$ 133 pm) are both much smaller than Cs^+ ($\approx$ 167 pm) and I^- ($\approx$ 220 pm). Since lattice energy $\propto 1/r$ and LiF has the much smaller sum of ionic radii, LiF **has the higher lattice energy** (and correspondingly the higher melting point: LiF melts at $845°$C vs. CsI at $621°$C).

Bài tập luyện tập

A metallurgist alloys pure gold (Au, radius ≈ 144 pm) with a small amount of silver (Ag, radius ≈ 144 pm) to make white gold-like jewelry alloys, and separately alloys iron (Fe, radius ≈ 126 pm) with a small amount of carbon (C, radius ≈ 77 pm) to make steel. Classify each alloy type and explain the reasoning.

Lời giải chi tiết

Au + Ag: the atomic radii are essentially identical (144 pm each), so Ag atoms can directly replace Au atoms at regular lattice positions — this is a **substitutional alloy**.
Fe + C: carbon's atomic radius (77 pm) is far smaller than iron's (126 pm) — too small to substitute at a regular lattice site, but small enough to fit into the interstitial gaps between the larger Fe atoms — this is an **interstitial alloy**. In both cases, the intruding atoms disrupt the uniform stacking of the pure metal, making the alloy harder and less malleable than the pure metal.

Bài tập luyện tập

Explain, using the electron-sea model, why metals conduct electricity in both the solid and molten states, while ionic compounds conduct electricity only when molten or dissolved (not as solids).

Lời giải chi tiết

In a metal, valence electrons are delocalized over the *entire* lattice and are free to drift under an applied electric field regardless of whether the cations are held in a rigid solid lattice or free to move in a liquid — the mobile electron sea itself is what carries current, so both phases conduct. In an ionic solid, the charge carriers would have to be the ions themselves (there is no delocalized electron sea), but the ions are locked into fixed lattice positions and cannot move to carry current; only when the lattice is disrupted by melting or dissolution can the ions move freely and carry current.

Bài tập luyện tập

For the molecule OF_2: (a) draw the Lewis structure, (b) state the number of valence electrons, (c) determine electron-domain and molecular geometry, (d) determine hybridization on O, (e) predict polarity.

Lời giải chi tiết

(b) Valence electrons $= 6(\text{O}) + 2 \times 7(\text{F}) = 6 + 14 = 20$.
(a) O central, bonded to 2 F by single bonds (4 electrons); each F gets 3 lone pairs (12 electrons); remaining 4 electrons $= 2$ lone pairs on O. Structure: F $-$ O $-$ F with 2 lone pairs on O and 3 lone pairs on each F.
(c) 2 bonding $+2$ lone pairs on O $= 4$ domains: electron-domain geometry **tetrahedral**; molecular geometry **bent** (angle $\approx 103^\circ$C, compressed by the two lone pairs).
(d) 4 domains $\Rightarrow sp^3$ hybridized O.
(e) Both O–F bonds are polar ($\Delta\text{EN} = |3.98 - 3.44| = 0.54$) and point toward the more electronegative F; because the molecule is bent, not linear, the two bond dipoles do not cancel. OF_2 **is polar.**

Bài tập luyện tập

Which of the following molecules is an exception to the octet rule due to an *incomplete* octet on the central atom?

(A) SF_6
(B) BCl_3
(C) PCl_5
(D) CO_2

Lời giải chi tiết

(B). BCl_3: valence electrons $= 3 + 3(7) = 24$; three B–Cl single bonds (6 e$^-$) plus 3 lone pairs on each Cl (18 e$^-$) uses all 24, leaving boron with only 3 bonding pairs (6 electrons) — an incomplete octet, characteristic of group-13 boron. SF_6 and PCl_5 are expanded-octet examples; CO_2 satisfies the octet rule normally.

Bài tập luyện tập

Draw the Lewis structure of NO_2 (nitrogen dioxide) and explain why it cannot satisfy the octet rule on nitrogen.

Lời giải chi tiết

Valence electrons $= 5(\text{N}) + 2 \times 6(\text{O}) = 5 + 12 = 17$, an **odd** number. Since electrons can only be arranged as bonding pairs or lone pairs (each contributing an even number, 2, to any single atom's total), an odd overall electron count makes it impossible for every atom to reach a filled-shell (even) electron count simultaneously. A reasonable structure places one N=O double bond and one N–O single bond, with one unpaired (lone) electron remaining on N (giving N a total of $4 + 2 + 1 = 7$ electrons around it, one short of an octet). NO_2 is therefore a stable odd-electron free radical.

Bài tập luyện tập

Draw the best Lewis structure for the cyanide ion, CN^-, including formal charges on both atoms, and state the C–N bond order.

Lời giải chi tiết

Valence electrons $= 4(\text{C}) + 5(\text{N}) + 1(\text{charge}) = 10$. To give both C and N an octet with only 10 electrons, a triple bond is required: $:\text{C} \equiv \text{N}:^-$, with one lone pair on C and one lone pair on N.
FC on C (1 lone pair $= 2$ nonbonding e$^-$; triple bond $= 6$ bonding e$^-$): $4 - 2 - \frac{1}{2}(6) = 4 - 2 - 3 = -1$.
FC on N (1 lone pair $= 2$ nonbonding e$^-$; triple bond $= 6$ bonding e$^-$): $5 - 2 - \frac{1}{2}(6) = 5 - 2 - 3 = 0$.
Sum: $-1 + 0 = -1$, matching the overall ion charge ✓. This is the preferred structure since it places the formal negative charge on carbon (less electronegative — this initially seems less ideal, but any structure without the triple bond leaves an atom without an octet, which is strongly disfavored; the triple-bond structure with formal charges -1 on C and 0 on N is the accepted best Lewis structure for cyanide). **C–N bond order** $= 3$ (triple bond, no resonance needed since only one skeleton is possible).

Bài tập luyện tập

For the ion SCN^- (thiocyanate, skeleton S–C–N), one valid resonance structure places a S=C double bond and a C≡N triple bond. Verify the total valence electron count and compute the formal charge on every atom.

Lời giải chi tiết

Valence electrons $= 6(\text{S}) + 4(\text{C}) + 5(\text{N}) + 1(\text{charge}) = 16$.
Structure: $\text{S} = \text{C} = \text{N}^-$ would be one resonance form, but let's verify the stated form S=C, C≡N is not simultaneously possible on the same carbon (carbon can have at most 4 bonds total). The consistent resonance structure is $^-\text{S} - \text{C} \equiv \text{N}$ (single S–C, triple C–N) or $\text{S} = \text{C} = \text{N}^-$ (double S=C, double C=N). Using $^-\text{S} - \text{C} \equiv \text{N}$: S has 1 single bond $+3$ lone pairs (6 nonbonding e$^-$); C has 1 single bond $+1$ triple bond (0 lone pairs); N has 1 triple bond $+1$ lone pair.
Electron count: S–C single (2) + C≡N triple (6) + S lone pairs (6) + N lone pair (2) $= 2+6+6+2 = 16$ ✓.
FC on S (3 lone pairs, 1 single bond): $6 - 6 - \frac{1}{2}(2) = -1$.

FC on C (0 lone pairs, 1 single $+1$ triple $= 4$ bonding pairs, 8 bonding e$^-$): $4 - 0 - \frac{1}{2}(8) = 0$.
FC on N (1 lone pair, 1 triple bond): $5 - 2 - \frac{1}{2}(6) = 0$.
Sum: $-1 + 0 + 0 = -1$ ✓, matching the ion's charge. This structure (negative charge on S, the less electronegative but larger, more polarizable atom of the terminal pair) is generally considered the major resonance contributor for thiocyanate.

Bài tập luyện tập

What is the electron-domain geometry, molecular geometry, and hybridization of the central atom in ClF_3?

(A) Trigonal bipyramidal, T-shaped, sp^3d
(B) Tetrahedral, trigonal pyramidal, sp^3
(C) Octahedral, square planar, sp^3d^2
(D) Trigonal bipyramidal, seesaw, sp^3d

Lời giải chi tiết

(A). Valence electrons on Cl (central) $= 7 + 3(7) = 28$; three Cl–F single bonds (6 e$^-$), each F gets 3 lone pairs (18 e$^-$), remaining 4 electrons $= 2$ lone pairs on Cl. Total domains on Cl: 3 bonding $+2$ lone pairs $= 5$ domains $\Rightarrow$ trigonal bipyramidal electron-domain geometry, sp^3d hybridization. With 2 lone pairs occupying equatorial positions (to minimize $90°$C repulsions) and 3 F atoms in the remaining positions, the molecular shape is **T-shaped**.

Bài tập luyện tập

Predict the molecular polarity of CCl_4 and $CHCl_3$, and explain why they differ despite both having a tetrahedral electron-domain geometry.

Lời giải chi tiết

CCl_4: C is bonded to 4 identical Cl atoms with no lone pairs — perfectly symmetric tetrahedral arrangement of 4 identical bond dipoles, which cancel exactly by vector symmetry. **Nonpolar**, despite each individual C–Cl bond being polar.
$CHCl_3$: C is bonded to 3 Cl and 1 H — the terminal atoms are *not* all identical, so the tetrahedral symmetry required for cancellation is broken (the C–H bond dipole points opposite to the net pull of the three C–Cl dipoles, but the magnitudes differ so they do not fully cancel). **Polar.**
The lesson: having the same geometry *name* does not guarantee the same polarity outcome — identical terminal atoms are required for dipole cancellation.

Bài tập luyện tập

A student claims that because SF_4 has a trigonal bipyramidal electron-domain geometry — the same electron-domain geometry as PCl_5, a nonpolar molecule — SF_4 must also be nonpolar. Evaluate this claim.

Lời giải chi tiết

The claim is **incorrect**. PCl_5 has 5 bonding domains and 0 lone pairs on P, giving a molecular geometry identical to its electron-domain geometry (trigonal bipyramidal) with perfect symmetry among 5 identical Cl atoms, so its bond dipoles cancel. SF_4, by contrast, has 4 bonding domains $+1$ lone pair on S (5 total electron domains, also trigonal bipyramidal electron-domain geometry), but the lone pair occupies one equatorial position, leaving a **seesaw** molecular ge-

ometry. The lone pair breaks the symmetry that would otherwise allow the S–F bond dipoles to cancel, so the seesaw arrangement's dipoles sum to a nonzero net dipole. SF_4 **is polar**, despite sharing the same electron-domain geometry (and same central-atom hybridization, sp^3d) as the nonpolar PCl_5. Molecular polarity must be judged from the molecular geometry (including lone-pair effects), not the electron-domain geometry alone.

Bài tập luyện tập

Which of the following correctly lists the number of sigma and pi bonds in a molecule of formaldehyde, $H_2C=O$?

(A) $2\,\sigma, 2\,\pi$
(B) $3\,\sigma, 1\,\pi$
(C) $4\,\sigma, 0\,\pi$
(D) $3\,\sigma, 2\,\pi$

Lời giải chi tiết

(B). Formaldehyde has 2 C–H single bonds ($1\,\sigma$ each $= 2\,\sigma$) and 1 C=O double bond ($1\,\sigma + 1\,\pi$). Total: $3\,\sigma$ bonds and $1\,\pi$ bond. Carbon is sp^2 hybridized (3 electron domains: 2 C–H bonds + 1 C=O domain), with one unhybridized p orbital forming the π bond with oxygen.

Bài tập luyện tập

Rank $MgCl_2$, MgO, and NaCl in order of *decreasing* melting point, and justify using lattice energy reasoning.

Lời giải chi tiết

Charges: MgO is $2+/2-$; $MgCl_2$ is $2+/1-$ (per ion pair, effectively $Q_1Q_2 = 2\times 1 = 2$); NaCl is $1+/1-$. Since lattice energy (and thus melting point) is dominated by the charge product, MgO ($Q_1Q_2 = 4$) > $MgCl_2$ ($Q_1Q_2 = 2$) > NaCl ($Q_1Q_2 = 1$). **Decreasing melting point:** MgO (**2852°C**) > $MgCl_2$ (**714°C**) > NaCl (**801°C**). (Note: $MgCl_2$'s melting point is actually slightly lower than NaCl's in real data because ionic radius and some covalent character in Mg–Cl bonding modify the simple Coulombic prediction — but MgO's dramatically higher Q_1Q_2 correctly predicts it as the clear highest-melting compound of the three.)

Bài tập luyện tập

Determine the Lewis structure, molecular geometry, hybridization, and polarity of the ion NH_4^+.

Lời giải chi tiết

Valence electrons $= 5(\text{N}) + 4(1)(\text{H}) - 1(\text{charge, cation}) = 5 + 4 - 1 = 8$. N is central, bonded to 4 H by single bonds (8 electrons total), using all 8 electrons — no lone pairs on N.
Electron domains: 4 bonding, 0 lone pairs $\Rightarrow$ tetrahedral electron-domain and molecular geometry, bond angle $109.5°$C, sp^3 hybridization.
FC on N: $5 - 0 - \frac{1}{2}(8) = 5 - 4 = +1$, matching the overall $+1$ charge (each H has FC $= 1 - 0 - \frac{1}{2}(2) = 0$).
Polarity: 4 identical H atoms symmetrically arranged around N with no lone pairs — bond dipoles cancel by symmetry. **Nonpolar** (as a standalone symmetric ion; its charge, not a permanent dipole, is what drives its interactions).

Bài tập luyện tập

A Lewis structure for PO_4^{3-} can be drawn with all four P–O bonds as single bonds; this gives formal charges of $+1$ on P and -1 on each of the four O atoms. An alternative structure places one P=O double bond and three P–O single bonds (using an expanded octet on P). Compute the formal charges for the alternative structure and state which is preferred.

Lời giải chi tiết

Valence electrons: $5(\text{P}) + 4 \times 6(\text{O}) + 3(\text{charge}) = 5 + 24 + 3 = 32$.
All-single-bond structure: P has 4 bonding pairs $+0$ lone pairs: FC $= 5 - 0 - \frac{1}{2}(8) = +1$. Each O (single bond, 3 lone pairs): FC $= 6 - 6 - \frac{1}{2}(2) = -1$. Sum $= +1 + 4(-1) = -3$ ✓, but this places 5 nonzero formal charges (magnitude 1 each) spread across the ion.
Double-bond structure: P now has 4 bonding pairs total (1 double $+3$ single $= 4$ bonding domains, 8 bonding electrons, 0 lone pairs — expanded to 10 electrons is not needed here since the double bond does not add extra domains, only extra shared electrons): bonding electrons around P $= 2(2) + 3(2) = 10$; FC(P) $= 5 - 0 - \frac{1}{2}(10) = 5 - 5 = 0$. FC on the double-bonded O (2 lone pairs, 1 double bond): $6 - 4 - \frac{1}{2}(4) = 0$. FC on each of the three single-bonded O (3 lone pairs, 1 single bond): $6 - 6 - \frac{1}{2}(2) = -1$. Sum: $0 + 0 + 3(-1) = -3$ ✓.
Conclusion: the double-bond structure gives P a formal charge of exactly 0 (vs. $+1$) and reduces the total number of atoms bearing nonzero formal charge from 5 to 3, so by the "minimize formal charge magnitude" rule it is the **preferred** structure. (As with sulfate, resonance actually delocalizes the double-bond character equally among all four oxygens in real PO_4^{3-}, giving an average P–O bond order of 1.25.)

Bài tập luyện tập

Which molecular geometry and hybridization describes the central Be atom in gaseous $BeCl_2$?

(A) Bent, sp^3
(B) Trigonal planar, sp^2
(C) Linear, sp
(D) Tetrahedral, sp^3

Lời giải chi tiết

(C). Valence electrons $= 2(\text{Be}) + 2 \times 7(\text{Cl}) = 16$; Be forms 2 single bonds to Cl using 4 electrons, and the remaining 12 electrons become 3 lone pairs on each Cl. Be ends up with 0 lone pairs and 2 bonding domains — an incomplete octet (only 4 electrons around Be), 2 electron domains $\Rightarrow$ **linear** geometry, $180°$C bond angle, sp hybridization.

Bài tập luyện tập

Determine the Lewis structure, electron-domain geometry, molecular geometry, hybridization, and polarity of CH_4.

Lời giải chi tiết

Valence electrons $= 4(\text{C}) + 4(1)(\text{H}) = 8$. C is central, bonded to 4 H by single bonds, using all 8 electrons — no lone pairs on C.
Electron domains: 4 bonding, 0 lone pairs $\Rightarrow$ electron-domain geometry $=$ molecular geometry $=$ **tetrahedral**, bond angle $109.5°$C, sp^3 hybridization.
Polarity: 4 identical H atoms arranged symmetrically around C with no lone pairs to break

the symmetry — the (weakly polar, $\Delta\text{EN} = 0.35$) C–H bond dipoles cancel exactly. CH_4 **is nonpolar.**

Bài tập luyện tập

Determine the Lewis structure, electron-domain geometry, molecular geometry, hybridization, and polarity of NH_3.

Lời giải chi tiết

Valence electrons $= 5(\text{N}) + 3(1)(\text{H}) = 8$. N is central, bonded to 3 H by single bonds (6 electrons), leaving 2 electrons as 1 lone pair on N.
Electron domains: 3 bonding $+1$ lone pair $= 4$ domains $\Rightarrow$ electron-domain geometry **tetrahedral**, sp^3 hybridization.
Molecular geometry: with 1 domain a lone pair, the 4 atoms (N and 3 H) form a **trigonal pyramidal** shape, bond angle $\approx 107^\circ$C (compressed from 109.5°C by the lone pair).
Polarity: the three N–H bond dipoles point toward the more electronegative N, and the lone pair breaks the symmetry that would otherwise allow cancellation (unlike a hypothetical planar NH_3, the pyramidal shape means the three dipoles combine into a net dipole along the axis through N and the lone pair). NH_3 **is polar.**

Bài tập luyện tập

An unknown period-3 central atom X forms the neutral molecule XF_6 with no lone pairs on X. What is the electron-domain geometry, molecular geometry, and hybridization of X, and which specific real molecule does this describe?

(A) Octahedral, octahedral, sp^3d^2; describes SF_6
(B) Trigonal bipyramidal, seesaw, sp^3d; describes SF_4
(C) Octahedral, square pyramidal, sp^3d^2; describes BrF_5
(D) Tetrahedral, tetrahedral, sp^3; describes CF_4

Lời giải chi tiết

(A). Six bonding domains and zero lone pairs on X requires exactly 6 electron domains, giving an **octahedral** electron-domain geometry (identical to molecular geometry, since there are no lone pairs), with 90°C bond angles and sp^3d^2 hybridization. A period-3 (or lower) central atom forming 6 bonds to fluorine with no lone pairs is exactly the case of SF_6, sulfur hexafluoride.

Bài tập luyện tập

Draw the resonance structures of ozone, O_3 (skeleton O–O–O, bent), compute the formal charge on every atom in one resonance structure, and state the average O–O bond order.

Lời giải chi tiết

Valence electrons: $3 \times 6 = 18$.
Structure: central O bonded to two terminal O atoms, one by a double bond and one by a single bond, to satisfy octets on all three with 18 electrons: central O has 1 lone pair, double-bonded terminal O has 2 lone pairs, single-bonded terminal O has 3 lone pairs. Electron count: 1 double bond (4) $+1$ single bond (2) $+1$ lone pair on central O (2) $+2$ lone pairs on double-bond

O (4) $+3$ lone pairs on single-bond O $(6) = 4+2+2+4+6 = 18$ ✓.
FC on central O (1 lone pair, 3 bonding pairs [1 double + 1 single] $= 6$ bonding e$^-$): $6-2-\frac{1}{2}(6) = 6-2-3 = +1$.
FC on double-bonded terminal O (2 lone pairs, 1 double bond): $6-4-\frac{1}{2}(4) = 0$.
FC on single-bonded terminal O (3 lone pairs, 1 single bond): $6-6-\frac{1}{2}(2) = -1$.
Sum: $+1+0+(-1) = 0$ ✓, matching the neutral molecule. A second, equivalent resonance structure swaps which terminal O carries the double bond; the true structure is the resonance hybrid, with both O–O bonds of **equal length**, average bond order $= \dfrac{2+1}{2} = 1.5$.

Bài tập luyện tập

Which of the following correctly identifies the hybridization of the central atom and the molecular geometry of BrF_5?

(A) sp^3d, seesaw
(B) sp^3d^2, square pyramidal
(C) sp^3d^2, octahedral
(D) sp^3d, T-shaped

Lời giải chi tiết

(B). Valence electrons on Br (central) $= 7+5(7) = 42$; five Br–F single bonds (10 e$^-$), each F gets 3 lone pairs (30 e$^-$), remaining 2 electrons $= 1$ lone pair on Br. Total domains on Br: 5 bonding $+1$ lone pair $= 6$ domains $\Rightarrow$ octahedral electron-domain geometry, sp^3d^2 hybridization. With 1 lone pair occupying one of the six octahedral positions, the remaining 5 F atoms form a **square pyramidal** molecular shape.

Bài tập luyện tập

Two isoelectronic-type ionic compounds, KCl and CaS, have similar ionic radii ($K^+ \approx 138$ pm, $Ca^{2+} \approx 100$ pm, $Cl^- \approx 181$ pm, $S^{2-} \approx 184$ pm). Predict which has the higher lattice energy and higher melting point, and justify.

Lời giải chi tiết

KCl is a $1+/1-$ pair ($Q_1Q_2 = 1$); CaS is a $2+/2-$ pair ($Q_1Q_2 = 4$). The sum of ionic radii is comparable for both compounds (KCl: $138+181 = 319$ pm; CaS: $100+184 = 284$ pm — actually slightly smaller for CaS, reinforcing the same conclusion), so the charge term dominates decisively. CaS **has the much higher lattice energy** (its Q_1Q_2 is $4\times$ larger, and its ionic radii sum is if anything smaller) and correspondingly the higher melting point (CaS melts at 2525°C vs. KCl at 770°C).

Bài tập luyện tập

A covalent-network solid such as quartz (SiO_2) has a melting point of 1713°C, while the molecular solid iodine (I_2) melts at only 114°C, even though both are held together by bonds involving shared electrons. Explain the enormous difference in melting point.

Lời giải chi tiết

In SiO_2, every Si and O atom throughout the entire crystal is connected by strong covalent bonds in a continuous three-dimensional network — melting requires breaking a large fraction

of these strong covalent (Si–O) bonds throughout the lattice, which demands a very large amount of energy. In solid I_2, by contrast, the covalent bonds are only *within* each discrete I_2 molecule (very strong, but few in number and irrelevant to melting); the molecules themselves are held to each other in the solid only by weak London dispersion forces. Melting I_2 only requires overcoming these weak intermolecular forces between molecules, not breaking any covalent bond, so its melting point is far lower than a covalent-network solid's.

Bài tập luyện tập

Rank the following central-atom electron-domain counts with their correct hybridization: (i) 2 domains, (ii) 5 domains, (iii) 6 domains, (iv) 3 domains.

(A) (i) sp, (ii) sp^3d, (iii) sp^3d^2, (iv) sp^2

(B) (i) sp^2, (ii) sp^3, (iii) sp^3d, (iv) sp

(C) (i) sp^3, (ii) sp^3d^2, (iii) sp^3d, (iv) sp^2

(D) (i) sp, (ii) sp^3d^2, (iii) sp^3d, (iv) sp^2

Lời giải chi tiết

(A). The number of hybrid orbitals always equals the number of electron domains: $2 \to sp$, $3 \to sp^2$, $4 \to sp^3$, $5 \to sp^3d$, $6 \to sp^3d^2$. Matching: (i) $2 \to sp$, (ii) $5 \to sp^3d$, (iii) $6 \to sp^3d^2$, (iv) $3 \to sp^2$.

Bài tập luyện tập

For the molecule HCN (skeleton H–C≡N, linear): (a) draw the Lewis structure and verify the electron count, (b) state the hybridization of C, (c) count the total number of σ and π bonds, (d) predict polarity.

Lời giải chi tiết

(a) Valence electrons $= 1(\text{H}) + 4(\text{C}) + 5(\text{N}) = 10$. C is central: one C–H single bond (2 e$^-$) and one C≡N triple bond (6 e$^-$) uses 8 electrons; the remaining 2 electrons form 1 lone pair on N. Check: $2 + 6 + 2 = 10$ ✓.
(b) C has 2 electron domains (the C–H bond and the C≡N domain) $\Rightarrow$ sp hybridized, linear, $180°$C.
(c) C–H single bond: $1\,\sigma$. C≡N triple bond: $1\,\sigma + 2\,\pi$. **Total: $2\,\sigma$ and $2\,\pi$ bonds.**
(d) The molecule is linear with two different terminal atoms (H and N) on either side of C, so the C–H and C≡N bond dipoles do not cancel (they are not identical in magnitude, and even if the molecule is linear, the two bonds are chemically different). HCN **is polar.**

Bài tập luyện tập

Which pair of substances would you expect to have the most similar melting points, based on the type of solid each forms: (I) CO_2 (dry ice) and SiO_2 (quartz); (II) NaCl and KBr; (III) Fe (iron) and Ar (solid argon)?

(A) Pair I, because both contain the same elements

(B) Pair II, because both are ionic solids with comparable Q_1Q_2 and similar ionic radii

(C) Pair III, because both are elements

(D) All three pairs should be similar

Lời giải chi tiết

(B). CO_2 is a molecular solid (held by weak LDF, melts/sublimes around -78°C) while SiO_2 is a covalent-network solid (melts near 1713°C) — despite superficially similar formulas, these are governed by completely different types of forces and have wildly different melting points, ruling out Pair I. Fe is a metallic solid (melts at 1538°C) while Ar is a molecular (atomic) solid held only by very weak LDF (melts at -189°C) — ruling out Pair III. NaCl and KBr are both $1+/1-$ ionic solids with comparable ionic radii and identical charge products, so Coulombic lattice energies (and melting points: NaCl 801°C, KBr 734°C) are indeed the most similar of the three pairs.

Intermolecular Forces and Properties

Mục tiêu Unit: Nhận diện và so sánh các lực liên phân tử (London, lưỡng cực–lưỡng cực, liên kết hydro, ion–lưỡng cực); phân loại chất rắn và tính chất; đọc giản đồ pha; sử dụng phương trình khí lý tưởng $PV = nRT$ và định luật Dalton; thuyết động học phân tử và phân bố Maxwell–Boltzmann; định luật Graham; sai lệch của khí thực; nồng độ dung dịch (molarity, % khối lượng, ppm, phần mol) và pha loãng; quy tắc độ tan và các phương pháp tách hỗn hợp; quang phổ điện từ, hiệu ứng quang điện, và định luật Beer–Lambert.

3.1 Intermolecular forces

The physical properties of a substance in its condensed phases — melting point, boiling point, viscosity, surface tension, vapor pressure — are governed not by the strong covalent or ionic bonds *within* a molecule or formula unit, but by the much weaker attractive forces *between* particles. These are collectively called **intermolecular forces** (IMFs), or more generally **van der Waals forces**. Because IMFs are typically 10–100 times weaker than covalent or ionic bonds, condensed phases held together by IMFs alone (molecular solids, liquids) melt and boil at far lower temperatures than ionic or covalent-network solids.

3.1.1 London dispersion forces

Every atom and molecule, polar or nonpolar, possesses **London dispersion forces (LDF)**, also called induced-dipole–induced-dipole forces. At any instant, the electron cloud surrounding a nucleus is not perfectly symmetric; a fleeting, **instantaneous dipole** forms as electron density momentarily concentrates on one side of the atom or molecule. This instantaneous dipole induces a matching **induced dipole** in a neighboring particle, and the two weakly attract. Because these dipoles flicker in and out of existence on a femtosecond timescale, LDF is a fluctuating, statistical effect — but averaged over time it produces a real, always-attractive net force.

Khái niệm cốt lõi

The strength of LDF depends on how easily a particle's electron cloud can be distorted — its **polarizability**. Polarizability increases with:

- **Larger electron count / molar mass**: more electrons, especially loosely-held outer electrons far from the nucleus, are easier to displace into a temporary dipole.
- **Larger surface area / molecular shape**: elongated, chain-like molecules can align surface-to-surface, maximizing contact and instantaneous-dipole interaction, whereas compact, spherical isomers of the same molar mass pack more tightly and touch over a smaller area, giving *weaker* net LDF.

Consequently, LDF strength (and hence boiling point) generally rises down a family of nonpolar substances of increasing molar mass — e.g. the halogens F_2 (gas) $\rightarrow$ Cl_2 (gas) $\rightarrow$ Br_2 (liquid) $\rightarrow$ I_2 (solid) at room temperature, or the noble gases He through Rn.

VN **GIẢI THÍCH TIẾNG VIỆT**

Lực phân tán London (LDF) tồn tại ở **mọi** phân tử, kể cả phân tử không phân cực, vì tại một thời điểm bất kỳ đám mây electron có thể lệch tạm thời sang một phía, tạo ra lưỡng cực tức thời, từ đó cảm ứng lưỡng cực ở phân tử bên cạnh. LDF càng mạnh khi phân tử càng **nhiều electron** (khối lượng mol lớn) và có **diện tích bề mặt tiếp xúc lớn** (phân tử dài, mạch thẳng mạnh hơn phân tử cầu gọn cùng khối lượng mol, vì mạch thẳng áp sát nhau tốt hơn).

3.1.2 Dipole–dipole forces

A **polar molecule** has a permanent dipole moment because of unevenly distributed electron density (asymmetric distribution of polar bonds — see Unit 2 for VSEPR/polarity). **Dipole–dipole forces** arise when the positive end of one polar molecule is attracted to the negative end of a neighboring polar molecule. Because this attraction is a *permanent*, oriented interaction rather than a fluctuating one, dipole–dipole forces are generally stronger than LDF between molecules of comparable size and mass — though LDF is always present as well, superimposed on the dipole–dipole attraction.

Comparing boiling points of similar-mass molecules

N_2 ($M = 28.0$ g/mol, nonpolar) boils at -196°C; CO ($M = 28.0$ g/mol, polar, small dipole from the C–O bond) boils at -192°C. Explain the difference.

Both molecules have essentially identical molar mass, so their LDF contributions are nearly equal. CO has a permanent (if modest) dipole moment due to the electronegativity difference between C and O, adding a dipole–dipole component absent in the perfectly symmetric, non-polar N_2. The extra attractive force in CO raises its boiling point slightly above that of N_2, even though the difference is small because the C–O dipole itself is weak.

VN **GIẢI THÍCH TIẾNG VIỆT**

Lực lưỡng cực–lưỡng cực chỉ xuất hiện giữa các phân tử **phân cực** (có mô-men lưỡng cực vĩnh viễn, do hình học phân tử không đối xứng). Đây là lực định hướng ổn định (đầu dương hút đầu âm của phân tử kế bên), nên thường mạnh hơn LDF ở các phân tử có khối lượng mol tương đương. Tuy nhiên phân tử phân cực vẫn có LDF — hai loại lực này cộng dồn với nhau.

3.1.3 Hydrogen bonding

Hydrogen bonding is an especially strong type of dipole–dipole attraction that occurs specifically when a hydrogen atom is bonded *directly* to one of the three highly electronegative, small atoms **N, O, or F**, and that H interacts with a lone pair on an N, O, or F atom of a neighboring molecule. The N–H, O–H, and F–H bonds are extremely polar (large ΔEN, small atomic size concentrates the partial positive charge on H into a very small area), and the small size of N, O, F allows very close approach, so the resulting dipole–dipole attraction is unusually strong — roughly 5–10% the strength of a covalent bond, far stronger than typical dipole–dipole forces.

Hydrogen bonding requires *both* conditions simultaneously: H covalently bonded to N, O, or F *and* a nearby N, O, or F (with a lone pair) on another molecule. A C–H bond, even in a molecule that also contains O or N elsewhere, does not itself hydrogen-bond (C is not electronegative enough and the bond is not polar enough).

Hydrogen bonding anomaly in Group 16 and 17 hydrides

Explain why H_2O ($M = 18.0$ g/mol) boils at 100°C, dramatically higher than H_2S ($M = 34.1$ g/mol, boils at -60°C), even though H_2S has the larger molar mass.

Molar mass alone would predict H_2S (heavier, more polarizable) to have the higher boiling point from LDF considerations. But O–H bonds in water hydrogen-bond extensively (each water molecule can form up to 4 hydrogen bonds via its 2 O–H bonds and 2 lone pairs), while S is too large and insufficiently electronegative for S–H to hydrogen-bond. The extra, very strong hydrogen-bonding network in water overwhelms the mass/LDF trend, giving water an anomalously high boiling point among the Group 16 hydrides.

VN **GIẢI THÍCH TIẾNG VIỆT**

Liên kết hydro là dạng **đặc biệt mạnh** của lực lưỡng cực–lưỡng cực, chỉ xảy ra khi H liên kết trực tiếp với N, O, hoặc F (nhớ quy tắc "N-H, O-H, F-H"), và H đó tương tác với cặp electron riêng của N/O/F ở phân tử khác. Đây là lý do nước (H_2O) có điểm sôi bất thường cao so với các hydride cùng nhóm 16 khác (H_2S, H_2Se, H_2Te) — chỉ có nước hình thành mạng lưới liên kết hydro rộng khắp.

3.1.4 Ion–dipole forces

An **ion–dipole force** is the attraction between a charged ion and the oppositely-charged end of a polar molecule's dipole. This is the dominant force responsible for the dissolution of ionic compounds in water: water molecules orient their partially negative O atom toward dissolved cations and their partially positive H atoms toward dissolved anions, a process called **hydration**. Ion–dipole forces are stronger than any purely-molecular IMF (hydrogen bonding included) because they involve a full ionic charge rather than just a partial charge.

Relative strength ordering (typical): ion–dipole $>$ hydrogen bonding $>$ dipole–dipole $>$ London dispersion. This ordering assumes comparable particle sizes; a sufficiently large, highly polarizable nonpolar molecule can have stronger net IMF (via LDF alone) than a small polar molecule — e.g. large nonpolar I_2 is a solid at room temperature while small polar HCl is a gas.

(!) Lỗi thường gặp: A very common error is thinking that polar molecules "don't have" London dispersion forces, or that only nonpolar molecules have LDF. **Every** atom and molecule has LDF — it is present in addition to any dipole–dipole or hydrogen-bonding interactions a polar molecule may also have. When ranking total IMF strength, do not ignore the LDF contribution even in strongly polar or hydrogen-bonding substances; for large polar molecules, LDF can be the single largest contributor to the total intermolecular attraction.

Ranking IMF strength across a mixed set

Rank the following in order of *increasing* boiling point, with reasoning: Ne, HCl, CH_3OH (methanol), NaCl.

Ne: nonpolar noble gas atom, only very weak LDF (few electrons) $\Rightarrow$ lowest b.p. (-246°C).
HCl: polar, LDF + dipole–dipole (no H-bonding, since Cl is not N/O/F) $\Rightarrow$ b.p. -85°C.
CH_3OH: has an O–H bond, so hydrogen bonds in addition to LDF and dipole–dipole $\Rightarrow$ b.p. 65°C.
NaCl: an ionic solid, held by full ionic (Coulombic) bonding throughout an extended lattice — far stronger than any intermolecular force $\Rightarrow$ b.p. 1465°C.
Order: Ne $<$ HCl $<$ CH_3OH $<$ NaCl.

3.2 Properties of solids

Compound	IMFs present	Notes
CH_4 (b.p. -161.5°C)	LDF only	Nonpolar, small, low polarizability
C_8H_{18} (octane, b.p. 126°C)	LDF only (stronger)	Same family as CH_4; far more electrons/surface area
PH_3 (b.p. -88°C)	LDF + weak dipole–dipole	P–H not a hydrogen-bond donor
H_2S (b.p. -60°C)	LDF + dipole–dipole	S–H not a hydrogen-bond donor
NH_3 (b.p. -33°C)	LDF + dipole–dipole + H-bond	N–H hydrogen-bonds
H_2O (b.p. 100°C)	LDF + dipole–dipole + H-bond ($\times 2$ donors, $\times 2$ acceptors)	Extensive H-bond network
HF (b.p. 20°C)	LDF + dipole–dipole + H-bond	Smallest hydrogen halide, yet highest b.p. among HX

Table 3.1: *

Boiling-point trends illustrating IMF type and strength. Note NH_3 boils lower than H_2O despite both hydrogen-bonding: H_2O has two O–H donors *and* two lone pairs, forming a denser hydrogen-bond network per molecule than NH_3's one lone pair.

3.2.1 Crystalline versus amorphous solids

In a **crystalline solid**, particles (atoms, ions, or molecules) are arranged in a highly ordered, repeating three-dimensional pattern called a **crystal lattice**. Crystalline solids have sharp, well-defined melting points because all the particle-particle interactions being broken are essentially identical, so they all give way at the same temperature. In an **amorphous solid** (e.g. glass, many plastics, rubber), particles are arranged with no long-range order — a "frozen liquid" structure. Amorphous solids soften gradually over a range of temperatures rather than melting sharply, because the variety of local particle environments means different regions break down at slightly different temperatures.

3.2.2 The four types of crystalline solids

Crystalline solids are classified by the type of particle at each lattice point and the force holding them together.

Khái niệm cốt lõi

- **Ionic solids**: lattice points are cations and anions, held by strong, nondirectional Coulombic (ionic) attraction throughout the lattice. Example: NaCl, CaF_2.
- **Molecular solids**: lattice points are discrete molecules, held together by intermolecular forces (LDF, dipole–dipole, hydrogen bonding) — the covalent bonds *within* each molecule are strong, but the forces *between* molecules are comparatively weak. Example: ice (H_2O), dry ice (CO_2), sucrose.
- **Network covalent (covalent-network) solids**: every atom is joined to its neighbors by covalent bonds extending throughout the entire crystal — essentially one giant covalently-bonded molecule. Example: diamond (C), quartz (SiO_2), silicon carbide.
- **Metallic solids**: lattice points are metal cations immersed in a delocalized "sea" of valence electrons free to move throughout the structure. Example: Cu, Fe, alloys.

Solid type	Melting point	Electrical conductivity	Hardness	Solubility
Ionic	High	Poor as solid; **good molten or aqueous** (mobile ions)	Hard, brittle	Often soluble in water (polar solvent)
Molecular	Low to moderate	Poor (no free charge carriers)	Soft	Soluble in solvents of similar polarity ("like dissolves like")
Network covalent	Very high	Usually poor (exception: graphite conducts *within* its layers)	Very hard	Insoluble in virtually all solvents
Metallic	Variable (low, e.g. Hg, to very high, e.g. W)	**Excellent**, solid or molten (delocalized electrons)	Variable; malleable/-ductile	Insoluble (except in other liquid metals)

VN **GIẢI THÍCH TIẾNG VIỆT**

Bốn loại chất rắn kết tinh: **ion** (mạng ion, dẫn điện khi nóng chảy/hoà tan vì ion di chuyển tự do, nhưng KHÔNG dẫn điện ở trạng thái rắn); **phân tử** (các phân tử liên kết với nhau bằng lực liên phân tử yếu, nên nhiệt độ nóng chảy thấp, mềm); **cộng hoá trị mạng lưới** (toàn bộ tinh thể là một mạng liên kết cộng hoá trị liên tục, cực kỳ cứng và nóng chảy ở nhiệt độ rất cao, ví dụ kim cương, thạch anh); **kim loại** (mạng cation kim loại trong "biển electron" tự do, dẫn điện tốt ở mọi trạng thái, dẻo, dễ dát mỏng).

(!) Lỗi thường gặp: Graphite is a network covalent solid but conducts electricity — an apparent exception. Within each hexagonal carbon layer, one electron per carbon is delocalized across the sheet (similar to metallic bonding confined to two dimensions), allowing conduction *parallel* to the layers; conduction *perpendicular* to the layers is poor because adjacent layers are held only by weak LDF. Do not generalize "network covalent = never conducts" without noting this exception.

Classifying an unknown solid from its properties

A solid has a melting point of 3550°C, does not conduct electricity as a solid or when melted, and is insoluble in water. Classify its solid type.

Extremely high melting point rules out molecular (too low) and most ionic solids (typically 300–1000°C). No conductivity even when molten rules out ionic (molten ionic solids conduct via mobile ions) and metallic (always conducts). The combination of very high melting point, no conductivity in any state, and insolubility is characteristic of a **network covalent solid** (this description matches diamond).

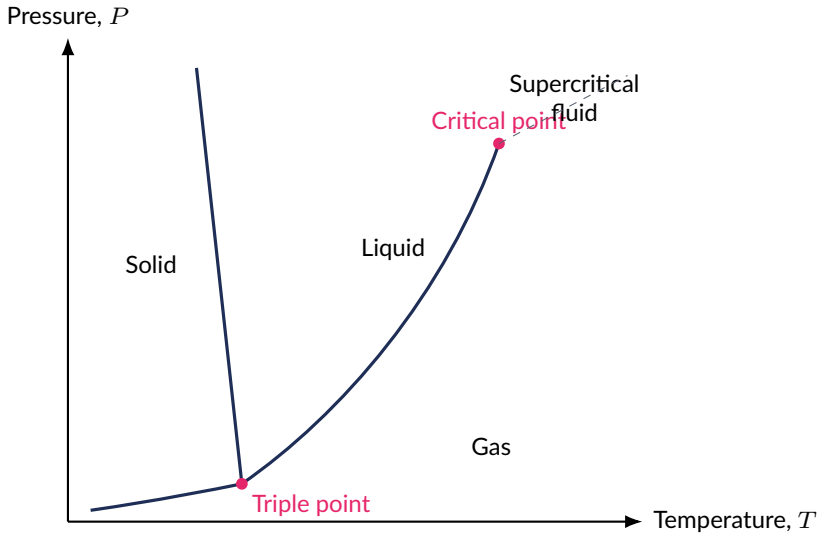
3.3 Solids, liquids, and gases

The three common states of matter differ in the average spacing between particles, the strength of the forces holding them in place, and the freedom of particle motion.

- **Solid**: particles are closely packed in fixed, ordered (or amorphous) positions; they vibrate in place but do not translate freely. Solids have a fixed shape and fixed volume, and are essentially incompressible.
- **Liquid**: particles remain close together (similar spacing to a solid) but are free to slide past one another. Liquids have a fixed volume but take the shape of their container, and are nearly incompressible.
- **Gas**: particles are separated by large distances (roughly $10\times$ the particle diameter or more) and move independently at high speed, with negligible attractive forces between them under ordinary conditions. Gases expand to fill their container's volume and shape completely and are highly compressible.

3.3.1 Phase diagrams

A **phase diagram** plots pressure (vertical axis) against temperature (horizontal axis) and shows which phase (solid, liquid, or gas) is thermodynamically stable at each (P, T) combination. Lines on the diagram represent conditions of two-phase equilibrium; a point where two phases coexist means both are present simultaneously.



Generic phase diagram: solid, liquid, and gas regions meet at the *triple point* (all three phases coexist in equilibrium); the liquid–gas boundary terminates at the *critical point*, beyond which no distinct liquid/gas phase boundary exists (supercritical fluid).

Triple point: the unique (P, T) at which solid, liquid, and gas coexist in equilibrium simultaneously. **Critical point**: the (P, T) beyond which the liquid and gas phases become indistinguishable (a **supercritical fluid**) — above the critical temperature, no amount of pressure can condense the gas into a distinct liquid phase. Moving vertically at fixed T (increasing P) or horizontally at fixed P (increasing T) traces a path across the diagram that crosses phase boundaries, predicting phase changes.

VN **GIẢI THÍCH TIẾNG VIỆT**

Giản đồ pha biểu diễn miền tồn tại của rắn, lỏng, khí theo áp suất và nhiệt độ. **Điểm ba** (triple point) là nơi cả ba pha cùng tồn tại cân bằng. **Điểm tới hạn** (critical point) là giới hạn trên của đường lỏng–khí; vượt qua điểm này, không còn phân biệt được pha lỏng và khí (gọi là chất lưu siêu tới hạn). Đường ranh giới rắn–lỏng của nước có độ dốc **âm** (nghiêng trái) — điểm bất thường vì đá kém đặc hơn nước lỏng, nên tăng áp suất tại nhiệt độ gần 0°C có thể làm đá tan

chảy thay vì đông đặc thêm.

Reading a phase diagram

Using the generic phase diagram above (triple point near low P, T; critical point at higher P, T), a substance sits initially in the liquid region at moderate P and T. If temperature is held constant while pressure is steadily decreased, which phase transition(s) will it undergo?

Moving straight down (decreasing P at constant T) starting from the liquid region eventually crosses the liquid–gas boundary line; below that boundary lies the gas region. The substance therefore undergoes **vaporization** (liquid → gas) as pressure drops below the equilibrium vapor pressure at that temperature. If the constant-T vertical line is drawn to the left of the triple point's temperature, decreasing pressure from a solid starting point instead crosses directly into the gas region without passing through liquid — this is **sublimation**.

3.4 The ideal gas law, $PV = nRT$

The **ideal gas law** relates the four macroscopic state variables of a gas sample:

$$PV = nRT,$$

where P is pressure (atm), V is volume (L), n is amount (mol), T is absolute temperature (K, *never* °C), and $R = 0.08206$ L·atm/(mol·K) is the ideal gas constant (equivalently $R = 8.314$ J/(mol·K) when using SI pressure/volume units). This single equation subsumes Boyle's Law ($P_1V_1 = P_2V_2$ at constant n, T), Charles's Law ($V_1/T_1 = V_2/T_2$ at constant n, P), Gay-Lussac's Law ($P_1/T_1 = P_2/T_2$ at constant n, V), and Avogadro's Law ($V_1/n_1 = V_2/n_2$ at constant P, T).

Combined gas law (fixed amount of gas, n constant): $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$. At **STP** ($0$°C $= 273.15$ K, 1 atm), one mole of an *ideal* gas occupies exactly 22.4 L — the standard molar volume. This value applies *only* at 0°C and 1 atm; it is a common error to apply 22.4 L/mol at room temperature (25°C) or any other condition.

(!) Lỗi thường gặp: 22.4 L/mol is valid *only* at STP (0°C, 1 atm) for an ideal gas. At room temperature (25°C $= 298$ K), one mole of ideal gas at 1 atm occupies $V = \dfrac{nRT}{P} = \dfrac{(1)(0.08206)(298)}{1} = 24.5$ L — noticeably different. Always check whether a problem specifies STP before reaching for 22.4 L/mol; when in doubt, use $PV = nRT$ directly with the given temperature and pressure.

Solving for pressure

A rigid 5.00 L cylinder contains 0.750 mol of N_2 gas at 22°C. Find the pressure inside the cylinder.

Convert temperature to kelvin: $T = 22 + 273 = 295$ K.

$$P = \frac{nRT}{V} = \frac{(0.750)(0.08206)(295)}{5.00} = \frac{18.16}{5.00} = 3.63 \text{ atm}.$$

Solving for volume

How many liters does 2.50 mol of CO_2 gas occupy at 1.20 atm and 310 K?

$$V = \frac{nRT}{P} = \frac{(2.50)(0.08206)(310)}{1.20} = \frac{63.60}{1.20} = 53.0 \text{ L}.$$

Solving for moles and mass

A sealed flask holds O_2 gas at 3.00 atm and 290 K in a volume of 8.00 L. Find the number of moles and the mass of O_2 present.

$$n = \frac{PV}{RT} = \frac{(3.00)(8.00)}{(0.08206)(290)} = \frac{24.00}{23.80} = 1.008 \text{ mol}.$$

Mass: $m = n \times M = (1.008)(32.00 \text{ g/mol}) = 32.3$ g.

Molar mass and density of a gas from PV=nRT

A 0.622 g sample of an unknown gas occupies 500.0 mL at 1.00 atm and $25.0°$C. Find the molar mass of the gas.

$T = 25.0 + 273 = 298$ K; $V = 0.5000$ L. First find moles:

$$n = \frac{PV}{RT} = \frac{(1.00)(0.5000)}{(0.08206)(298)} = \frac{0.5000}{24.45} = 0.02045 \text{ mol}.$$

Molar mass:

$$M = \frac{m}{n} = \frac{0.622 \text{ g}}{0.02045 \text{ mol}} = 30.4 \text{ g/mol}.$$

This value is close to the molar mass of NO (30.0 g/mol), a plausible identity for the unknown gas.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương trình khí lý tưởng $PV = nRT$ là công cụ trung tâm: từ đây suy ra công thức tính **khối lượng mol** của khí chưa biết bằng cách tìm n từ P, V, T rồi chia khối lượng mẫu cho n: $M = \frac{mRT}{PV}$. Luôn đổi nhiệt độ sang Kelvin ($T(K) = T(°\text{C}) + 273$) trước khi thay vào công thức — đây là lỗi sai phổ biến nhất khi giải bài tập khí.

3.4.1 Dalton's Law of partial pressures

In a mixture of non-reacting gases, each gas exerts a **partial pressure** P_i — the pressure it would exert alone in the same container at the same temperature. **Dalton's Law** states that the total pressure is the sum of the partial pressures:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots$$

Because each gas occupies the full container volume at the same temperature, mole fraction and pressure fraction are equal: $P_i = \chi_i \, P_{\text{total}}$, where $\chi_i = n_i / n_{\text{total}}$.

Dalton's Law: partial pressures from moles

A 10.0 L tank at 300 K contains 0.400 mol N_2, 0.100 mol O_2, and 0.0500 mol CO_2. Find the partial pressure of each gas and the total pressure.

Total moles: $n_{\text{total}} = 0.400 + 0.100 + 0.0500 = 0.550$ mol.

$$P_{\text{total}} = \frac{n_{\text{total}}RT}{V} = \frac{(0.550)(0.08206)(300)}{10.0} = \frac{13.54}{10.0} = 1.354 \text{ atm}.$$

Mole fractions: $\chi(N_2) = \dfrac{0.400}{0.550} = 0.727$, $\chi(O_2) = \dfrac{0.100}{0.550} = 0.182$, $\chi(CO_2) = \dfrac{0.0500}{0.550} = 0.0909$.

$P(N_2) = 0.727(1.354) = 0.985$ atm, $P(O_2) = 0.182(1.354) = 0.246$ atm, $P(CO_2) = 0.0909(1.354) = 0.123$ a

Check: $0.985 + 0.246 + 0.123 = 1.354$ atm $= P_{\text{total}}$. ✓

VN **GIẢI THÍCH TIẾNG VIỆT**

Định luật Dalton: áp suất tổng của hỗn hợp khí bằng tổng áp suất riêng phần của từng khí thành phần, và áp suất riêng phần của một khí tỉ lệ với **phần mol** của nó trong hỗn hợp ($P_i = \chi_i P_{\text{total}}$). Bài toán "khí thu qua nước" (collected over water) thường yêu cầu trừ áp suất hơi nước bão hoà khỏi áp suất tổng đo được để tìm áp suất khí khô.

3.5 Kinetic molecular theory

The **kinetic molecular theory (KMT)** of gases explains macroscopic gas behavior (pressure, the gas laws) in terms of particle-level motion, resting on several idealized postulates.

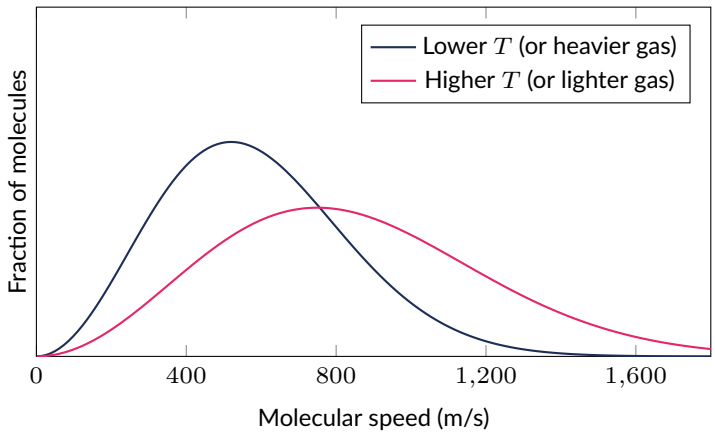
Postulates of KMT

1. Gas particles are in constant, random, straight-line motion until they collide.
2. The volume of the gas particles themselves is negligible compared to the volume of the container (particles are treated as point masses).
3. Gas particles exert no attractive or repulsive forces on one another (no intermolecular forces).
4. Collisions between particles, and between particles and container walls, are perfectly **elastic** — no kinetic energy is lost in a collision.
5. The average kinetic energy of gas particles is directly proportional to the **absolute temperature** (in kelvin) of the gas, and is the *same* for all gases at a given temperature regardless of molar mass: $\overline{KE} = \frac{3}{2}RT$ (per mole).

Because average kinetic energy depends only on absolute temperature and $\overline{KE} = \frac{1}{2}m\overline{v^2}$, at a fixed temperature a *lighter* gas particle must move *faster*, on average, than a heavier one to have the same average kinetic energy.

3.5.1 The Maxwell–Boltzmann speed distribution

Not all particles in a gas sample move at the same speed; collisions constantly redistribute kinetic energy among particles. The **Maxwell–Boltzmann distribution** plots the fraction of particles (vertical axis) against particle speed (horizontal axis), producing a characteristic asymmetric curve: it rises from zero (very few particles are at rest), climbs to a peak at the **most probable speed**, then tails off gradually toward high speed (a long right-hand tail, since no upper speed limit exists, but very few particles reach extremely high speeds).



Maxwell–Boltzmann speed distributions. Raising temperature (or decreasing molar mass) shifts the peak to higher speed, broadens and flattens the curve, and shifts more of the area under the curve into the high-speed tail — while the total area (100% of particles) stays fixed.

Effect of increasing temperature (fixed gas): the curve shifts right (higher most-probable speed) and flattens/broadens (a wider spread of speeds), because more particles gain enough energy to move quickly.

Effect of increasing molar mass (fixed temperature): the curve shifts left (lower most-probable speed) and narrows/sharpens, because heavier particles move slower on average and the spread of possible speeds is more constrained at the same average kinetic energy.

VN **GIẢI THÍCH TIẾNG VIỆT**

Đường phân bố Maxwell–Boltzmann mô tả tỉ lệ phần trăm phân tử khí có một tốc độ nhất định. Khi **tăng nhiệt độ**, đỉnh đường cong dịch sang phải (tốc độ phổ biến tăng) và đường cong dẹt/rộng ra (đa dạng tốc độ hơn). Khi so sánh hai khí ở **cùng nhiệt độ**, khí có khối lượng mol **nhỏ hơn** sẽ có đường cong dịch sang phải hơn (tốc độ trung bình lớn hơn) — vì động năng trung bình như nhau ở cùng T, khối lượng nhỏ hơn buộc tốc độ phải lớn hơn để bù lại.

3.5.2 Graham's Law of effusion

Effusion is the escape of gas particles through a tiny opening into a vacuum (or region of lower pressure). **Graham's Law** states that the rate of effusion of a gas is inversely proportional to the square root of its molar mass:

$$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{M_2}{M_1}}.$$

Lighter gases effuse (and diffuse) faster than heavier gases, directly reflecting their higher average speeds at a given temperature.

Graham's Law: ratio of effusion rates

Compare the effusion rate of H_2 ($M = 2.02$ g/mol) to that of O_2 ($M = 32.00$ g/mol) at the same temperature.

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

Hydrogen gas effuses about 3.98 times faster than oxygen gas under identical conditions.

Graham's Law: finding an unknown molar mass

An unknown gas effuses 0.462 times as fast as O_2 gas at the same temperature and pressure. Find the molar mass of the unknown gas.

$$\frac{\text{rate(unk)}}{\text{rate}(O_2)} = \sqrt{\frac{M(O_2)}{M(\text{unk})}} \Rightarrow 0.462 = \sqrt{\frac{32.00}{M(\text{unk})}}.$$

Square both sides: $0.2134 = \dfrac{32.00}{M(\text{unk})} \Rightarrow M(\text{unk}) = \dfrac{32.00}{0.2134} = 150.0$ g/mol.

VN **GIẢI THÍCH TIẾNG VIỆT**

Định luật Graham: tốc độ thoát khí (effusion) tỉ lệ nghịch với căn bậc hai của khối lượng mol. Khí càng nhẹ thoát ra càng nhanh. Công thức $\dfrac{\text{rate}_1}{\text{rate}_2} = \sqrt{\dfrac{M_2}{M_1}}$ — chú ý khối lượng mol nằm **chéo** so với tốc độ (khí 1 ở tử số tốc độ nhưng M_1 ở mẫu số căn), đây là điểm học sinh dễ nhầm khi thay số.

3.6 Deviation from ideal gas behavior

Real gases only approximate the ideal gas law; deviations become significant under conditions that violate the KMT assumptions of negligible particle volume and no intermolecular attraction.

Real gases deviate most from ideal behavior at:

- **High pressure**: particles are forced close together, so their own finite volume becomes a non-negligible fraction of the total volume, and intermolecular attractions (which act at short range) become significant.
- **Low temperature**: particles move more slowly, spending more time near one another, so intermolecular attractive forces have more effect on their trajectories and can no longer be ignored. Near the point of condensation, deviation is most severe.

The **van der Waals equation** adds two correction terms to the ideal gas law to account for these effects qualitatively:

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT.$$

The term an^2/V^2 is added back to the measured pressure because intermolecular attractions pull particles toward each other and away from the container walls, making the *measured* pressure lower than what an ideal gas at the same n, V, T would exert — the correction compensates for this "lost" pressure. The term nb is subtracted from the container volume because the particles themselves occupy real volume, so the space actually available for particle motion is less than the full container volume V.

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Khí thực lệch khỏi khí lý tưởng nhiều nhất ở **áp suất cao** (thể tích riêng của phân tử không còn bỏ qua được) và **nhiệt độ thấp** (lực hút giữa các phân tử trở nên đáng kể vì phân tử chuyển động chậm, ở gần nhau lâu hơn). Phương trình van der Waals hiệu chỉnh hai yếu tố này: cộng thêm an^2/V^2 vào áp suất đo được (bù cho áp suất "mất đi" do lực hút phân tử), và trừ nb khỏi thể tích bình chứa (bù cho thể tích riêng của phân tử).

Ranking gases by ideality

Rank He, CH_4, and NH_3 from *most* to *least* ideal behavior at the same moderate pressure and temperature.

Ideal behavior is favored by small particle size (small b) and weak intermolecular attraction (small a). He is a small, monatomic, nonpolar noble gas with minimal LDF — closest to ideal. CH_4 is nonpolar but larger, with somewhat stronger LDF than He. NH_3 is polar and hydrogen-bonds, giving it the strongest intermolecular attractions of the three and the largest deviation from ideal behavior. Order (most to least ideal): He $>$ CH_4 $>$ NH_3.

(!) Lỗi thường gặp: Do not assume that a gas with a *larger* molar mass automatically deviates more from ideality — the size/volume correction (b) does tend to increase with molar mass, but the *attraction* correction (a) depends on polarity and hydrogen-bonding ability, not simply mass. A small polar/hydrogen-bonding gas like NH_3 ($M = 17.0$ g/mol) deviates more than a larger but nonpolar gas like CH_4 ($M = 16.0$ g/mol) would suggest from mass alone — always consider IMF type, not just size.

3.7 Solutions and mixtures

A **solution** is a homogeneous mixture in which one substance (the **solute**, present in smaller amount) is dispersed uniformly throughout another (the **solvent**, present in larger amount) at the molecular or ionic level. Solutions can form from combinations of any two phases: gas-in-gas (air), gas-in-liquid (carbonated water, CO_2 in water), liquid-in-liquid (ethanol in water), solid-in-liquid (salt water), and solid-in-solid (metal alloys such as brass).

3.7.1 Molarity and dilution

The most common concentration unit in AP Chemistry is **molarity**:

$$M = \frac{\text{mol solute}}{\text{L solution}}.$$

When a solution is diluted by adding solvent, the *moles* of solute stay constant, so $M_1V_1 = M_2V_2$ (moles before $=$ moles after).

Molarity from mass and volume

A solution is prepared by dissolving 14.6 g of NaCl ($M = 58.44$ g/mol) in enough water to make 250.0 mL of solution. Find its molarity.

$$n(\text{NaCl}) = \frac{14.6}{58.44} = 0.2499 \text{ mol}.$$

$$M = \frac{0.2499 \text{ mol}}{0.2500 \text{ L}} = 1.00 \text{ M}.$$

Dilution calculation

How many milliliters of 6.00 M H_2SO_4 stock solution are needed to prepare 250.0 mL of 0.500 M H_2SO_4?

$$M_1V_1 = M_2V_2 \;\Rightarrow\; V_1 = \frac{M_2V_2}{M_1} = \frac{(0.500)(250.0)}{6.00} = 20.8 \text{ mL}.$$

Measure 20.8 mL of the 6.00 M stock and dilute with water to a total volume of 250.0 mL.

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Molarity $M = \dfrac{\text{mol chất tan}}{\text{L dung dịch}}$ — chú ý mẫu số là thể tích **dung dịch**, không phải thể tích dung môi. Khi pha loãng, số mol chất tan **không đổi**, chỉ có thể tích tăng lên, dẫn đến công thức $M_1V_1 = M_2V_2$. Đây là công thức dùng cực nhiều trong phòng thí nghiệm để pha dung dịch chuẩn từ dung dịch gốc (stock solution).

3.7.2 Solubility rules for ionic compounds (qualitative)

Generally soluble: compounds of Na^+, K^+, NH_4^+ (nearly all salts of these cations); all nitrates (NO_3^-) and acetates; most chlorides, bromides, iodides (exceptions: Ag^+, Pb^{2+}, Hg_2^{2+}); most sulfates (exceptions: Ba^{2+}, Sr^{2+}, Pb^{2+}, Ca^{2+} is only slightly soluble).

Generally insoluble: most carbonates, phosphates, hydroxides, and sulfides (exceptions again include Na^+, K^+, NH_4^+ salts, which remain soluble).

3.8 Representations of solutions

3.8.1 Particulate representations

At the particulate level, a dissolved **ionic** solute is represented as fully separated, individually hydrated cations and anions dispersed throughout the solvent (reflecting complete dissociation of a strong electrolyte). A dissolved **molecular** solute (e.g. glucose, ethanol) is represented as intact, whole molecules dispersed throughout the solvent — the molecule does not break apart into ions, since no ionic bonds exist to dissociate.

(!) Lỗi thường gặp: When asked to draw or interpret a particulate diagram of a dissolved ionic compound like $MgCl_2$, do NOT draw intact "$MgCl_2$" formula units floating in solution. A strong electrolyte dissociates completely: the correct picture shows separate Mg^{2+} ions and *twice as many* Cl^- ions (reflecting the $1{:}2$ stoichiometry), each individually surrounded by oriented water molecules.

3.8.2 Concentration units beyond molarity

Khái niệm cốt lõi

- **Mass percent**: $\%\text{(m/m)} = \dfrac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$.
- **Parts per million / billion**: for very dilute solutions, $\text{ppm} = \dfrac{\text{mass solute}}{\text{mass solution}} \times 10^6$; $\text{ppb} = \dfrac{\text{mass solute}}{\text{mass solution}} \times 10^9$. For aqueous solutions near room temperature, 1 ppm ≈ 1 mg solute per liter of solution (since 1 L of dilute aqueous solution has a mass of ≈ 1000 g).
- **Mole fraction**: $\chi_i = \dfrac{n_i}{n_{\text{total}}}$ (dimensionless; all mole fractions in a mixture sum to 1).

Mass percent and ppm

A solution contains 0.0250 g of lead dissolved in 500.0 g of water. Express the concentration as mass percent and as ppm.

Total solution mass $\approx 500.0 + 0.0250 = 500.0$ g (solute mass is negligible next to solvent mass

here).

$$\%\text{(m/m)} = \frac{0.0250}{500.0} \times 100 = 0.00500\%.$$

$$\text{ppm} = \frac{0.0250}{500.0} \times 10^6 = 50.0 \text{ ppm}.$$

Mole fraction

A solution is made from 36.0 g of water ($M = 18.0$ g/mol) and 46.0 g of ethanol, C_2H_5OH ($M = 46.0$ g/mol). Find the mole fraction of ethanol.

$$n(H_2O) = \frac{36.0}{18.0} = 2.00 \text{ mol}, \qquad n(C_2H_5OH) = \frac{46.0}{46.0} = 1.00 \text{ mol}.$$

$$\chi(\text{ethanol}) = \frac{1.00}{2.00 + 1.00} = \frac{1.00}{3.00} = 0.333.$$

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Ba đơn vị nồng độ hay bị nhầm lẫn: **% khối lượng** dùng khối lượng chất tan chia khối lượng **dung dịch** (không phải dung môi); **ppm/ppb** là mở rộng của % khối lượng cho dung dịch rất loãng (nhân 10^6 hoặc 10^9 thay vì 100); **phần mol** χ_i dùng **số mol**, không phải khối lượng, và luôn nằm trong khoảng 0 đến 1, tổng các phần mol trong hỗn hợp luôn bằng 1.

(!) Lỗi thường gặp: A frequent mistake is computing mole fraction using masses directly (as if it were mass percent) instead of converting to moles first. Mole fraction *requires* a mole-based ratio; two solutes of very different molar mass can have very different mole fractions even with identical masses present.

3.9 Separation of solutions and mixtures

Different physical methods separate mixtures by exploiting differences in physical properties between the components.

Khái niệm cốt lõi

- **Filtration**: separates an insoluble solid from a liquid (or solution) by passing the mixture through a porous barrier that retains solid particles but allows liquid to pass through.
- **Distillation**: separates components of a liquid mixture based on differences in **boiling point**. The mixture is heated; the component with the lower boiling point vaporizes preferentially, and the vapor is then cooled and condensed separately, enriching the distillate in the more volatile component. **Fractional distillation** uses a column with many theoretical "plates" to achieve sharper separation between components of similar boiling point.
- **Chromatography**: separates components of a mixture based on differences in how strongly each component interacts with a **stationary phase** versus a moving **mobile phase**. Components that interact more strongly with the stationary phase travel more slowly (lag behind); components that partition more into the mobile phase travel farther/faster.

3.9.1 Chromatography and the retention factor

In **paper** or **thin-layer chromatography**, a spot of the mixture is placed near the bottom of a strip (stationary phase, e.g. paper or a silica-coated plate), and the bottom edge is dipped in a solvent (mobile phase) that travels up the strip by capillary action, carrying the mixture's components at different rates. The **retention factor** R_f quantifies how far a given component traveled relative to the solvent front:

$$R_f = \frac{\text{distance traveled by the spot}}{\text{distance traveled by the solvent front}}.$$

R_f is always between 0 (component does not move at all — very strongly retained by the stationary phase) and 1 (component moves exactly with the solvent front — essentially no retention). Under fixed conditions (same solvent, same stationary phase, same temperature), R_f is a characteristic, reproducible property of a given substance, useful for identification.

Calculating retention factor

On a chromatography plate, the solvent front travels 8.40 cm from the origin. A particular compound's spot is found 5.46 cm from the origin. Find its R_f value.

$$R_f = \frac{5.46}{8.40} = 0.650.$$

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Sắc ký (chromatography) tách hỗn hợp dựa trên mức độ tương tác khác nhau giữa từng thành phần với pha tĩnh (stationary phase) và pha động (mobile phase, thường là dung môi di chuyển). Hệ số lưu (retention factor) $R_f = \dfrac{\text{quãng đường vết di chuyển}}{\text{quãng đường dung môi di chuyển}}$, luôn nằm trong khoảng 0 đến 1. Chưng cất (distillation) tách hỗn hợp lỏng dựa trên **khác biệt điểm sôi**; lọc (filtration) tách rắn không tan khỏi lỏng dựa trên kích thước hạt.

3.10 Solubility

3.10.1 "Like dissolves like"

The general principle governing solubility is that substances with **similar types of intermolecular forces** tend to be miscible/soluble in one another, while substances with very different IMF character tend to be immiscible/insoluble. Polar solutes (and ionic compounds) dissolve readily in polar solvents (like water) because the solvent's dipoles or ion–dipole attractions can effectively replace the solute-solute attractions being broken. Nonpolar solutes dissolve in nonpolar solvents (like hexane) because only comparable-strength LDF need to be overcome and re-formed.

Predicting solubility from structure

Predict whether I_2 (nonpolar) is more soluble in water (polar) or in carbon tetrachloride, CCl_4 (nonpolar).

I_2 is a nonpolar molecule held together only by LDF. Dissolving it in water would require breaking water's extensive hydrogen-bond network to accommodate a nonpolar solute that cannot form comparably strong ion–dipole or hydrogen-bonding interactions with water — energetically unfavorable. In CCl_4, only LDF-type interactions are involved on both sides, so the solute can dissolve without disrupting stronger interactions. I_2 is far more soluble in CCl_4 than in water.

3.10.2 Temperature and pressure effects on solubility

Solid solutes in liquids: solubility usually **increases** with increasing temperature (dissolution of most ionic/molecular solids is endothermic; adding heat shifts the dissolution equilibrium toward more dissolved solute), though there are exceptions.

Gas solutes in liquids: solubility usually **decreases** with increasing temperature. Dissolving a gas is generally exothermic (the gas particles lose significant kinetic energy/entropy on entering the liquid), so increasing temperature drives dissolved gas back out of solution — this is why a warm carbonated beverage goes flat faster and why heated water releases dissolved air as tiny bubbles before it even boils.

Pressure effect on gas solubility — Henry's Law: the solubility of a gas in a liquid is directly proportional to the partial pressure of that gas above the liquid: $C_{\text{gas}} = k_H P_{\text{gas}}$. Higher partial pressure of a gas above a liquid drives more of that gas into solution (this is why carbonated beverages are bottled under high CO_2 pressure, and why deep-sea divers must decompress slowly to avoid excess dissolved N_2 forming bubbles in the blood as pressure drops).

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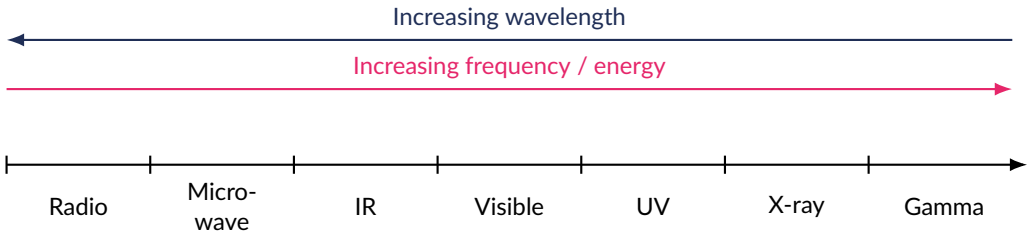
Độ tan của **chất rắn** trong chất lỏng thường **tăng** khi nhiệt độ tăng. Ngược lại, độ tan của **chất khí** trong chất lỏng thường **giảm** khi nhiệt độ tăng (nước ấm giữ ít khí hoà tan hơn nước lạnh). Định luật Henry: độ tan của khí tỉ lệ thuận với áp suất riêng phần của khí đó phía trên bề mặt chất lỏng — áp suất càng cao, khí hoà tan càng nhiều (ứng dụng: nước ngọt có ga được đóng chai dưới áp suất CO_2 cao).

3.11 Spectroscopy and the electromagnetic spectrum

Electromagnetic radiation carries energy in discrete packets called **photons**. The energy of a photon relates to its frequency f and wavelength λ by:

$$E = hf = \frac{hc}{\lambda},$$

where $h = 6.626 \times 10^{-34}$ J·s (Planck's constant) and $c = 3.00 \times 10^{8}$ m/s (speed of light). Because E and f are directly proportional while E and λ are inversely proportional, **higher-frequency (shorter-wavelength) radiation carries more energy per photon**.



The electromagnetic spectrum, arranged from lowest energy/frequency (radio, longest wavelength) to highest energy/frequency (gamma rays, shortest wavelength).

Order of increasing energy/frequency (decreasing wavelength) across the EM spectrum: radio $<$ microwave $<$ infrared (IR) $<$ visible $<$ ultraviolet (UV) $<$ X-ray $<$ gamma ray. Within the visible region, red light has the longest wavelength/lowest energy and violet light has the shortest wavelength/highest energy.

Photon energy from wavelength

Find the energy of a single photon of green light with $\lambda = 520$ nm.
Convert to meters: $\lambda = 520 \times 10^{-9}$ m $= 5.20 \times 10^{-7}$ m.

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})(3.00 \times 10^{8})}{5.20 \times 10^{-7}} = \frac{1.988 \times 10^{-25}}{5.20 \times 10^{-7}} = 3.82 \times 10^{-19} \text{ J}.$$

3.11.1 Absorption and emission spectra; electronic transitions

When an atom or molecule absorbs a photon whose energy exactly matches the energy gap between two allowed electronic energy levels, an electron is promoted from a lower to a higher energy level — this produces dark lines (missing wavelengths) in an **absorption spectrum** viewed against a continuous light source. When an electron relaxes from a higher to a lower energy level, it emits a photon of energy exactly equal to the gap between those levels, producing bright lines at specific wavelengths in an **emission spectrum**. Because energy levels in an atom are quantized (only specific discrete values are allowed), both absorption and emission spectra consist of sharp lines at characteristic wavelengths rather than a continuous range — each element has a unique spectral "fingerprint."

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Năng lượng photon $E = hf = \frac{hc}{\lambda}$: tần số càng cao (bước sóng càng ngắn) thì năng lượng mỗi photon càng lớn. Thứ tự năng lượng tăng dần trên phổ điện từ: radio < vi sóng < hồng ngoại < ánh sáng khả kiến < tử ngoại < tia X < tia gamma. **Phổ hấp thụ** xuất hiện vạch tối khi electron nhảy lên mức năng lượng cao hơn (hấp thụ photon đúng năng lượng); **phổ phát xạ** xuất hiện vạch sáng khi electron rơi xuống mức thấp hơn (phát ra photon). Mỗi nguyên tố có phổ vạch đặc trưng riêng vì các mức năng lượng bị lượng tử hoá.

3.12 The photoelectric effect

The **photoelectric effect** is the emission of electrons from a metal surface when light of sufficiently high frequency strikes it. Each metal has a characteristic **work function** ϕ — the minimum energy needed to eject an electron from that metal's surface. Light below a certain **threshold frequency** f_0 (where $hf_0 = \phi$) cannot eject any electrons at all, no matter how intense the light is, because no single photon carries enough energy to overcome ϕ (photons do not "add up" their energy from different absorption events). Above the threshold frequency, any excess photon energy beyond ϕ becomes the ejected electron's kinetic energy:

$$KE_{\text{max}} = hf - \phi.$$

Increasing light intensity at a fixed frequency above threshold increases the *number* of photons striking the surface per second, and therefore the *number* of electrons ejected per second (photocurrent) — but does *not* change the maximum kinetic energy of each individual ejected electron, since each electron is ejected by a single photon of the same fixed energy hf. Only *increasing the frequency* of the light increases KE_{max}.

Threshold frequency and work function

The work function of sodium metal is $\phi = 3.65 \times 10^{-19}$ J. Find the threshold frequency below which the photoelectric effect cannot occur.

$$f_0 = \frac{\phi}{h} = \frac{3.65 \times 10^{-19}}{6.626 \times 10^{-34}} = 5.51 \times 10^{14} \text{ Hz}.$$

Maximum kinetic energy of ejected electrons

Light of wavelength 200.0 nm strikes a metal with work function $\phi = 4.20 \times 10^{-19}$ J. Find the maximum kinetic energy of the ejected electrons.

First find the photon energy: $\lambda = 2.000 \times 10^{-7}$ m.

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})(3.00 \times 10^{8})}{2.000 \times 10^{-7}} = 9.939 \times 10^{-19} \text{ J}.$$

$$KE_{\text{max}} = E_{\text{photon}} - \phi = 9.939 \times 10^{-19} - 4.20 \times 10^{-19} = 5.74 \times 10^{-19} \text{ J}.$$

Since $E_{\text{photon}} > \phi$, ejection does occur, and the excess energy above the work function becomes the electron's kinetic energy.

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Hiệu ứng quang điện: chỉ khi tần số ánh sáng vượt **tần số ngưỡng** f_0 (ứng với công thoát $\phi = hf_0$) thì electron mới bị bật ra khỏi bề mặt kim loại, vì mỗi electron chỉ hấp thụ năng lượng từ **một photon duy nhất** (không cộng dồn từ nhiều photon yếu). **Tăng cường độ ánh sáng** (số photon/giây) ở cùng tần số chỉ làm tăng **số lượng** electron bật ra (dòng quang điện), KHÔNG làm tăng động năng cực đại của mỗi electron — chỉ **tăng tần số** mới làm tăng $KE_{\text{max}} = hf - \phi$.

(!) Lỗi thường gặp: A very common mistake is assuming brighter (more intense) light ejects *faster* electrons. Intensity only controls the *number* of photons per second, not the energy of each individual photon. KE_{max} depends solely on frequency (via $hf - \phi$); intensity affects only the *rate* of electron ejection (photocurrent), never KE_{max}.

3.13 The Beer--Lambert Law

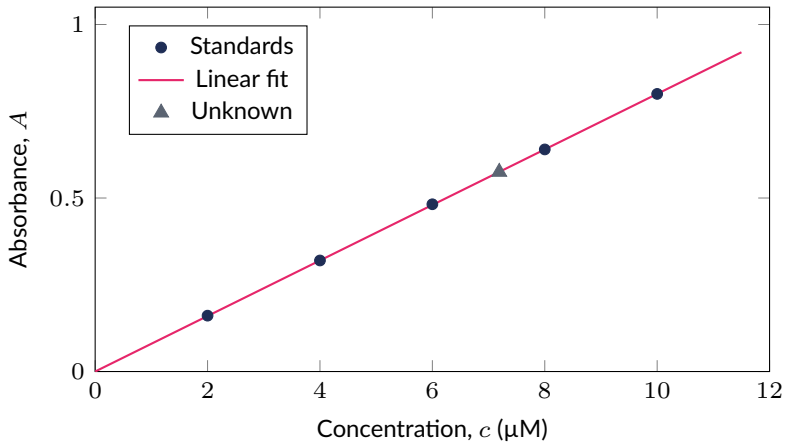
The **Beer–Lambert Law** relates how much light a solution absorbs to its concentration, forming the basis of quantitative spectrophotometric analysis:

$$A = \varepsilon b c,$$

where A is absorbance (dimensionless), ε is the **molar absorptivity** ($\text{M}^{-1}\text{cm}^{-1}$, a constant specific to the absorbing species at a given wavelength), b is the **path length** of light through the sample (cm, typically the width of a standard cuvette, 1.00 cm), and c is the molar concentration of the absorbing species (M). Because A is directly proportional to c at fixed ε and b, absorbance measurements provide a direct, convenient way to determine unknown concentrations.

3.13.1 Calibration curves

In practice, ε is often not known precisely, so a **calibration curve** is constructed: several solutions of *known* concentration are prepared, their absorbances are measured, and A is plotted against c. Because the Beer–Lambert Law predicts a straight line through the origin (slope $= \varepsilon b$), a linear regression fit to the standards gives an equation $A = (\text{slope})\, c + (\text{intercept})$. The absorbance of an unknown sample is then measured under the same conditions, and its concentration is read directly off the calibration line (interpolated, not extrapolated, for reliable results).



Beer–Lambert calibration curve: five standards of known concentration give a linear fit $A = 0.0800\,c$ ($\text{M}^{-1} \cdot \mu\text{M}$ units combine into a fitted slope through the origin). An unknown sample with measured $A = 0.575$ is read off the line at $c \approx 7.19\ \mu\text{M}$.

Finding concentration directly from $A = \varepsilon b c$

A solution has measured absorbance $A = 0.512$ at a wavelength where the molar absorptivity is $\varepsilon = 8.60 \times 10^3\ \text{M}^{-1}\text{cm}^{-1}$, measured in a standard 1.00 cm cuvette. Find the concentration.

$$c = \frac{A}{\varepsilon b} = \frac{0.512}{(8.60 \times 10^3)(1.00)} = 5.95 \times 10^{-5}\ \text{M}.$$

Using a calibration curve to find an unknown concentration

A calibration curve constructed from five standard solutions gives the linear regression equation $A = 0.0800\,c + 0.002$ (with c in μM and the intercept near zero, as expected from Beer's Law). An unknown sample measured under the same conditions gives $A = 0.575$. Find its concentration.

Solve the regression equation for c:

$$c = \frac{A - 0.002}{0.0800} = \frac{0.575 - 0.002}{0.0800} = \frac{0.573}{0.0800} = 7.16\ \mu\text{M}.$$

This matches (within rounding) the value read directly off the calibration graph above.

VN **GIẢI THÍCH TIẾNG VIỆT**

Định luật Beer–Lambert $A = \varepsilon b c$: độ hấp thụ quang tỉ lệ thuận với nồng độ (khi ε, b cố định). Trong thực hành, người ta thường KHÔNG tính trực tiếp bằng công thức mà dựng **đường chuẩn** (calibration curve): đo độ hấp thụ của một dãy dung dịch chuẩn đã biết nồng độ, vẽ đồ thị A theo c, tìm phương trình hồi quy tuyến tính, rồi đo độ hấp thụ mẫu chưa biết và **nội suy** (không ngoại suy) nồng độ từ đường chuẩn đó.

(!) Lỗi thường gặp: Reading a concentration off a calibration curve by *extrapolating* far beyond the range of the standard solutions used to build it is unreliable — the linear relationship of Beer's Law can break down at high concentration (light scattering, instrument saturation), so an unknown's absorbance should fall *within* the measured range of standards whenever possible. If it does not, the standards should be re-prepared to bracket the unknown, or the unknown should be diluted into range.

3.14 Practice Problems

Bài tập luyện tập

Which of the following best explains why Br_2 is a liquid at room temperature while Cl_2 is a gas, given that neither molecule is polar?

(A) Br_2 has stronger dipole–dipole forces

(B) Br_2 has a larger, more polarizable electron cloud, giving stronger London dispersion forces

(C) Br_2 forms hydrogen bonds

(D) Br_2 has ion–dipole forces with itself

Lời giải chi tiết

Both Cl_2 and Br_2 are nonpolar, so only LDF applies to either. Br_2 has more electrons and a larger, more easily distorted electron cloud than Cl_2, producing stronger LDF and hence a higher boiling point (sufficient to be liquid at room temperature). **(B)**.

Bài tập luyện tập

Explain, in terms of intermolecular forces, why n-pentane (b.p. $= 36^\circ$C) has a higher boiling point than its branched isomer neopentane (b.p. $= 9.5^\circ$C), even though both have the identical molecular formula C_5H_{12} (identical molar mass).

Lời giải chi tiết

Both molecules are nonpolar and have identical molar mass, so they experience LDF of comparable intrinsic strength based on electron count. However, n-pentane's long, straight chain allows extended surface-to-surface contact between neighboring molecules, maximizing the net LDF attraction. Neopentane's compact, nearly spherical shape (a central carbon with four methyl branches) minimizes the contact surface area between molecules, weakening the net LDF and lowering its boiling point relative to the straight-chain isomer.

Bài tập luyện tập

A 3.00 L container holds 0.500 mol of an ideal gas at 27°C. Find the pressure in atm.

(A) 3.42 atm

(B) 4.10 atm

(C) 1.37 atm

(D) 8.21 atm

Lời giải chi tiết

$T = 27 + 273 = 300$ K. $P = \dfrac{nRT}{V} = \dfrac{(0.500)(0.08206)(300)}{3.00} = \dfrac{12.31}{3.00} = 4.10$ atm. **(B)**.

Bài tập luyện tập

A gas sample occupies 12.0 L at 1.50 atm and 290 K. If the temperature is raised to 350 K and the pressure is increased to 2.00 atm, find the new volume.

Lời giải chi tiết

Combined gas law: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$.

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{(1.50)(12.0)(350)}{(290)(2.00)} = \frac{6300}{580} = \boxed{10.9\text{ L}}.$$

Bài tập luyện tập

A gas mixture at a total pressure of 2.20 atm contains He and Ar in a $3{:}1$ mole ratio. Find the partial pressure of each gas.

Lời giải chi tiết

Mole fractions: $\chi(\text{He}) = \frac{3}{4} = 0.750$, $\chi(\text{Ar}) = \frac{1}{4} = 0.250$.

$$P(\text{He}) = 0.750(2.20) = \boxed{1.65\text{ atm}}, \qquad P(\text{Ar}) = 0.250(2.20) = \boxed{0.550\text{ atm}}.$$

Bài tập luyện tập

A 1.243 g sample of an unknown gas occupies 750.0 mL at 0.985 atm and 27.0°C. Find its molar mass.

(A) 28.0 g/mol
(B) 32.6 g/mol
(C) 40.9 g/mol
(D) 44.1 g/mol

Lời giải chi tiết

$T = 300$ K. $n = \frac{PV}{RT} = \frac{(0.985)(0.7500)}{(0.08206)(300)} = \frac{0.7388}{24.62} = 0.03001$ mol. $M = \frac{1.243}{0.03001} = 41.4$ g/mol, closest to **(C)** 40.9 g/mol.

Bài tập luyện tập

Compare the root-mean-square speeds of He atoms and Ar atoms in the same container at the same temperature. Which statement is correct?

(A) They have equal speeds since T is the same
(B) He atoms move faster because they have lower molar mass
(C) Ar atoms move faster because they have more electrons
(D) Cannot be determined without pressure

Lời giải chi tiết

At equal T, average kinetic energy is equal for both gases ($\overline{KE} = \frac{3}{2}RT$, independent of identity). Since $KE = \frac{1}{2}mv^2$, the lighter atom (He, $M = 4.00$) must have a higher average speed than the heavier atom (Ar, $M = 39.95$) to share the same kinetic energy. **(B)**.

Bài tập luyện tập

Use Graham's Law to find the ratio of effusion rates of CH_4 ($M = 16.0$ g/mol) to CO_2 ($M = 44.0$ g/mol) at the same temperature.

Lời giải chi tiết

$$\frac{\text{rate}(CH_4)}{\text{rate}(CO_2)} = \sqrt{\frac{M(CO_2)}{M(CH_4)}} = \sqrt{\frac{44.0}{16.0}} = \sqrt{2.75} = \boxed{1.66}.$$

Methane effuses about 1.66 times faster than carbon dioxide.

Bài tập luyện tập

An unknown gas effuses 1.34 times faster than Cl_2 gas ($M = 70.90$ g/mol) under identical conditions. Find the molar mass of the unknown gas.

(A) 39.5 g/mol
(B) 52.9 g/mol
(C) 95.0 g/mol
(D) 127 g/mol

Lời giải chi tiết

$\frac{\text{rate(unk)}}{\text{rate}(Cl_2)} = \sqrt{\frac{M(Cl_2)}{M(\text{unk})}} \Rightarrow 1.34 = \sqrt{\frac{70.90}{M(\text{unk})}}$. Squaring: $1.796 = \frac{70.90}{M(\text{unk})} \Rightarrow M(\text{unk}) = \frac{70.90}{1.796} = 39.5$ g/mol. **(A)**.

Bài tập luyện tập

Which set of conditions causes a real gas to deviate *most* from ideal behavior?

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

Lời giải chi tiết

Deviation is greatest when particle volume and intermolecular attraction both matter most: high pressure crowds particles together (volume effect), and low temperature slows them down, letting attractive forces act (attraction effect). **(D)**.

Bài tập luyện tập

A student states that SF_6 should deviate from ideal gas behavior less than H_2O vapor at comparable conditions, despite SF_6's much larger molar mass. Evaluate this claim.

Lời giải chi tiết

The claim is reasonable. Although SF_6 ($M = 146.1$ g/mol) is far heavier than H_2O ($M = 18.0$ g/mol) and therefore has a larger excluded-volume correction b, SF_6 is a nonpolar, symmetric octahedral molecule with only LDF between its molecules. Water vapor, by contrast, hydrogen-bonds extensively, giving it a much larger attractive-force correction a per particle relative to its small size. Since deviation from ideality depends on *both* particle volume and attractive-

force strength, water's strong hydrogen bonding can make it deviate more than the larger but weakly-interacting SF_6, especially near water's condensation point. **The claim can be correct**, illustrating that molar mass alone does not predict ideality — IMF character matters at least as much.

Bài tập luyện tập

25.0 mL of 4.00 M stock KOH is diluted to a final volume of 1.00 L. Find the resulting molarity.

(A) 0.0400 M
(B) 0.100 M
(C) 0.400 M
(D) 1.00 M

Lời giải chi tiết

$M_2 = \dfrac{M_1 V_1}{V_2} = \dfrac{(4.00)(25.0)}{1000} = 0.100$ M. **(B).**

Bài tập luyện tập

A solution is prepared by dissolving 22.0 g of $CaCl_2$ ($M = 110.98$ g/mol) in enough water to make 400.0 mL of solution. Find the molarity of $CaCl_2$ and the molarity of chloride ion, Cl^-, in the solution.

Lời giải chi tiết

$n(CaCl_2) = \dfrac{22.0}{110.98} = 0.1982$ mol. $M(CaCl_2) = \dfrac{0.1982}{0.4000} = \boxed{0.496\ \text{M}}$.
Each formula unit releases 2 Cl^- ions on complete dissociation: $M(Cl^-) = 2 \times 0.496 = \boxed{0.991\ \text{M}}$.

Bài tập luyện tập

Predict the qualitative solubility (soluble / insoluble) in water of: (a) $AgNO_3$, (b) $PbSO_4$, (c) K_2CO_3, (d) $CaCO_3$.

Lời giải chi tiết

(a) $AgNO_3$: all nitrates are soluble regardless of cation ⇒ **soluble**.
(b) $PbSO_4$: sulfates are soluble except with Ba^{2+}, Sr^{2+}, Pb^{2+}, Ca^{2+} ⇒ **insoluble**.
(c) K_2CO_3: carbonates are generally insoluble, but K^+ salts are always soluble ⇒ **soluble**.
(d) $CaCO_3$: a carbonate with no soluble-cation exception ⇒ **insoluble**.

Bài tập luyện tập

A solution contains 0.0180 g of a trace contaminant in 600.0 g of total solution. Express its concentration in ppm.

(A) 3.00 ppm
(B) 30.0 ppm
(C) 300 ppm
(D) 0.0300 ppm

Lời giải chi tiết

ppm $= \dfrac{0.0180}{600.0} \times 10^6 = 30.0$ ppm. **(B).**

Bài tập luyện tập

A mixture of 18.0 g water and 90.0 g glucose ($C_6H_{12}O_6$, $M = 180.0$ g/mol) is prepared. Find the mole fraction of water.

(A) 0.667
(B) 0.500
(C) 0.167
(D) 0.833

Lời giải chi tiết

$n(H_2O) = \dfrac{18.0}{18.0} = 1.00$ mol; $n(\text{glucose}) = \dfrac{90.0}{180.0} = 0.500$ mol. Total moles $= 1.50$ mol.

$$\chi(H_2O) = \frac{1.00}{1.50} = \boxed{0.667}.$$

(A). (Choices (C) 0.167 and (D) 0.833 are the *mass* fractions of water and glucose, respectively — a common mix-up between mass fraction and mole fraction; choice (B) 0.500 comes from incorrectly treating the two components as present in equal moles.)

Bài tập luyện tập

Classify the following solid by its expected properties: melting point 1085°C, excellent electrical conductivity both as a solid and when molten, malleable (can be hammered into sheets without shattering).

(A) Ionic solid
(B) Molecular solid
(C) Network covalent solid
(D) Metallic solid

Lời giải chi tiết

Conductivity in the *solid* state (not just molten) rules out ionic solids (which only conduct molten/dissolved) and network covalent solids (generally nonconductors). Malleability (bends/deforms without breaking) rules out the brittle ionic and hard, brittle network-covalent options. Delocalized electrons allow both solid-state conductivity and malleability — characteristic of a **metallic solid** (this description matches copper). **(D).**

Bài tập luyện tập

Quartz (SiO_2) has an extremely high melting point (1713°C), is very hard, and does not conduct electricity in any state. Explain these properties in terms of its solid-state structure.

Lời giải chi tiết

Quartz is a **network covalent solid**: every Si atom is covalently bonded to four O atoms (and each O bridges two Si atoms) in a continuous three-dimensional covalent network extending throughout the entire crystal. Melting requires breaking a very large number of strong covalent Si–O bonds throughout the lattice (not just overcoming weak intermolecular forces), which de-

mands enormous thermal energy — hence the very high melting point. The rigid, fully-bonded network resists deformation, giving high hardness. Because all valence electrons are localized in fixed covalent bonds (none delocalized), there are no mobile charge carriers, so quartz does not conduct electricity as a solid; unlike an ionic solid, melting it does not free mobile ions either, since the bonding remains covalent throughout, so it remains a nonconductor even molten.

Bài tập luyện tập

On the generic phase diagram (triple point at low P, T; solid–liquid boundary with a steep positive slope; critical point at higher P, T), a sample begins in the solid region at a pressure below the triple-point pressure. Holding pressure constant, temperature is slowly increased. Which phase transition occurs?

(A) Melting (solid → liquid)
(B) Sublimation (solid → gas)
(C) Deposition (gas → solid)
(D) No phase change occurs

Lời giải chi tiết

At a pressure below the triple-point pressure, there is no temperature at which the liquid phase is stable — the horizontal path (constant P, increasing T) starting in the solid region crosses directly into the gas region, skipping the liquid phase entirely. This transition is **sublimation**. **(B)**.

Bài tập luyện tập

Water's solid–liquid phase boundary has a negative slope (unlike most substances). Explain what this implies about the relative densities of ice and liquid water, and predict what happens to an ice cube at 0°C when subjected to a large increase in pressure at constant temperature.

Lời giải chi tiết

A negative-slope solid–liquid boundary means that, moving from the solid region across the boundary into the liquid region requires an *increase* in pressure at constant temperature (or the boundary tilts left with increasing P, so the liquid region expands to lower temperatures as P rises). Since increasing pressure favors the phase with *smaller* volume (denser phase), and increasing pressure pushes the system from solid into liquid here, liquid water must be **denser than ice**. Consequently, applying sufficient pressure to an ice cube sitting exactly at 0°C can push the system across the solid–liquid boundary into the liquid region, **causing the ice to melt** under pressure alone, with no change in temperature.

Bài tập luyện tập

A mixture of two colored dyes is spotted onto chromatography paper. After development, the solvent front has traveled 9.60 cm from the origin. Dye A's spot is 7.68 cm from the origin; dye B's spot is 2.40 cm from the origin. Find the R_f value of each dye, and state which dye interacts more strongly with the stationary phase.

Lời giải chi tiết

$$R_f(\text{A}) = \frac{7.68}{9.60} = \boxed{0.800}, \qquad R_f(\text{B}) = \frac{2.40}{9.60} = \boxed{0.250}.$$

Dye B has the smaller R_f, meaning it traveled a much shorter relative distance — it is more strongly retained by (interacts more strongly with) the stationary phase, while dye A partitions more readily into the mobile phase and travels closer to the solvent front.

Bài tập luyện tập

A chemist needs to separate ethanol (b.p. 78°C) from water (b.p. 100°C) in a homogeneous liquid mixture, and separately needs to remove suspended, insoluble sand particles from a saltwater mixture. Identify the best separation technique for each task.

(A) Distillation for both

(B) Filtration for both

(C) Distillation for the ethanol/water mixture; filtration for the sand/saltwater mixture

(D) Filtration for the ethanol/water mixture; distillation for the sand/saltwater mixture

Lời giải chi tiết

The ethanol/water mixture is a homogeneous solution of two liquids with different boiling points — this calls for **distillation**, which separates based on volatility differences. Sand is an insoluble solid suspended in a liquid (saltwater) — this calls for **filtration**, which separates based on physical state/particle size, not boiling point (filtration cannot separate ethanol from water, since both pass through a filter as a homogeneous solution). **(C)**.

Bài tập luyện tập

Rank the following types of electromagnetic radiation from *lowest* to *highest* photon energy: visible light, X-ray, radio wave, ultraviolet.

(A) radio $<$ visible $<$ UV $<$ X-ray

(B) X-ray $<$ UV $<$ visible $<$ radio

(C) visible $<$ radio $<$ UV $<$ X-ray

(D) radio $<$ UV $<$ visible $<$ X-ray

Lời giải chi tiết

Photon energy increases with frequency (decreases with wavelength) in the order radio $<$ microwave $<$ IR $<$ visible $<$ UV $<$ X-ray $<$ gamma. Selecting from this ordering: radio $<$ visible $<$ UV $<$ X-ray. **(A)**.

Bài tập luyện tập

An X-ray photon has wavelength $\lambda = 0.154$ nm (a wavelength commonly used in X-ray diffraction). Find its energy in joules.

Lời giải chi tiết

$\lambda = 0.154 \times 10^{-9}$ m $= 1.54 \times 10^{-10}$ m.

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34})(3.00 \times 10^{8})}{1.54 \times 10^{-10}} = \frac{1.988 \times 10^{-25}}{1.54 \times 10^{-10}} = \boxed{1.29 \times 10^{-15}\ \text{J}}.$$

This is roughly 10^4 times more energetic than a visible-light photon, consistent with X-rays lying far to the high-energy end of the EM spectrum.

Bài tập luyện tập

A metal has a threshold frequency of 4.60×10^{14} Hz. If light of frequency 7.50×10^{14} Hz strikes the metal, find (a) the work function of the metal and (b) the maximum kinetic energy of the ejected electrons.

Lời giải chi tiết

(a) $\phi = hf_0 = (6.626 \times 10^{-34})(4.60 \times 10^{14}) = \boxed{3.05 \times 10^{-19}\ \text{J}}$.
(b) $KE_{\text{max}} = hf - \phi = (6.626 \times 10^{-34})(7.50 \times 10^{14}) - 3.05 \times 10^{-19} = 4.970 \times 10^{-19} - 3.05 \times 10^{-19} = \boxed{1.92 \times 10^{-19}\ \text{J}}$.

Bài tập luyện tập

In a photoelectric-effect experiment, the frequency of incident light is held constant above the threshold frequency while the intensity is doubled. What happens to (a) the number of electrons ejected per second and (b) the maximum kinetic energy of the ejected electrons?

(A) Both double
(B) (a) doubles, (b) stays the same
(C) (a) stays the same, (b) doubles
(D) Both stay the same

Lời giải chi tiết

Intensity reflects the number of photons striking the surface per second, not the energy per photon. Doubling intensity doubles the number of photons (and hence roughly doubles the number of electrons ejected per second, since each ejection event still consumes one photon). Because each photon still carries the same fixed energy hf (frequency unchanged), $KE_{\text{max}} = hf - \phi$ is unaffected. **(B)**.

Bài tập luyện tập

A calibration curve for a colored complex gives the linear regression $A = 1.25 \times 10^4\, c$ (c in M, with the fit forced through the origin as expected from Beer's Law, path length 1.00 cm). An unknown sample of this complex gives $A = 0.665$. Find its concentration.

(A) 5.32×10^{-5} M
(B) 8.31×10^{3} M
(C) 1.88×10^{-4} M
(D) 5.32×10^{-4} M

Lời giải chi tiết

$$c = \frac{A}{\text{slope}} = \frac{0.665}{1.25 \times 10^4} = 5.32 \times 10^{-5}\ \text{M}.$$

(A).

Bài tập luyện tập

Two solutions of the same absorbing species are measured in cuvettes of different path length: solution 1 in a 1.00 cm cuvette gives $A = 0.400$; solution 2, at the *same* concentration, is measured in a 2.50 cm cuvette. Predict A for solution 2.

Lời giải chi tiết

Since $A = \varepsilon bc$ and ε, c are identical between the two measurements, A scales directly with path length b:

$$A_2 = A_1 \times \frac{b_2}{b_1} = 0.400 \times \frac{2.50}{1.00} = \boxed{1.00}.$$

Bài tập luyện tập

Rank the following compounds from *lowest* to *highest* boiling point, briefly justifying the order: CH_3F ($M = 34.0$), CH_3OH ($M = 32.0$), C_2H_6 ($M = 30.1$).

Lời giải chi tiết

C_2H_6: nonpolar (symmetric, C–H and C–C bonds only), LDF only $\Rightarrow$ lowest boiling point (-89°C).
CH_3F: polar (C–F bond dipole not canceled), LDF + dipole–dipole, but F is not bonded to H so no hydrogen bonding $\Rightarrow$ intermediate boiling point (-78°C).
CH_3OH: has an O–H bond, so it hydrogen-bonds in addition to LDF and dipole–dipole, despite having the *smallest* molar mass of the three $\Rightarrow$ highest boiling point (65°C).
Order: $C_2H_6 < CH_3F < CH_3OH$. This illustrates that hydrogen bonding can dominate over both molar mass and simple bond polarity in determining relative boiling points.

Bài tập luyện tập

A nonpolar organic solute is added separately to (i) hexane (C_6H_{14}, nonpolar) and (ii) water (polar, hydrogen-bonding). In which solvent is the solute expected to be more soluble, and why?

(A) Water, because water is a universal solvent

(B) Hexane, by the "like dissolves like" principle

(C) Equal solubility in both

(D) Neither — nonpolar solutes are always insoluble

Lời giải chi tiết

"Like dissolves like": a nonpolar solute disperses readily among nonpolar solvent molecules held together only by comparably weak LDF, requiring no disruption of strong solvent–solvent interactions. Dissolving it in water would require breaking part of water's extensive hydrogen-bond network without gaining comparably strong solute–water attractions in return (a nonpolar solute cannot hydrogen-bond or align favorably with water's dipoles) — energetically unfavorable. **(B)**.

Bài tập luyện tập

A can of carbonated soda is sealed under high CO_2 partial pressure. Using Henry's Law and the temperature-dependence of gas solubility, explain (a) why the soda fizzes vigorously when opened, and (b) why a warm can of soda goes flat faster than a cold one even while both remain sealed and then opened similarly.

Lời giải chi tiết

(a) Henry's Law: dissolved gas concentration is proportional to the partial pressure of that gas above the liquid, $C_{CO_2} = k_H P_{CO_2}$. Before opening, the sealed can maintains a high partial pressure of CO_2 in the headspace, keeping a correspondingly high concentration of dissolved CO_2 in solution at equilibrium. Opening the can releases the pressurized headspace gas, sharply dropping P_{CO_2} to roughly atmospheric levels; the dissolved CO_2 concentration is now far above its new equilibrium solubility, so excess gas rapidly leaves solution as visible bubbles (fizzing). (b) Gas solubility in a liquid *decreases* as temperature increases (dissolution of a gas is generally exothermic). A warm can therefore holds less dissolved CO_2 at equilibrium even at the same sealed pressure, and loses its dissolved gas to the headspace/atmosphere more readily once opened — going flat faster than a cold can, which can hold more dissolved gas at the same pressure.

Bài tập luyện tập

A 250.0 mL flask contains O_2 gas collected over water at 24.0°C and a total (measured) pressure of 0.995 atm. The vapor pressure of water at 24.0°C is 0.0298 atm. Find the partial pressure of dry O_2 gas and the number of moles of O_2 collected.

Lời giải chi tiết

By Dalton's Law, the measured total pressure of gas collected over water is the sum of the partial pressure of the dry gas and the vapor pressure of water at that temperature: $P_{\text{total}} = P_{O_2} + P_{H_2O}$. Solving for the partial pressure of dry O_2:

$$P_{O_2} = P_{\text{total}} - P_{H_2O} = 0.995 - 0.0298 = \boxed{0.965 \text{ atm}}.$$

Converting temperature to Kelvin, $T = 24.0 + 273 = 297$ K, and using $V = 0.2500$ L, apply the ideal gas law to the dry O_2 alone (the water vapor has already been removed via its partial pressure):

$$n = \frac{PV}{RT} = \frac{(0.9652)(0.2500)}{(0.08206)(297)} = \frac{0.2413}{24.37} = \boxed{9.90 \times 10^{-3} \text{ mol}}.$$

Chemical Reactions

Mục tiêu Unit: Nhận biết bằng chứng của phản ứng hoá học và áp dụng định luật bảo toàn khối lượng để cân bằng phương trình hoá học; viết phương trình phân tử, phương trình ion đầy đủ và phương trình ion thu gọn dựa trên quy tắc độ tan; phân biệt biến đổi vật lý và biến đổi hoá học; giải bài toán chất giới hạn (limiting reactant), hiệu suất lý thuyết và hiệu suất phần trăm; thực hiện tính toán chuẩn độ acid–base để xác định nồng độ chưa biết; phân loại phản ứng (tổng hợp, phân huỷ, thế đơn dựa trên dãy hoạt động hoá học, thế đôi, đốt cháy); nắm định nghĩa acid–base theo Brønsted–Lowry và cặp acid–base liên hợp; gán số oxi hoá và cân bằng phương trình oxi hoá–khử bằng phương pháp bán phản ứng trong môi trường acid, xác định chất oxi hoá và chất khử.

4.1 Introduction to reactions

A **chemical reaction** converts one or more **reactants** into one or more **products** through the breaking and forming of chemical bonds, rearranging atoms into new substances with new chemical and physical properties. A **chemical equation** is the symbolic shorthand for this process: reactant formulas on the left, product formulas on the right, connected by a reaction arrow ($\rightarrow$), with state symbols (s), (l), (g), (aq) indicating the physical state of each species.

4.1.1 Evidence of chemical change

Because a chemical reaction produces genuinely new substances, it is typically detectable through one or more observable signs. No single sign is proof by itself (each can also accompany a purely physical process), but their combination is strong evidence that a reaction has occurred.

Observable evidence of a chemical reaction

- **Color change** — a new substance often absorbs/reflects light differently than the reactants (e.g. colorless $Pb^{2+}(aq)$ and $I^{-}(aq)$ combining to form bright yellow solid PbI_2).
- **Gas evolution** — bubbling or fizzing not caused by boiling (e.g. $Zn(s)$ reacting with acid to release $H_2(g)$).
- **Precipitate formation** — an insoluble solid appears from two clear solutions.
- **Temperature change** — heat is absorbed (endothermic) or released (exothermic) as bonds break and form, changing the internal chemical energy of the system.
- **Light emission** — chemiluminescence or a flame.
- **Odor change** — formation of a volatile substance with a new smell.

VN **GIẢI THÍCH TIẾNG VIỆT**

Một phản ứng hoá học thường đi kèm các dấu hiệu quan sát được: đổi màu, sủi bọt khí, xuất hiện kết tủa, thay đổi nhiệt độ (toả nhiệt/thu nhiệt), phát sáng, hoặc đổi mùi. Tuy nhiên, từng dấu hiệu riêng lẻ không phải là bằng chứng tuyệt đối (ví dụ đun sôi nước cũng sinh bọt khí nhưng đó chỉ là biến đổi vật lý) — cần xem xét tổng thể và đối chiếu với việc có hình thành chất mới hay không.

4.1.2 Conservation of mass

The **law of conservation of mass** states that mass is neither created nor destroyed in a chemical reaction: the total mass of all reactants consumed equals the total mass of all products formed. At the atomic level, this is because a chemical reaction only rearranges existing atoms into new bonding patterns — no atoms are created, destroyed, or converted into other elements. Consequently, a correctly balanced chemical equation must show the *same number of atoms of each element* on the reactant and product sides.

> Conservation of mass at the macroscopic level (total mass reactants = total mass products) and conservation of atoms at the particulate level (same count of each element on both sides of a balanced equation) are two expressions of the same underlying principle. A coefficient in a balanced equation reports the relative number of *moles* (or particles) reacting/forming — never a mass ratio directly, since different substances have different molar masses.

4.1.3 Balancing chemical equations

Balancing an equation means inserting whole-number **coefficients** in front of each formula so that the atom count of every element matches on both sides. Only coefficients may be adjusted — never the subscripts within a formula, since changing a subscript changes the identity of the substance itself (e.g. changing H_2O to H_2O_2 produces hydrogen peroxide, a completely different compound).

Systematic balancing strategy

1. Balance elements that appear in only one reactant and one product first, saving elements that appear in multiple species (often H and O) for later.
2. Balance polyatomic ions that survive unchanged through the reaction as a single unit rather than atom-by-atom, when possible.
3. For combustion reactions specifically, balance C, then H, then O last (O frequently requires a coefficient adjustment on O_2, sometimes fractional before scaling to whole numbers).
4. If a fractional coefficient is unavoidable partway through, multiply every coefficient in the equation by the fraction's denominator to clear it.
5. Verify by counting every atom of every element on both sides — and, for equations involving ions, verify that total charge also balances (Section 4.3).

VN **GIẢI THÍCH TIẾNG VIỆT**

Cân bằng phương trình hoá học nghĩa là thêm **hệ số** (không phải chỉ số) trước mỗi công thức sao cho số nguyên tử mỗi nguyên tố ở hai vế bằng nhau. Chiến lược thường dùng cho phản ứng đốt cháy: cân bằng C trước, rồi H, để O lại sau cùng vì O xuất hiện ở nhiều chất; nếu hệ số ra phân số (thường gặp với O_2), nhân toàn bộ phương trình với mẫu số để đưa về số nguyên nhỏ nhất.

Balancing a combustion equation

Balance the combustion of propane, C_3H_8, with oxygen gas to form carbon dioxide and water.

Step 1 — write the skeleton equation.

$$C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Step 2 — balance carbon. There are 3 C atoms in C_3H_8, so place a coefficient of 3 on CO_2:

$$C_3H_8 + O_2 \rightarrow 3CO_2 + H_2O$$

Step 3 — balance hydrogen. There are 8 H atoms in C_3H_8; each H_2O carries 2 H atoms, so 4 waters are needed:

$$C_3H_8 + O_2 \rightarrow 3CO_2 + 4H_2O$$

Step 4 — balance oxygen last. The right side now has $3(2) + 4(1) = 6 + 4 = 10$ O atoms, all supplied by O_2 on the left, so the coefficient on O_2 is $10/2 = 5$:

$$\boxed{C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)}$$

Check: C: $3 = 3$; H: $8 = 8$; O: $5(2) = 10$ and $3(2) + 4(1) = 10$. Balanced.

4.2 Net ionic equations

Many important reactions in chemistry occur in **aqueous solution**, where ionic compounds and certain molecular compounds separate into freely-moving ions. Writing every spectator ion out in full obscures which species actually participate in the chemistry — the **net ionic equation** strips away everything that does not change, showing only the actual chemical transformation.

4.2.1 Strong electrolytes and dissociation

A **strong electrolyte** dissociates (or ionizes) essentially completely into ions when dissolved in water, producing a solution that conducts electricity well. Strong electrolytes include:

Categories of strong electrolytes

- **Soluble ionic compounds** (salts) — apply the solubility rules (Section 4.2, table below) to decide whether a given ionic compound dissolves; if soluble, it dissociates 100% into its constituent ions.
- **Strong acids** — HCl, HBr, HI, HNO_3, H_2SO_4 (first proton), $HClO_4$, $HClO_3$ — ionize completely, e.g. $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$.
- **Strong bases** — Group 1 hydroxides (LiOH, NaOH, KOH, ...) and $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$ — whatever amount dissolves, dissociates completely into metal cation and OH^-.

By contrast, **weak electrolytes** (weak acids, weak bases) ionize only partially and remain predominantly as intact molecules in solution, while **nonelectrolytes** (most molecular compounds — sugars, alcohols, and other covalent compounds without acid/base character) dissolve without forming any ions at all. Weak and nonelectrolyte species are written as intact molecular formulas in every version of an equation, never split into ions.

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Chất điện li mạnh phân li **hoàn toàn** thành ion trong nước: muối tan (theo quy tắc độ tan), acid mạnh (7 acid mạnh cần nhớ: $HCl, HBr, HI, HNO_3, H_2SO_4$ (nấc 1), $HClO_4, HClO_3$), và base mạnh (hydroxide nhóm 1 và $Ca(OH)_2, Sr(OH)_2, Ba(OH)_2$). Chất điện li yếu (acid yếu, base yếu) chỉ phân li một phần — viết dưới dạng phân tử nguyên vẹn trong phương trình ion, KHÔNG được tách thành ion.

4.2.2 Solubility rules

Ion	Solubility	Exceptions
Group 1 cations (Li^+, Na^+, K^+, Rb^+, Cs^+), NH_4^+	Soluble	none
Nitrate NO_3^-, acetate $C_2H_3O_2^-$	Soluble	none
Chloride, bromide, iodide (Cl^-, Br^-, I^-)	Soluble	Ag^+, Pb^{2+}, Hg_2^{2+} insoluble
Sulfate SO_4^{2-}	Soluble	$BaSO_4$, $PbSO_4$ insoluble; $CaSO_4$ slightly soluble
Carbonate CO_3^{2-}, phosphate PO_4^{3-}	Insoluble	soluble only with Group 1 cations or NH_4^+
Hydroxide OH^-	Insoluble	soluble with Group 1 cations; $Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$ slightly soluble

Table 4.1: *
Reference solubility rules for common ionic compounds in water. To predict whether mixing two aqueous solutions produces a precipitate, identify the two possible new ionic pairings (double replacement) and check each against this table.

4.2.3 Molecular, complete ionic, and net ionic equations

Three levels of representation

- **Molecular equation**: every compound written as a whole neutral formula, exactly as one would measure it out in the lab.
- **Complete ionic equation**: every strong electrolyte is rewritten as its separated ions; substances that are solid, liquid, gaseous, weak, or nonelectrolytic remain as full formulas.
- **Net ionic equation**: any ion appearing *identically* on both sides of the complete ionic equation — a **spectator ion** — is cancelled, leaving only the species that actually undergo chemical change.

Molecular, complete ionic, and net ionic equations for a precipitation reaction

Write the molecular, complete ionic, and net ionic equations for mixing aqueous calcium chloride and aqueous sodium carbonate.

Molecular equation. Predict the double-replacement products: Ca^{2+} pairs with CO_3^{2-} (carbonate, insoluble except Group 1/NH_4^+ — so $CaCO_3$ precipitates), and Na^+ pairs with Cl^- (soluble):

$$CaCl_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaCl(aq)$$

Complete ionic equation. Dissociate every soluble strong electrolyte ($CaCl_2$, Na_2CO_3, NaCl); the precipitate $CaCO_3(s)$ stays as a solid formula unit:

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) + 2Na^+(aq) + 2Cl^-(aq)$$

Net ionic equation. Cancel the spectator ions Na^+ and Cl^-, which appear unchanged on both sides:

$$\boxed{Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)}$$

Charge check: left side $(+2) + (-2) = 0$; right side (neutral solid) $= 0$. Balanced in both atoms and charge.

(!) Lỗi thường gặp: A frequent mistake is dissociating *every* compound in the complete ionic equation, including weak acids, weak bases, molecular gases, and insoluble solids. Only *soluble strong electrolytes* are split into ions. A weak acid like CH_3COOH, a gas like $CO_2(g)$, water $H_2O(l)$, and any precipitate marked (s) must all be written as full, undissociated formulas in the complete ionic equation — treating them as if they were strong electrolytes produces an incorrect net ionic equation.

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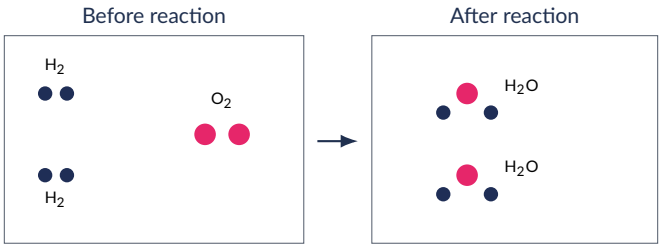
Phương trình ion đầy đủ chỉ tách các chất điện li mạnh **tan** thành ion; các chất khí, chất lỏng nguyên chất (nước), chất kết tủa (rắn), và chất điện li yếu vẫn giữ nguyên dạng phân tử. Phương trình ion thu gọn (net ionic equation) loại bỏ các ion khán giả (spectator ions) — ion xuất hiện giống hệt ở cả hai vế mà không tham gia phản ứng thực sự — chỉ giữ lại các tiểu phân thực sự biến đổi.

4.3 Representations of reactions

4.3.1 Particulate-level diagrams

Chemical equations describe reactions at the macroscopic and formula level, but chemists also reason at the **particulate (molecular) level** — visualizing individual atoms and molecules rearranging. A particulate diagram represents each species as a small circle or cluster of circles (color-coded by element), showing a "before" box of reactant particles and an "after" box of product particles.



Particulate representation of $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$: two H_2 molecules (navy pairs) and one O_2 molecule (pink pair) rearrange into two H_2O molecules. Atom count is conserved on both sides: 4 H atoms and 2 O atoms.

Translating between formula equations and particulate diagrams

- The *number of discrete particles drawn* in a box should be in the smallest whole-number ratio matching the balanced equation's coefficients (or an exact multiple of it).
- Molecules that do not react (excess reactant, or a spectator species present but uninvolved) appear unchanged in both the "before" and "after" boxes.
- A correct particulate diagram never creates or destroys individual atoms — every atom present in the "before" box must be accounted for, bonded differently, in the "after" box.
- Diagrams can also depict a mixture that has *not yet* reacted completely, useful for identifying which reactant is limiting purely from particle counts (Section 4.5).

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Sơ đồ hạt (particulate diagram) biểu diễn phản ứng ở cấp độ phân tử: mỗi vòng tròn là một nguyên tử, mã màu theo nguyên tố. Số hạt vẽ trong hộp "trước phản ứng" và "sau phản ứng" phải theo đúng tỉ lệ hệ số cân bằng (hoặc bội số của tỉ lệ đó). Nguyên tắc quan trọng: tổng số nguyên tử mỗi loại phải giữ nguyên — không hạt nào biến mất hay xuất hiện thêm.

4.3.2 Balancing verified by atom count and charge

For *molecular* equations, a correct balance requires only that atom counts match on both sides. For equations that include *ions* (complete ionic and net ionic equations), a second, independent check is required: **total charge must also balance** — the sum of all ionic charges on the reactant side must equal the sum on the product side, even though the total charge need not be zero.

Verifying a redox equation by both atom count and charge

Confirm that the following net ionic equation is correctly balanced: $\mathrm{Zn(s)} + 2\mathrm{Ag^+(aq)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\mathrm{Ag(s)}$.

Atom check: 1 Zn atom on each side; 2 Ag atoms on each side. Atoms balance.
Charge check: left side, $\mathrm{Zn(s)}$ is neutral (0) and $2\mathrm{Ag^+}$ contributes $2(+1) = +2$, for a total of $+2$. Right side, $\mathrm{Zn^{2+}}$ contributes $+2$ and $2\mathrm{Ag(s)}$ is neutral (0), for a total of $+2$. Both sides equal $+2$ — charge balances.
Both checks pass, confirming this is a validly balanced net ionic (and, as will be shown in Section 4.9, redox) equation.

4.4 Physical and chemical changes

4.4.1 Distinguishing physical and chemical change

A **physical change** alters the form, phase, or arrangement of a substance without changing its chemical identity — no bonds within molecules or formula units are broken or newly formed between different substances, and the same molecules/ions present at the start are still present at the end (though possibly in a different phase or physically mixed with other particles). A **chemical change** breaks and forms chemical bonds, converting reactants into products with different chemical formulas, different molecular structure, and different physical/chemical properties.

Physical vs. chemical change: key examples

- **Phase changes** (melting, freezing, boiling, condensing, subliming) — physical. The substance's formula and bonding are unchanged; only the spacing/organization/kinetic energy of the particles changes.
- **Dissolution of an ionic compound** — physical. When $\mathrm{NaCl(s)}$ dissolves in water, the ionic lattice separates into hydrated $\mathrm{Na^+(aq)}$ and $\mathrm{Cl^-(aq)}$ ions — these ions already existed as discrete charged species within the solid lattice; no new substance is formed, and evaporating the water regenerates the original NaCl.
- **Mixing without reaction** (e.g. stirring sand into water) — physical; components retain their individual identities and can be separated by physical means.
- **Any process forming a new substance** with a new chemical formula — rusting, combustion, precipitation, gas evolution from a reaction, digestion of food — chemical. Bonds within the reactant molecules break, and new bonds form to create products with fundamentally different composition.

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Biến đổi vật lý (physical change) chỉ thay đổi hình dạng/trạng thái/cách sắp xếp của chất — không có liên kết hoá học nào bị phá vỡ hay hình thành giữa các chất khác nhau, chất vẫn giữ nguyên bản chất hoá học. Ví dụ: nóng chảy, sôi, hoà tan muối ăn vào nước (các ion $\mathrm{Na^+}$, $\mathrm{Cl^-}$ vốn đã tồn tại sẵn trong mạng tinh thể, chỉ được hydrat hoá chứ không tạo ra chất mới). Biến đổi hoá học (chemical change) tạo ra chất mới với công thức và tính chất hoàn toàn khác — ví

dụ gỉ sắt, đốt cháy, tạo kết tủa.

4.4.2 Conservation of atoms across both types of change

Whether a change is physical or chemical, the **total number of atoms of each element is always conserved** — atoms are neither created nor destroyed by ordinary physical or chemical processes (only nuclear reactions change elemental identity, which lies outside the scope of chemical reactions). The distinguishing question is not "are atoms conserved?" (they always are) but "are the atoms bonded together in the same molecular/ionic arrangement before and after?" A physical change answers yes; a chemical change answers no.

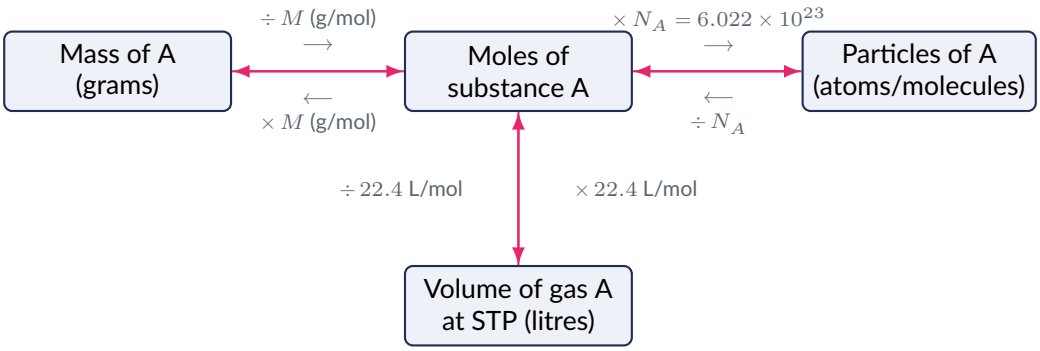
Classifying changes and applying conservation of atoms

Classify each process as physical or chemical, and state what is conserved in each case: (a) ice melting at 0°C; (b) $AgNO_3(aq)$ mixed with $NaCl(aq)$ forming a white precipitate; (c) dissolving CO_2 gas into water to make carbonated water (no reaction, simple physical dissolution of a gas).

(a) **Physical.** H_2O molecules are identical in the solid and liquid phase; only the rigid hydrogen-bonded lattice breaks down into a more disordered, mobile arrangement. The number of H_2O molecules (and H, O atoms) is unchanged.
(b) **Chemical.** New ionic bonding arrangement forms: Ag^+ and Cl^-, previously each surrounded by water and other counter-ions, combine into a new solid, $AgCl(s)$, with distinct physical properties (insoluble, white) from either reactant. Atom counts (Ag, N, O, Na, Cl) are conserved throughout, but the bonding pattern is entirely different from the reactants.
(c) **Physical.** CO_2 molecules remain intact and chemically unchanged; they are simply dispersed among water molecules (a small fraction does react reversibly to form carbonic acid, H_2CO_3, but the bulk dissolution process itself, and the classic "dissolving a gas in a liquid" description, is physical).

4.5 Stoichiometry

Stoichiometry is the quantitative study of the mole relationships between reactants and products in a balanced chemical equation. The coefficients of a balanced equation give the exact **mole ratio** in which substances react and form — this ratio is the conversion factor for every stoichiometric calculation.



The stoichiometry "mole map": moles is the central hub connecting mass (via molar mass M), particle count (via Avogadro's number N_A), and gas volume at STP only (via 22.4 L/mol, valid strictly at 0°C and 1 atm). To convert between two *different* substances (A to B), always pass through moles of each and apply the mole ratio from the balanced equation.

4.5.1 Mole ratios from balanced equations

General stoichiometric roadmap

To convert a known quantity of substance A into a quantity of substance B using a balanced equation:

1. Convert the given quantity of A into **moles of A** (using molar mass, Avogadro's number, or 22.4 L/mol at STP, as appropriate).
2. Multiply by the **mole ratio** $\frac{\text{coefficient of B}}{\text{coefficient of A}}$ from the balanced equation to obtain moles of B.
3. Convert moles of B into whatever final unit is requested (mass, particles, volume at STP, or concentration).

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Sơ đồ mol (mole map) đặt **số mol** làm trung tâm: từ khối lượng (chia cho khối lượng mol M), số hạt (nhân với số Avogadro N_A), hoặc thể tích khí ở đktc (22.4 L/mol — chỉ áp dụng ở 0°C, 1 atm) đều quy về số mol trước, rồi mới dùng **tỉ lệ hệ số** trong phương trình cân bằng để chuyển sang số mol chất khác.

4.5.2 Limiting reactant

When reactants are not combined in the exact stoichiometric mole ratio required by the balanced equation, one reactant will be completely consumed first — this is the **limiting reactant** (or limiting reagent), and it determines the maximum possible amount of product, the **theoretical yield**. Any reactant remaining unconsumed when the limiting reactant runs out is the **excess reactant**.

Identifying the limiting reactant

Convert every given reactant quantity into moles. Then, for each reactant, calculate how many moles of a chosen product *would* form if that reactant were used up completely (dividing by its own coefficient and multiplying by the product's coefficient). The reactant that predicts the *smaller* amount of product is the limiting reactant — it runs out first and caps the reaction. Equivalently, divide moles of each reactant by its own coefficient in the balanced equation; the smallest resulting value identifies the limiting reactant.

(!) Lỗi thường gặp: A very common error is assuming the reactant present in the smaller *mass* (grams) — or the smaller number of grams given in the problem — is automatically the limiting reactant. Limiting reactant is determined by **mole ratios**, not raw mass. A reactant can be present as fewer grams yet still be in stoichiometric excess if its molar mass is much smaller than the other reactant's, or if the balanced equation requires many fewer moles of it. Always convert to moles and compare against the balanced coefficients before drawing a conclusion.

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Chất giới hạn (limiting reactant) là chất phản ứng hết trước, quyết định lượng sản phẩm tối đa (hiệu suất lý thuyết — theoretical yield). **Lỗi thường gặp:** học sinh hay nhầm chất có khối lượng gam nhỏ hơn là chất giới hạn — đây là sai lầm, vì phải quy đổi về **số mol** và so với tỉ lệ hệ số trong phương trình mới xác định được chất nào hết trước.

Limiting reactant and theoretical yield

When 50.0 g of N_2 is combined with 10.0 g of H_2 and allowed to react completely according to $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, determine the limiting reactant and the theoretical yield of NH_3 in grams.

Convert to moles. $M(N_2) = 2(14.01) = 28.02$ g/mol; $M(H_2) = 2(1.008) = 2.016$ g/mol.

$$n(N_2) = \frac{50.0}{28.02} = 1.784 \text{ mol}, \qquad n(H_2) = \frac{10.0}{2.016} = 4.960 \text{ mol}$$

Determine the limiting reactant. The equation requires 3 mol H_2 per 1 mol N_2. For all 1.784 mol N_2 to react, $1.784 \times 3 = 5.353$ mol H_2 would be needed — but only 4.960 mol H_2 is available. Since the available H_2 falls short of what full reaction of the N_2 would require, H_2 **is the limiting reactant** (and N_2 is in excess).

Theoretical yield of NH_3, based entirely on the limiting reactant H_2 (mole ratio $NH_3 : H_2 = 2 : 3$):

$$n(NH_3) = 4.960 \text{ mol } H_2 \times \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2} = 3.307 \text{ mol } NH_3$$

$M(NH_3) = 14.01 + 3(1.008) = 17.034$ g/mol, so

$$\boxed{m(NH_3) = 3.307 \text{ mol} \times 17.034 \text{ g/mol} = 56.33 \text{ g (theoretical yield)}}$$

4.5.3 Percent yield

In practice, real reactions rarely achieve their full theoretical yield — side reactions, incomplete reactions, and mechanical loss during transfer/purification all reduce the actual mass of product recovered, the **actual yield**. The **percent yield** quantifies reaction efficiency:

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Percent yield calculation

In the reaction of Example above ($N_2 + 3H_2 \rightarrow 2NH_3$, theoretical yield 56.33 g NH_3), a chemist actually collects 42.5 g of NH_3. Calculate the percent yield.

$$\% \text{ yield} = \frac{42.5 \text{ g}}{56.33 \text{ g}} \times 100\% = \boxed{75.4\%}$$

A percent yield below 100% is expected and normal; it reflects real experimental losses (e.g. some product lost during filtration, an equilibrium reaction that does not go fully to completion, or a competing side reaction). Percent yield can never exceed 100% for a correctly identified theoretical yield — an apparent yield over 100% signals a measurement or purity error (Section *Practice Problems*, Problem 31).

VN **GIẢI THÍCH TIẾNG VIỆT**

Hiệu suất phần trăm $= \dfrac{\text{lượng thực tế thu được}}{\text{lượng lý thuyết tính toán}} \times 100\%$. Hiệu suất luôn nhỏ hơn hoặc bằng 100% trong điều kiện lý tưởng — nếu tính ra hiệu suất vượt quá 100%, nguyên nhân thường là sản phẩm thu được còn lẫn tạp chất (chưa sấy khô hoàn toàn, còn nước hoặc chất phản ứng dư), chứ không phải phản ứng tạo ra nhiều sản phẩm hơn giới hạn lý thuyết cho phép.

4.5.4 Mass-to-mass and gas stoichiometry

Mass-to-mass stoichiometry

How many grams of CO_2 are produced by the complete combustion of 25.0 g of propane, C_3H_8, according to $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ (excess O_2 assumed)?
$M(C_3H_8) = 3(12.01) + 8(1.008) = 44.094$ g/mol.

$$n(C_3H_8) = \frac{25.0}{44.094} = 0.5670 \text{ mol}$$

Mole ratio $CO_2 : C_3H_8 = 3 : 1$:

$$n(CO_2) = 0.5670 \text{ mol} \times \frac{3}{1} = 1.701 \text{ mol}$$

$M(CO_2) = 12.01 + 2(16.00) = 44.01$ g/mol:

$$\boxed{m(CO_2) = 1.701 \text{ mol} \times 44.01 \text{ g/mol} = 74.86 \text{ g}}$$

Gas stoichiometry at STP

What volume of O_2 gas, measured at STP, is required to completely combust 10.0 g of methane, CH_4, via $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$?
$M(CH_4) = 12.01 + 4(1.008) = 16.042$ g/mol.

$$n(CH_4) = \frac{10.0}{16.042} = 0.6234 \text{ mol}$$

Mole ratio $O_2 : CH_4 = 2 : 1$:

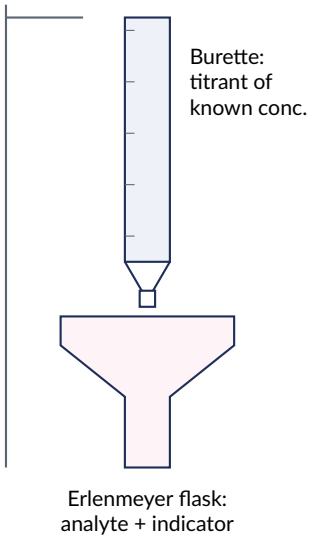
$$n(O_2) = 0.6234 \text{ mol} \times \frac{2}{1} = 1.247 \text{ mol}$$

At STP, 1 mol of any ideal gas occupies 22.4 L:

$$\boxed{V(O_2) = 1.247 \text{ mol} \times 22.4 \text{ L/mol} = 27.9 \text{ L}}$$

4.6 Introduction to titration

Titration is a laboratory technique for determining the unknown concentration (or amount) of one solution (the **analyte**) by reacting it, in a precisely measured and controlled way, with a solution of known concentration (the **titrant**). In an acid-base titration, titrant is added slowly from a **burette** into a flask containing a measured volume of analyte plus a few drops of **indicator**, a substance that changes color at (or very near) the point of complete reaction.



Titration setup: titrant of known molarity is added dropwise from the burette into the analyte until the indicator signals that the equivalence (end) point has been reached.

4.6.1 Equivalence point and titration calculations

The **equivalence point** is reached when the moles of titrant added have exactly reacted, in the stoichiometric ratio given by the balanced equation, with all the moles of analyte originally present. For a simple $1:1$ monoprotic acid-base reaction, this means moles acid $=$ moles base at equivalence; for reactions with other stoichiometric ratios, the mole ratio from the balanced equation must be applied.

Titration calculation procedure

1. Record the volume of titrant delivered at the equivalence point (from the burette).
2. Compute moles of titrant $= M_{\text{titrant}} \times V_{\text{titrant}}$.
3. Use the balanced equation's mole ratio to convert moles of titrant into moles of analyte.
4. Divide by the known volume of analyte to obtain its molarity (or, if a mass of solid analyte was used, divide by that mass to determine molar mass, or vice versa).

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Chuẩn độ (titration) xác định nồng độ chưa biết của dung dịch phân tích (analyte) bằng cách cho phản ứng với thể tích chính xác của dung dịch chuẩn (titrant) đã biết nồng độ, đến khi đạt **điểm tương đương** (equivalence point — chất chỉ thị đổi màu báo hiệu). Công thức cốt lõi: số mol titrant $= M \times V$, sau đó dùng tỉ lệ hệ số phương trình cân bằng để suy ra số mol analyte, rồi chia cho thể tích analyte để có nồng độ mol.

Titration calculation for unknown molarity

A 25.00 mL sample of an HCl solution of unknown concentration is titrated with 0.1050 M NaOH. The equivalence point is reached after 32.46 mL of NaOH has been added. Find the molarity of the HCl solution.

Balanced equation: $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$ — a $1:1$ mole ratio.

Moles of titrant (NaOH):

$$n(\text{NaOH}) = (0.03246\ \text{L})(0.1050\ \text{M}) = 3.408 \times 10^{-3}\ \text{mol}$$

Moles of analyte (HCl), using the $1:1$ ratio: $n(\text{HCl}) = 3.408 \times 10^{-3}$ mol.

Molarity of HCl:

$$M(\text{HCl}) = \frac{3.408 \times 10^{-3}\ \text{mol}}{0.02500\ \text{L}} = 0.1363\ \text{M}$$

4.7 Types of chemical reactions

Chemical reactions are commonly sorted into a small number of recognizable patterns. Recognizing the pattern helps predict products even before balancing.

Reaction type	General form	Example
Synthesis (combination)	$A + B \rightarrow AB$	$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
Decomposition	$AB \rightarrow A + B$	$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
Single replacement	$A + BC \rightarrow AC + B$	$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$
Double replacement	$AB + CD \rightarrow AD + CB$	$BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KCl(aq)$
Combustion	$C_xH_y(+O) + O_2 \rightarrow CO_2 + H_2O$	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

Table 4.2: *
The five commonly recognized reaction-type patterns. Double replacement reactions further subdivide by product type (below).

4.7.1 Synthesis (combination)

A **synthesis reaction** combines two or more simpler substances into a single, more complex product. Common examples include a metal reacting with a nonmetal to form an ionic compound, two nonmetals combining, or a metal oxide reacting with water to form a hydroxide, or a nonmetal oxide reacting with water to form an oxoacid.

4.7.2 Decomposition

A **decomposition reaction** breaks a single compound down into two or more simpler substances (elements or simpler compounds), typically requiring an input of energy (heat, light, or electricity) to drive the process, since it is generally the reverse of an exothermic synthesis. Common triggers include heating (thermal decomposition, indicated Δ over the arrow) and electrolysis.

4.7.3 Single replacement and the activity series

A **single replacement (displacement) reaction** occurs when one free element displaces another element from a compound: a more reactive metal displaces a less reactive metal (or hydrogen) from a compound in solution, or a more reactive halogen displaces a less reactive halogen from a halide salt. Whether a given single replacement actually proceeds depends on the relative reactivity of the free element versus the element it would displace, summarized by the **activity series**.

> To predict whether $A(s) + BC(aq) \rightarrow AC(aq) + B(s)$ proceeds, locate A and B in the activity series: the reaction proceeds only if A is *more* reactive (higher in the table) than B. If A is less reactive than B, no reaction occurs (written "NR"). The same logic (an analogous halogen activity series, $F_2 > Cl_2 > Br_2 > I_2$) governs single replacement among the halogens.

> VN **GIẢI THÍCH TIẾNG VIỆT**
> Phản ứng thế đơn (single replacement) chỉ xảy ra khi nguyên tố tự do **hoạt động mạnh hơn** nguyên tố nó thay thế, tra theo **dãy hoạt động hoá học**: Li, K, Ba, Ca, Na, Mg, Al, Zn, Fe, Ni,

Reactivity behavior	Metals (most → least active)
React vigorously with cold water and with dilute acids, releasing H_2	Li, K, Ba, Ca, Na
Do not react with cold water; react with steam and with dilute acids	Mg, Al
Do not react with water; react readily with dilute acids, displacing H_2	Zn, Fe, Ni, Sn, Pb
Reference point — dividing line for displacing H_2 from acid	H_2
Do not react with dilute non-oxidizing acids (HCl, dilute H_2SO_4)	Cu, Ag, Au

Table 4.3: *
Activity series of common metals, listed most to least reactive (top row to bottom row; left to right within a row). A free metal will displace the cation of any *less*-active metal (or displace H_2 from a non-oxidizing acid) that appears *below* it in the series; it will not displace a *more*-active metal or H_2 appearing above it.

Sn, Pb, (H_2), Cu, Ag, Au (từ mạnh đến yếu nhất). Kim loại đứng trước có thể đẩy kim loại đứng sau ra khỏi dung dịch muối, hoặc đẩy H_2 ra khỏi acid loãng nếu đứng trước H_2 trong dãy; kim loại đứng sau H_2 (Cu, Ag, Au) không phản ứng với acid loãng thông thường.

4.7.4 Double replacement: precipitation, gas-forming, and neutralization

A **double replacement (metathesis) reaction** exchanges the cations (or anions) between two ionic compounds in solution: $AB + CD \rightarrow AD + CB$. A double replacement reaction proceeds forward (produces an observable change) only if at least one of the following driving forces removes ions from solution:

Driving forces for double replacement

- **Precipitation**: one product is insoluble (check the solubility rules table, Section 4.2), removing ions from solution as a solid.
- **Gas formation**: one product is (or immediately decomposes into) a gas — e.g. a sulfide forms $H_2S(g)$ with acid, a carbonate/bicarbonate forms $CO_2(g) + H_2O(l)$ (via unstable H_2CO_3), a sulfite forms $SO_2(g) + H_2O(l)$.
- **Neutralization / weak-electrolyte formation**: an acid and a base combine to form water (a very weak electrolyte) plus a salt, effectively removing H^+ and OH^- from solution.

If *neither* possible product is insoluble, gaseous, or a weak electrolyte, no net reaction occurs — all four ions remain fully dissociated spectators, and the correct net ionic equation is simply "NR" (no reaction).

(!) Lỗi thường gặp: Do not assume every double replacement combination produces a precipitate. Always check *both* possible new pairings against the solubility rules before concluding a reaction occurs. For example, mixing $NaNO_3(aq)$ and $KCl(aq)$ gives the possible new pairings NaCl and KNO_3 — both fully soluble — so no precipitate forms and no net reaction takes place; all four ions remain spectators in solution.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phản ứng thế đôi (double replacement) chỉ thực sự xảy ra (có hiện tượng quan sát được) khi có một trong ba động lực: tạo **kết tủa** (tra bảng độ tan), tạo **khí** (ví dụ sulfide + acid tạo H_2S, carbonate + acid tạo CO_2), hoặc **trung hoà acid–base** tạo nước. Nếu cả hai sản phẩm có thể có đều tan tốt, phản ứng KHÔNG xảy ra (NR — no reaction) — đây là lỗi thường gặp khi học sinh mặc định luôn có kết tủa.

4.7.5 Combustion

A **combustion reaction** is the rapid reaction of a substance (most commonly a hydrocarbon or other organic compound) with O_2 gas, releasing energy as heat and light. Complete combustion of a hydrocarbon C_xH_y (or an oxygen-containing organic compound $C_xH_yO_z$) with sufficient O_2 always yields $CO_2(g)$ and $H_2O(g \text{ or } l)$ as the only products. (Incomplete combustion, with insufficient O_2, instead yields some CO or soot/carbon — outside the scope of the idealized combustion equations used here.)

Classifying a reaction by type

Classify each of the following balanced equations by reaction type.

(a) $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

(b) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

(c) $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

(d) $BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KCl(aq)$

(e) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

(a) Two elements combine into a single compound ⇒ **synthesis**.
(b) One compound breaks into two simpler substances (water and oxygen gas) ⇒ **decomposition**.
(c) Free element Zn displaces Cu from $CuSO_4$ (Zn is above Cu in the activity series) ⇒ **single replacement**.
(d) Cations/anions exchange between two ionic compounds, producing the insoluble precipitate $BaSO_4$ ⇒ **double replacement (precipitation)**.
(e) A hydrocarbon reacts with O_2 to give CO_2 and H_2O ⇒ **combustion**.

4.8 Introduction to acid-base reactions

4.8.1 The Brønsted–Lowry definition

The **Brønsted–Lowry theory** defines acids and bases by proton (H^+) transfer: a **Brønsted–Lowry acid** is a proton *donor*, and a **Brønsted–Lowry base** is a proton *acceptor*. This definition is broader than the Arrhenius definition (which restricts acids/bases to species that release H^+ or OH^- specifically in water) because it applies to any solvent and identifies species like NH_3 (which contains no OH^- but accepts a proton) as bases.

4.8.2 Conjugate acid-base pairs

Every Brønsted–Lowry acid-base reaction involves two **conjugate acid-base pairs**: when an acid donates a proton, what remains is its **conjugate base** (one fewer H^+, one more unit of negative charge); when a base accepts a proton, it becomes its **conjugate acid** (one more H^+, one more unit of positive charge).

Identifying conjugate acid-base pairs

Identify the Brønsted–Lowry acid, base, conjugate acid, and conjugate base in the equilibrium

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Reading left to right, H_2O donates a proton to NH_3. **Acid** (proton donor): H_2O. **Base** (proton acceptor): NH_3. After donating H^+, H_2O becomes OH^- — its **conjugate base**. After accepting H^+, NH_3 becomes NH_4^+ — its **conjugate acid**.

The two conjugate pairs are H_2O/OH^- and NH_4^+/NH_3 — each pair differs by exactly one H^+.

A species that can act as either a proton donor or a proton acceptor, depending on the reaction partner, is called **amphoteric** (or amphiprotic). Water is the classic example: it acts as a base (accepting H^+) toward a stronger acid, and as an acid (donating H^+) toward a stronger base. Polyprotic-acid intermediate species such as HCO_3^- are also amphoteric — able to donate a proton to form CO_3^{2-}, or accept one to re-form H_2CO_3.

VN **GIẢI THÍCH TIẾNG VIỆT**

Theo thuyết Brønsted–Lowry, acid là chất **cho proton** (H^+), base là chất **nhận proton**. Mỗi phản ứng acid–base tạo ra hai **cặp acid–base liên hợp**: acid sau khi cho H^+ trở thành base liên hợp (base "conjugate"); base sau khi nhận H^+ trở thành acid liên hợp. Chất **lưỡng tính** (amphoteric) như nước hoặc HCO_3^- có thể đóng vai trò acid hoặc base tuỳ chất phản ứng cùng.

4.8.3 Neutralization: acid + base → water + salt

A **neutralization reaction** between a strong (or weak) acid and a strong (or weak) base produces water and an ionic compound called a **salt**. When both the acid and base are strong, the net ionic equation reduces to the simple combination of the free ions:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Balancing a neutralization equation

Write the balanced molecular equation for the neutralization of phosphoric acid, H_3PO_4, by calcium hydroxide, $Ca(OH)_2$.

The salt formed pairs Ca^{2+} with PO_4^{3-}: charges must balance to 0, requiring 3 Ca^{2+} for every 2 PO_4^{3-}, giving the formula $Ca_3(PO_4)_2$. Balancing Ca first fixes the coefficient of $Ca(OH)_2$ at 3, and balancing P fixes the coefficient of H_3PO_4 at 2:

$$2H_3PO_4(aq) + 3Ca(OH)_2(aq) \rightarrow Ca_3(PO_4)_2(s) + 6H_2O(l)$$

Check: Ca: $3 = 3$. P: $2 = 2$. H: left $2(3) + 3(2) = 12$; right $6(2) = 12$. O: left $2(4) + 3(2) = 14$; right $2(4) + 6(1) = 14$.

$$\boxed{2H_3PO_4(aq) + 3Ca(OH)_2(aq) \rightarrow Ca_3(PO_4)_2(s) + 6H_2O(l)}$$

(Note $Ca_3(PO_4)_2$ is insoluble by the phosphate solubility rule, so this reaction also proceeds as a precipitation-driven double replacement.)

4.9 Oxidation-reduction (redox) reactions

An **oxidation-reduction (redox) reaction** involves the transfer of electrons between species, tracked through changes in **oxidation number** (oxidation state).

4.9.1 Assigning oxidation numbers

Rules for assigning oxidation numbers

1. A free element (uncombined) has oxidation number 0 (e.g. $Zn(s)$, O_2, P_4).
2. A monatomic ion has an oxidation number equal to its charge (e.g. $Na^+ = +1$, $S^{2-} = -2$).
3. Fluorine is always -1 in compounds.
4. Oxygen is usually -2, *except* in peroxides (O_2^{2-}, oxidation number -1 per O, e.g. H_2O_2) and when bonded to F.
5. Hydrogen is usually $+1$ when bonded to a nonmetal, but -1 in metal hydrides (e.g. NaH).
6. The sum of all oxidation numbers in a neutral compound is 0; the sum in a polyatomic ion equals the ion's overall charge.

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Quy tắc gán số oxi hoá: nguyên tố tự do $= 0$; ion đơn nguyên tử $=$ điện tích của nó; F luôn -1; O thường -2 (trừ peroxide O_2^{2-} là -1); H thường $+1$ (trừ hydride kim loại là -1); tổng số oxi hoá trong hợp chất trung hoà $= 0$, trong ion đa nguyên tử $=$ điện tích ion đó.

Oxidation numbers in polyatomic ions

Determine the oxidation number of the central atom in (a) $Cr_2O_7^{2-}$ (dichromate); (b) NO_3^- (nitrate); (c) SO_4^{2-} (sulfate).

(a) Let $x =$ oxidation number of Cr. Oxygen is -2 (no peroxide bonding indicated), and there are 2 Cr and 7 O, with overall charge -2:

$$2x + 7(-2) = -2 \;\Rightarrow\; 2x - 14 = -2 \;\Rightarrow\; 2x = 12 \;\Rightarrow\; \boxed{x = +6}$$

(b) $x + 3(-2) = -1 \;\Rightarrow\; x - 6 = -1 \;\Rightarrow\; \boxed{x = +5}$.
(c) $x + 4(-2) = -2 \;\Rightarrow\; x - 8 = -2 \;\Rightarrow\; \boxed{x = +6}$.

4.9.2 Oxidation, reduction, and identifying the agents

Oxidation is the *loss* of electrons, corresponding to an *increase* in oxidation number. **Reduction** is the *gain* of electrons, corresponding to a *decrease* in oxidation number. (Mnemonic: **OIL RIG** — Oxidation Is Loss, Reduction Is Gain, of electrons.) The species that is oxidized is called the **reducing agent** (it donates electrons, causing another species to be reduced); the species that is reduced is called the **oxidizing agent** (it accepts electrons, causing another species to be oxidized).

(!) Lỗi thường gặp: Students frequently reverse the agent labels. The **oxidizing agent** is not the species that is oxidized — it is the species that *causes* oxidation in something else by accepting electrons from it, meaning the oxidizing agent *itself* is reduced. Likewise the **reducing agent** is the species that is itself oxidized. Also remember oxygen is not *always* -2: in peroxides it is

-1, and metal hydrides give hydrogen -1 rather than the usual $+1$ — applying the default rule blindly in these cases gives an incorrect oxidation number.

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Oxi hoá là **mất electron** (số oxi hoá tăng); khử là **nhận electron** (số oxi hoá giảm). Chất khử (reducing agent) là chất **tự bị oxi hoá** (nhường electron); chất oxi hoá (oxidizing agent) là chất **tự bị khử** (nhận electron). Lỗi thường gặp: nhầm lẫn — chất oxi hoá KHÔNG phải là chất bị oxi hoá, mà chính là chất bị khử; hãy nhớ chất oxi hoá "làm chất khác oxi hoá" bằng cách tự nó nhận electron (tự bị khử).

Identifying oxidizing and reducing agents

For the reaction $\mathrm{Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)}$, assign oxidation numbers to each element and identify the oxidizing agent and reducing agent.

Zn: $0 \rightarrow +2$ (in $\mathrm{ZnCl_2}$) — oxidation number *increases*, so Zn is **oxidized**; Zn is the **reducing agent**.
H (in HCl): $+1 \rightarrow 0$ (in $\mathrm{H_2}$) — oxidation number *decreases*, so $\mathrm{H^+}$ is **reduced**; HCl (specifically its $\mathrm{H^+}$) is the **oxidizing agent**.
Cl: -1 in HCl and -1 in $\mathrm{ZnCl_2}$ — unchanged, so $\mathrm{Cl^-}$ is a spectator in the redox sense (though not a spectator ion in the overall reaction, since it remains part of the product salt).

4.9.3 Balancing redox equations: the half-reaction method (acidic solution)

Complex redox equations, especially those involving polyatomic oxidizing/reducing agents, are balanced most reliably by splitting the overall reaction into two **half-reactions** — one for oxidation, one for reduction — balancing each independently, then recombining.

Half-reaction method in acidic solution

1. Assign oxidation numbers and split the skeleton equation into an oxidation half-reaction and a reduction half-reaction.
2. Balance all atoms *other than* O and H in each half-reaction.
3. Balance O by adding $\mathrm{H_2O}$ to the side deficient in O.
4. Balance H by adding $\mathrm{H^+}$ to the side deficient in H.
5. Balance charge in each half-reaction by adding electrons (e^-) to the more positive side.
6. Multiply each half-reaction by the smallest whole number needed so that the number of electrons lost in oxidation equals the number gained in reduction.
7. Add the two half-reactions together, cancelling electrons and any identical species (e.g. excess $\mathrm{H_2O}$ or $\mathrm{H^+}$) that appear on both sides.
8. Verify: every atom balances, and total charge is identical on both sides.

VN **GIẢI THÍCH TIẾNG VIỆT**

Phương pháp bán phản ứng (half-reaction method) cân bằng phản ứng oxi hoá–khử trong môi trường acid theo các bước: tách thành hai bán phản ứng (oxi hoá và khử); cân bằng nguyên tố khác O, H; cân bằng O bằng $\mathrm{H_2O}$; cân bằng H bằng $\mathrm{H^+}$; cân bằng điện tích bằng electron e^-; nhân hệ số để số electron nhường bằng số electron nhận; cộng hai bán phản ứng, rút gọn các chất trùng lặp ở hai vế.

Balancing a redox equation via half-reactions

Balance the following redox reaction in acidic solution: $MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$.

Step 1 — oxidation numbers. Mn: $+7 \rightarrow +2$ (reduction, gains $5e^-$). Fe: $+2 \rightarrow +3$ (oxidation, loses $1e^-$).

Oxidation half-reaction:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

(Fe already balanced; charge: left $+2$, right $+3 - 1 = +2$ — balanced.)

Reduction half-reaction — balance Mn:

$$MnO_4^- \rightarrow Mn^{2+}$$

Balance O with H_2O (4 O on the left needs 4 H_2O on the right):

$$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$$

Balance H with H^+ (8 H needed on the left from the 4 H_2O):

$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

Balance charge with e^-: left charge $= -1 + 8 = +7$; right charge $= +2$; add $5e^-$ to the left:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Step 2 — equalize electrons. The reduction half-reaction transfers $5e^-$; the oxidation half-reaction transfers only $1e^-$, so multiply the oxidation half-reaction by 5:

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$$

Step 3 — add the half-reactions, cancelling $5e^-$ on each side:

$$\boxed{MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)}$$

Check — atoms: Mn: $1 = 1$; O: $4 = 4$; H: $8 = 8$; Fe: $5 = 5$.
Check — charge: left $-1 + 8 + 5(2) = -1 + 8 + 10 = 17$; right $2 + 0 + 5(3) = 2 + 15 = 17$. Balanced.

4.10 Practice Problems

Bài tập luyện tập

Balance the combustion of butane, C_4H_{10}, with O_2 to form CO_2 and H_2O, using the smallest whole-number coefficients. What is the sum of all the coefficients in the balanced equation?

(A) 25
(C) 31
(B) 29
(D) 33

Lời giải chi tiết

Balance C first: 4 C atoms in C_4H_{10} requires $4CO_2$. Balance H: 10 H atoms requires $5H_2O$. This gives, so far, $C_4H_{10} + O_2 \rightarrow 4CO_2 + 5H_2O$, with $4(2) + 5(1) = 13$ O atoms needed on the right. Since 13 is odd, a coefficient of $13/2$ on O_2 would balance it, but coefficients must be whole numbers — multiply the entire equation by 2:

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

Check: C: $8 = 8$; H: $20 = 20$; O: $13(2) = 26$ and $8(2) + 10(1) = 26$. Sum of coefficients $= 2 + 13 + 8 + 10 = 33$. **(D)**.

Bài tập luyện tập

Classify the reaction $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$.

(A) Synthesis
(B) Decomposition
(C) Single replacement
(D) Double replacement

Lời giải chi tiết

A single free element, Mg, displaces another element, H, from a compound, HCl, forming a new compound $MgCl_2$ and releasing free H_2. This pattern — one element replacing another within a compound — defines a single replacement reaction, consistent with Mg lying above H_2 in the activity series (so the displacement indeed proceeds). **(C)**.

Bài tập luyện tập

Write the molecular equation, complete ionic equation, and net ionic equation for the reaction between aqueous potassium phosphate and aqueous silver nitrate.

Lời giải chi tiết

Molecular equation. Ag^+ pairs with PO_4^{3-} (phosphate is insoluble except with Group 1/NH_4^+, so Ag_3PO_4 precipitates); K^+ pairs with NO_3^- (soluble). Balancing charges: 3 Ag^+ per PO_4^{3-}, and 3 KNO_3 to balance the 3 K and 3 NO_3^-:

$$K_3PO_4(aq) + 3AgNO_3(aq) \rightarrow Ag_3PO_4(s) + 3KNO_3(aq)$$

Complete ionic equation. Dissociate all soluble strong electrolytes:

$$3K^+(aq) + PO_4^{3-}(aq) + 3Ag^+(aq) + 3NO_3^-(aq) \rightarrow Ag_3PO_4(s) + 3K^+(aq) + 3NO_3^-(aq)$$

Net ionic equation. Cancel spectator ions K^+ and NO_3^-:

$$\boxed{3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s)}$$

Charge check: left $3(+1) + (-3) = 0$; right (neutral solid) $= 0$. Balanced.

Bài tập luyện tập

Predict whether mixing aqueous KOH with aqueous $MgSO_4$ produces a precipitate. If so, write the net ionic equation.

Lời giải chi tiết

Possible new pairings: Mg^{2+} with OH^-, and K^+ with SO_4^{2-}. Hydroxides are insoluble except with Group 1/NH_4^+ or as $Ba(OH)_2$/$Sr(OH)_2$/$Ca(OH)_2$ (slightly soluble); $Mg(OH)_2$ is therefore insoluble and precipitates. K_2SO_4 is soluble (Group 1 cation).
Molecular equation: $2KOH(aq) + MgSO_4(aq) \rightarrow Mg(OH)_2(s) + K_2SO_4(aq)$.
Net ionic equation (cancel spectators K^+, SO_4^{2-}):

$$\boxed{Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)}$$

Bài tập luyện tập

Which pair of aqueous solutions, when mixed, produces *no* precipitate?

(A) $Pb(NO_3)_2$ and NaCl
(B) $BaCl_2$ and Na_2SO_4
(C) $NaNO_3$ and KCl
(D) $AgNO_3$ and KBr

Lời giải chi tiết

Check each pair's possible new products against the solubility rules: (A) gives $PbCl_2$, insoluble (chloride exception) — precipitate forms. (B) gives $BaSO_4$, insoluble (sulfate exception) — precipitate forms. (C) gives NaCl and KNO_3, both soluble (Group 1 cations, and nitrate always soluble) — no precipitate. (D) gives AgBr, insoluble (halide exception with Ag^+) — precipitate forms. Only (C) produces no reaction. **(C)**.

Bài tập luyện tập

The thermite reaction, $2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(l)$, is carried out with 15.0 g of Al and 60.0 g of Fe_2O_3. (a) Determine the limiting reactant. (b) Calculate the theoretical yield of Fe, in grams.

Lời giải chi tiết

(a) $M(Al) = 26.98$ g/mol, $M(Fe_2O_3) = 2(55.85) + 3(16.00) = 159.70$ g/mol.

$$n(Al) = \frac{15.0}{26.98} = 0.5560 \text{ mol}, \qquad n(Fe_2O_3) = \frac{60.0}{159.70} = 0.3757 \text{ mol}$$

The equation requires 1 mol Fe_2O_3 per 2 mol Al. For all 0.5560 mol Al to react, only $0.5560/2 = 0.2780$ mol Fe_2O_3 is needed — far less than the 0.3757 mol available. So Fe_2O_3 is in excess, and Al **is the limiting reactant**.

(b) Mole ratio Fe : Al $= 2:2 = 1:1$, so $n(Fe) = 0.5560$ mol. $M(Fe) = 55.85$ g/mol:

$$\boxed{m(Fe) = 0.5560 \times 55.85 = 31.05 \text{ g (theoretical yield)}}$$

Bài tập luyện tập

In the thermite reaction of the previous problem, 26.4 g of iron is actually recovered. Calculate the percent yield.

Lời giải chi tiết

$$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{26.4}{31.05} \times 100\% = \boxed{85.0\%}$$

Bài tập luyện tập

Ethanol, C_2H_5OH, burns completely according to $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$. How many grams of CO_2 are produced from the complete combustion of 46.0 g of ethanol?

Lời giải chi tiết

$M(C_2H_5OH) = 2(12.01) + 6(1.008) + 16.00 = 46.068$ g/mol.

$$n(C_2H_5OH) = \frac{46.0}{46.068} = 0.9985 \text{ mol}$$

Mole ratio $CO_2 : C_2H_5OH = 2 : 1$:

$$n(CO_2) = 0.9985 \times 2 = 1.997 \text{ mol}$$

$M(CO_2) = 44.01$ g/mol:

$$\boxed{m(CO_2) = 1.997 \times 44.01 = 87.9 \text{ g}}$$

Bài tập luyện tập

Potassium chlorate decomposes on heating: $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$. What volume of O_2 gas, measured at STP, is produced from the complete decomposition of 24.5 g of $KClO_3$?

Lời giải chi tiết

$M(KClO_3) = 39.10 + 35.45 + 3(16.00) = 122.55$ g/mol.

$$n(KClO_3) = \frac{24.5}{122.55} = 0.1999 \text{ mol}$$

Mole ratio $O_2 : KClO_3 = 3 : 2$:

$$n(O_2) = 0.1999 \times \frac{3}{2} = 0.2999 \text{ mol}$$

$$\boxed{V(O_2) = 0.2999 \times 22.4 = 6.72 \text{ L}}$$

Bài tập luyện tập

In a reaction between A and B, exactly 2.00 mol of A reacts completely with 3.00 mol of B with nothing left over. If a chemist instead combines 2.00 mol of A with 4.50 mol of B, which statement is correct?

(A) A is limiting; 1.50 mol B remains unreacted

(B) B is limiting; some A remains unreacted

(C) Both are completely consumed, since more total moles are present

(D) The reaction cannot proceed because the ratio is not $1{:}1$

Lời giải chi tiết

The stoichiometric ratio is $A : B = 2.00 : 3.00 = 1 : 1.5$. With 2.00 mol A present, exactly $2.00 \times 1.5 = 3.00$ mol B is needed for complete reaction — and 4.50 mol B is available, i.e. 1.50 mol B in excess. All 2.00 mol of A reacts (A is limiting, fully consumed), leaving $4.50 - 3.00 = 1.50$ mol of B unreacted. **(A)**.

Bài tập luyện tập

A 20.00 mL sample of H_2SO_4 of unknown concentration is titrated with 0.200 M NaOH via $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$. The equivalence point is reached after 27.35 mL of NaOH is added. Find the molarity of the H_2SO_4 solution.

Lời giải chi tiết

$$n(\text{NaOH}) = (0.02735\ \text{L})(0.200\ \text{M}) = 5.470 \times 10^{-3}\ \text{mol}$$

Mole ratio $H_2SO_4 : NaOH = 1 : 2$:

$$n(H_2SO_4) = \frac{5.470 \times 10^{-3}}{2} = 2.735 \times 10^{-3}\ \text{mol}$$

$$\boxed{M(H_2SO_4) = \frac{2.735 \times 10^{-3}\ \text{mol}}{0.02000\ \text{L}} = 0.1368\ \text{M}}$$

Bài tập luyện tập

A 0.5104 g sample of pure potassium hydrogen phthalate, $KHC_8H_4O_4$ (KHP, $M = 204.22$ g/mol, a monoprotic acid), is dissolved in water and titrated to the equivalence point with 24.16 mL of NaOH solution via $KHC_8H_4O_4(aq) + NaOH(aq) \rightarrow KNaC_8H_4O_4(aq) + H_2O(l)$. Find the molarity of the NaOH solution.

Lời giải chi tiết

$$n(\text{KHP}) = \frac{0.5104\ \text{g}}{204.22\ \text{g/mol}} = 2.499 \times 10^{-3}\ \text{mol}$$

The $1 : 1$ mole ratio gives $n(\text{NaOH}) = 2.499 \times 10^{-3}$ mol.

$$\boxed{M(\text{NaOH}) = \frac{2.499 \times 10^{-3}\ \text{mol}}{0.02416\ \text{L}} = 0.1034\ \text{M}}$$

Bài tập luyện tập

In the equilibrium $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$, identify the conjugate acid of HCO_3^-.

(A) CO_3^{2-}
(B) H_2CO_3
(C) H_2O
(D) OH^-

Lời giải chi tiết

Reading the reaction, HCO_3^- accepts a proton from H_2O (it acts as a Brønsted–Lowry base here) and becomes H_2CO_3 — its conjugate acid, formed by gaining one H^+. **(B)**.

Bài tập luyện tập

For the reaction $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$, identify the Brønsted–Lowry acid, base, conjugate acid, and conjugate base.

Lời giải chi tiết

H_2O donates a proton to NH_3, so H_2O is the **acid** and NH_3 is the **base**. After donating H^+, H_2O becomes OH^-, its **conjugate base**. After accepting H^+, NH_3 becomes NH_4^+, its **conjugate acid**. The two conjugate pairs are H_2O/OH^- and NH_4^+/NH_3.

Bài tập luyện tập

Write the balanced molecular equation for the neutralization of aqueous phosphoric acid, H_3PO_4, with aqueous calcium hydroxide, $Ca(OH)_2$, and classify the reaction type(s) it represents.

Lời giải chi tiết

Balancing charge in the salt $Ca_3(PO_4)_2$ (3 Ca^{2+} per 2 PO_4^{3-}) and then balancing Ca, P, H, O:

$$\boxed{2H_3PO_4(aq) + 3Ca(OH)_2(aq) \rightarrow Ca_3(PO_4)_2(s) + 6H_2O(l)}$$

Check: Ca $3 = 3$; P $2 = 2$; H $2(3) + 3(2) = 12 = 6(2)$; O $2(4) + 3(2) = 14 = 2(4) + 6(1)$. This reaction is both a **neutralization** (acid + base → salt + water) and a **double replacement (precipitation)** reaction, since $Ca_3(PO_4)_2$ is insoluble by the solubility rules.

Bài tập luyện tập

What is the oxidation number of Mn in $KMnO_4$?

(A) $+2$
(B) $+4$
(C) $+6$
(D) $+7$

Lời giải chi tiết

K is $+1$, O is -2 (four O atoms). The compound is neutral, so:

$$(+1) + x + 4(-2) = 0 \;\Rightarrow\; x - 7 = 0 \;\Rightarrow\; x = +7$$

(D).

Bài tập luyện tập

Determine the oxidation number of chlorine in each of the following: NaCl, Cl_2, NaClO, $NaClO_2$, $NaClO_3$, $NaClO_4$.

Lời giải chi tiết

Using Na $= +1$ and O $= -2$ throughout, and solving each neutral-compound sum for Cl (or, for Cl_2, applying the free-element rule directly):
NaCl: $(+1) + x = 0 \Rightarrow x = \boxed{-1}$.
Cl_2: free element $\Rightarrow x = \boxed{0}$.
NaClO: $(+1) + x + (-2) = 0 \Rightarrow x = \boxed{+1}$.
$NaClO_2$: $(+1) + x + 2(-2) = 0 \Rightarrow x - 3 = 0 \Rightarrow x = \boxed{+3}$.
$NaClO_3$: $(+1) + x + 3(-2) = 0 \Rightarrow x - 5 = 0 \Rightarrow x = \boxed{+5}$.
$NaClO_4$: $(+1) + x + 4(-2) = 0 \Rightarrow x - 7 = 0 \Rightarrow x = \boxed{+7}$.
Chlorine's oxidation state rises steadily from -1 to $+7$ as increasing numbers of electronegative oxygen atoms are bonded to it, illustrating how the same element can occupy a wide range of oxidation states across a series of oxoacid/oxoanion salts.

Bài tập luyện tập

Balance the following redox reaction in acidic solution using the half-reaction method: $MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow Mn^{2+}(aq) + CO_2(g)$.

Lời giải chi tiết

Oxidation half-reaction (C: $+3 \rightarrow +4$, loses e^-; balance C, then charge):

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

(Charge check: left -2; right $0 - 2 = -2$. Balanced.)

Reduction half-reaction (Mn: $+7 \rightarrow +2$, gains $5e^-$): balance O with H_2O, H with H^+, then charge with e^-:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Equalize electrons. LCM of 2 and 5 is 10: multiply the oxidation half-reaction by 5 and the reduction half-reaction by 2:

$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$

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

Add and cancel $10e^-$:

$$\boxed{2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)}$$

Check atoms: Mn $2 = 2$; O: left $2(4) + 5(4) = 28$, right $8(1) + 10(2) = 28$; H $16 = 16$; C $5(2) = 10 = 10$.
Check charge: left $2(-1) + 16(+1) + 5(-2) = -2 + 16 - 10 = 4$; right $2(+2) = 4$. Balanced.

Bài tập luyện tập

For the reaction $2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$, identify the oxidizing agent and the reducing agent.

Lời giải chi tiết

Al: $0 \to +3$ (in $AlCl_3$) — oxidation number increases, so Al is **oxidized**; **Al is the reducing agent**. Cl: $0 \to -1$ (in $AlCl_3$) — oxidation number decreases, so Cl_2 is **reduced**; **Cl_2 is the oxidizing agent**.

Bài tập luyện tập

Which metal, when placed in dilute hydrochloric acid, will *not* produce a visible evolution of H_2 gas?

(A) Mg
(B) Zn
(C) Fe
(D) Cu

Lời giải chi tiết

Referring to the activity series, H_2 itself divides metals that displace hydrogen from a dilute non-oxidizing acid (all metals above H_2 in the series) from those that do not (Cu, Ag, Au, below H_2). Mg, Zn, and Fe all lie above H_2 and react readily; Cu lies below H_2 and does not react with dilute HCl. **(D)**.

Bài tập luyện tập

Iron metal is placed into an aqueous solution of copper(II) sulfate. (a) Write the balanced molecular equation, predicting whether a reaction occurs, using the activity series. (b) Write the net ionic equation.

Lời giải chi tiết

(a) Fe lies above Cu in the activity series (Fe is more reactive), so Fe displaces Cu^{2+} from solution:

$$\boxed{Fe(s) + CuSO_4(aq) \to FeSO_4(aq) + Cu(s)}$$

(b) SO_4^{2-} is a spectator ion (present unchanged on both sides, since both $FeSO_4$ and $CuSO_4$ are soluble):

$$\boxed{Fe(s) + Cu^{2+}(aq) \to Fe^{2+}(aq) + Cu(s)}$$

Bài tập luyện tập

Classify the reaction $Na_2S(aq) + 2HCl(aq) \to 2NaCl(aq) + H_2S(g)$, and state which driving force causes it to proceed.

(A) Single replacement, driven by precipitation
(B) Double replacement, driven by gas formation
(C) Synthesis, driven by neutralization
(D) Double replacement, driven by precipitation

Lời giải chi tiết

Cations (Na^+, H^+) and anions (S^{2-}, Cl^-) exchange partners — a double replacement pattern. The driving force is not precipitation (both possible chloride/sulfide-free products are soluble) but the escape of the volatile gas H_2S from solution, removing ions and pulling the reaction

forward. **(B)**.

Bài tập luyện tập

Solid ammonium nitrate decomposes on gentle heating: $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$. Verify this equation is balanced, and classify the reaction type.

Lời giải chi tiết

N: left 2 (1 from NH_4^+, 1 from NO_3^-); right 2 (in N_2O). Balanced.
H: left 4 (in NH_4^+); right $2(2) = 4$ (in $2H_2O$). Balanced.
O: left 3 (in NO_3^-); right 1 (in N_2O) $+2(1) = 2$ (in $2H_2O$) $= 3$. Balanced.
All three elements balance with the coefficients as given (no further adjustment needed). A single compound breaks apart into two simpler gaseous products $\Rightarrow$ **decomposition reaction**.

Bài tập luyện tập

A sealed container holds 6 molecules of H_2 gas and 3 molecules of O_2 gas, which react completely according to $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$. (a) How many molecules of each species are present after the reaction goes to completion? A second container instead holds 8 molecules of H_2 and 3 molecules of O_2. (b) Identify the limiting reactant by particle count, and state how many molecules of each species remain/form.

Lời giải chi tiết

(a) The required particle ratio is $H_2 : O_2 = 2 : 1$. Here $6 : 3 = 2 : 1$ exactly — both reactants are used up together, with no excess of either. All 6 H_2 and all 3 O_2 molecules are consumed, forming 6 molecules of H_2O (matching the $2 : 1 : 2$ overall particle ratio). Final count: 0 H_2, 0 O_2, 6 H_2O.

(b) For all 3 molecules of O_2 to react, $3 \times 2 = 6$ molecules of H_2 are required; 8 molecules of H_2 are available, more than enough, so O_2 is the **limiting reactant**. All 3 O_2 molecules react with 6 of the 8 H_2 molecules, leaving $8 - 6 = 2$ molecules of H_2 unreacted, and producing $2 \times 3 = 6$ molecules of H_2O. Final count: 2 H_2 (excess), 0 O_2, 6 H_2O.

Bài tập luyện tập

Which of the following best exemplifies a chemical change?

(A) Melting a block of ice

(B) Dissolving table sugar in warm water

(C) Iron nails developing reddish-brown rust when left outdoors

(D) Boiling water in an open pot

Lời giải chi tiết

Melting, dissolving sugar, and boiling water are all phase/dispersal changes that do not alter the chemical identity of the substance involved — the same molecules exist before and after. Rusting, however, is the reaction of iron metal with atmospheric O_2 and moisture to form iron(III) oxide compounds, a new substance with different chemical composition and properties (Fe metal is not the same substance as iron oxide). **(C)**.

Bài tập luyện tập

A 5.00 g strip of magnesium ribbon burns completely in air, forming magnesium oxide. If 8.29 g of MgO is collected, use the law of conservation of mass to find the mass of oxygen that combined with the magnesium, and verify this figure using the stoichiometry of $2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$.

Lời giải chi tiết

By conservation of mass: mass of O_2 combined = mass of product − mass of Mg $= 8.29 - 5.00 = \boxed{3.29\text{ g}}$.

Verification by stoichiometry: $M(\text{Mg}) = 24.31$ g/mol, so $n(\text{Mg}) = 5.00/24.31 = 0.2057$ mol. Mole ratio $\text{O}_2 : \text{Mg} = 1 : 2$, so $n(\text{O}_2) = 0.2057/2 = 0.1028$ mol; $m(\text{O}_2) = 0.1028 \times 2(16.00) = 0.1028 \times 32.00 = 3.29$ g. This matches the conservation-of-mass result exactly, confirming both the experimental data and the balanced equation are self-consistent.

Bài tập luyện tập

A 12.50 g sample of aluminum metal is added to 250.0 mL of 1.50 M $\text{CuSO}_4\text{(aq)}$; a single-replacement reaction deposits copper metal and forms aqueous aluminum sulfate. (a) Write the balanced molecular, complete ionic, and net ionic equations. (b) Determine the limiting reactant. (c) Calculate the theoretical yield of Cu, in grams. (d) If 19.8 g of Cu is actually recovered, calculate the percent yield. (e) Identify the oxidizing agent and the reducing agent.

Lời giải chi tiết

(a) **Molecular:** $2\text{Al(s)} + 3\text{CuSO}_4\text{(aq)} \rightarrow \text{Al}_2(\text{SO}_4)_3\text{(aq)} + 3\text{Cu(s)}$.
Complete ionic: $2\text{Al(s)} + 3\text{Cu}^{2+}\text{(aq)} + 3\text{SO}_4^{2-}\text{(aq)} \rightarrow 2\text{Al}^{3+}\text{(aq)} + 3\text{SO}_4^{2-}\text{(aq)} + 3\text{Cu(s)}$.
Net ionic (cancel spectator SO_4^{2-}): $\boxed{2\text{Al(s)} + 3\text{Cu}^{2+}\text{(aq)} \rightarrow 2\text{Al}^{3+}\text{(aq)} + 3\text{Cu(s)}}$.

(b) $M(\text{Al}) = 26.98$ g/mol: $n(\text{Al}) = 12.50/26.98 = 0.4633$ mol. $n(\text{CuSO}_4) = (0.2500\text{ L})(1.50\text{ M}) = 0.3750$ mol. The equation requires 3 mol Cu^{2+} per 2 mol Al; for all 0.4633 mol Al to react, $0.4633 \times 1.5 = 0.6950$ mol Cu^{2+} would be needed — but only 0.3750 mol is available. CuSO_4 **is the limiting reactant.**

(c) Mole ratio $\text{Cu} : \text{Cu}^{2+} = 3 : 3 = 1 : 1$, so $n(\text{Cu}) = 0.3750$ mol. $M(\text{Cu}) = 63.55$ g/mol:

$$\boxed{m(\text{Cu}) = 0.3750 \times 63.55 = 23.83\text{ g}}$$

(d)

$$\%\text{ yield} = \frac{19.8}{23.83} \times 100\% = \boxed{83.1\%}$$

(e) Cu: $+2 \rightarrow 0$, reduced ⇒ Cu^{2+} (i.e. CuSO_4) is the **oxidizing agent**. Al: $0 \rightarrow +3$, oxidized ⇒ **Al is the reducing agent**.

Bài tập luyện tập

In the reaction $\text{Zn(s)} + 2\text{Ag}^+\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + 2\text{Ag(s)}$, which species is the oxidizing agent?

(A) Zn(s)
(B) $\text{Ag}^+\text{(aq)}$
(C) $\text{Zn}^{2+}\text{(aq)}$
(D) Ag(s)

Lời giải chi tiết

Zn: $0 \to +2$ (oxidized, loses $2e^-$); Ag: $+1 \to 0$ (reduced, gains e^-). The oxidizing agent is the species that is itself reduced, namely $Ag^+(aq)$. **(B)**.

Bài tập luyện tập

Given the reaction $4Fe(s) + 3O_2(g) \to 2Fe_2O_3(s)$, how many moles of Fe_2O_3 form from 2.50 mol of Fe, assuming excess O_2?

Lời giải chi tiết

Mole ratio $Fe_2O_3 : Fe = 2 : 4 = 1 : 2$:

$$\boxed{n(Fe_2O_3) = 2.50 \text{ mol} \times \frac{1}{2} = 1.25 \text{ mol}}$$

Bài tập luyện tập

A student calculates a percent yield of 108% for a recrystallized solid product. Which explanation is most chemically reasonable?

(A) The reaction produced more product than is theoretically possible

(B) The limiting reactant was miscalculated as the reactant in excess

(C) The collected solid was not fully dried and still contained residual solvent, inflating its measured mass

(D) The molar mass used in the calculation was too large

Lời giải chi tiết

Percent yield cannot legitimately exceed 100%, since the theoretical yield already represents the maximum mass obtainable if the limiting reactant reacted with perfect efficiency and the product were perfectly pure. An apparent yield over 100% is a strong signal that the "product" mass is inflated by an impurity — most commonly residual solvent or water not fully removed during drying — rather than evidence that more product formed than stoichiometry allows. (A misidentified limiting reactant, choice B, would shift the theoretical yield but not directly explain an over-100% result unless compounded with another error; the most direct and common explanation is impure/wet product.) **(C)**.

Bài tập luyện tập

A 50.0 g sample of C_3H_8 is burned in 175.0 g of O_2 via $C_3H_8(g) + 5O_2(g) \to 3CO_2(g) + 4H_2O(g)$. Determine the limiting reactant and calculate the volume of CO_2 produced, measured at STP.

Lời giải chi tiết

$M(C_3H_8) = 44.094$ g/mol: $n(C_3H_8) = 50.0/44.094 = 1.134$ mol. $n(O_2) = 175.0/32.00 = 5.469$ mol.
The equation requires 5 mol O_2 per mol C_3H_8; for all 1.134 mol C_3H_8 to react, $1.134 \times 5 = 5.670$ mol O_2 is needed — more than the 5.469 mol available. O_2 **is the limiting reactant.**

Mole ratio $CO_2 : O_2 = 3 : 5$:

$$n(CO_2) = 5.469 \times \frac{3}{5} = 3.281 \text{ mol}$$

$$\boxed{V(CO_2) = 3.281 \times 22.4 = 73.5 \text{ L}}$$

Bài tập luyện tập

A 50.00 mL sample of HCl solution of unknown concentration is exactly neutralized by 36.44 mL of 0.150 M $Ba(OH)_2$ solution via $Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$. Find the molarity of the HCl solution.

Lời giải chi tiết

$$n(Ba(OH)_2) = (0.03644 \text{ L})(0.150 \text{ M}) = 5.466 \times 10^{-3} \text{ mol}$$

Mole ratio $HCl : Ba(OH)_2 = 2 : 1$:

$$n(HCl) = 2 \times 5.466 \times 10^{-3} = 1.093 \times 10^{-2} \text{ mol}$$

$$\boxed{M(HCl) = \frac{1.093 \times 10^{-2} \text{ mol}}{0.05000 \text{ L}} = 0.2186 \text{ M}}$$

Kinetics

Mục tiêu Unit: Viết và áp dụng biểu thức tốc độ trung bình và tức thời theo hệ số tỉ lượng; xác định bậc phản ứng riêng phần, bậc phản ứng toàn phần và hằng số tốc độ k (kèm đơn vị đúng) bằng phương pháp tốc độ đầu; sử dụng định luật tốc độ tích phân (bậc 0, bậc 1, bậc 2) để tính nồng độ theo thời gian và chu kỳ bán rã $t_{1/2}$; xác định bậc phản ứng bằng đồ thị tuyến tính hoá; phân biệt phản ứng đơn giản (elementary) với cơ chế nhiều bước; áp dụng thuyết va chạm, phân bố Maxwell–Boltzmann và phương trình Arrhenius; suy luận định luật tốc độ từ một cơ chế đề xuất (kể cả khi cần xấp xỉ tiền cân bằng — pre-equilibrium); đọc và giải thích giản đồ năng lượng phản ứng nhiều bước; phân biệt rõ chất xúc tác và chất trung gian phản ứng.

5.1 Reaction rates

The **rate of a chemical reaction** measures how quickly reactants are consumed or products are formed, expressed as a change in concentration per unit time. For a homogeneous reaction in solution or in the gas phase, rate is normally reported in units of molarity per second, M/s (equivalently mol $\mathrm{L}^{-1}\mathrm{s}^{-1}$), although minutes or other time units are used when a reaction is slow.

5.1.1 Average rate and stoichiometry

For a reaction monitored between two times t_1 and t_2, the **average rate** of disappearance of a reactant A or appearance of a product B is

$$\text{average rate of } A = -\frac{\Delta[A]}{\Delta t}, \qquad \text{average rate of } B = +\frac{\Delta[B]}{\Delta t}.$$

A reactant's concentration decreases with time, so $\Delta[A] = [A]_2 - [A]_1$ is negative; the leading minus sign makes the reported rate a positive quantity. A product's concentration increases, so no sign change is needed for $\Delta[B]$.

Different species in the same reaction change concentration at different numerical rates whenever their stoichiometric coefficients differ, because for every mole of reaction that occurs, each species is consumed or produced in proportion to its coefficient. For the general reaction

$$aA + bB \rightarrow cC + dD,$$

dividing each species' rate of change by its own coefficient gives a single, unambiguous **rate of reaction** that is the same number no matter which species is tracked:

$$\text{rate of reaction} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}.$$

Khái niệm cốt lõi

To convert between the rate of change of one species and another in the same reaction, use the stoichiometric coefficients as a mole-ratio bridge, exactly as in stoichiometry calculations:

$$(\text{rate of } X) = \frac{\text{coefficient of } X}{\text{coefficient of } Y} \times (\text{rate of } Y)\,.$$

This relationship holds for average rates and for instantaneous rates alike.

VN **GIẢI THÍCH TIẾNG VIỆT**

Tốc độ trung bình của một chất được tính bằng độ biến thiên nồng độ chia cho khoảng thời gian; dùng dấu trừ cho chất phản ứng (vì nồng độ giảm dần) để tốc độ luôn là số dương. Vì các chất trong phản ứng biến đổi theo tỉ lệ hệ số cân bằng phương trình, tốc độ của từng chất khác nhau về giá trị số nếu hệ số khác nhau — nhưng khi chia tốc độ mỗi chất cho hệ số tỉ lượng của chính nó, ta thu được **tốc độ phản ứng** chung, giống nhau dù tính theo chất nào.

Average rate and stoichiometric conversion

Dinitrogen pentoxide decomposes as $2\mathrm{N_2O_5}(g) \rightarrow 4\mathrm{NO_2}(g) + \mathrm{O_2}(g)$. In one experiment $[\mathrm{N_2O_5}]$ falls from 0.0300 M at $t = 0$ s to 0.0222 M at $t = 200$ s. Find (a) the average rate of disappearance of $\mathrm{N_2O_5}$, (b) the average rate of the reaction, and (c) the average rate of formation of $\mathrm{NO_2}$ and of $\mathrm{O_2}$.

(a) $\Delta[\mathrm{N_2O_5}] = 0.0222 - 0.0300 = -0.0078$ M over $\Delta t = 200$ s, so

$$-\frac{\Delta[\mathrm{N_2O_5}]}{\Delta t} = \frac{0.0078}{200} = 3.90 \times 10^{-5}\ \text{M/s}.$$

(b) Rate of reaction $= \dfrac{1}{2}\left(3.90 \times 10^{-5}\right) = 1.95 \times 10^{-5}$ M/s (divide by the coefficient of $\mathrm{N_2O_5}$, which is 2).

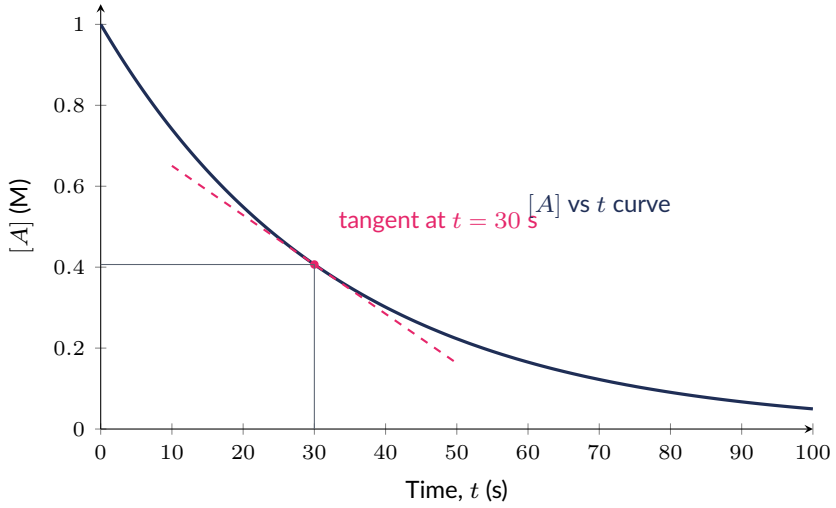
(c) Rate of $\mathrm{NO_2}$ formation $= 4 \times (1.95 \times 10^{-5}) = 7.80 \times 10^{-5}$ M/s (coefficient 4). Rate of $\mathrm{O_2}$ formation $= 1 \times (1.95 \times 10^{-5}) = 1.95 \times 10^{-5}$ M/s (coefficient 1, equal to the rate of reaction).

5.1.2 Instantaneous rate

The average rate over a finite interval Δt is only an approximation to the true rate at any single moment, because the rate of most reactions is not constant — it typically decreases as reactants are used up. The **instantaneous rate** at a specific time t is the rate at that exact moment, defined as the slope of the tangent line to the concentration-versus-time curve at that point:

$$\text{instantaneous rate of } A = -\lim_{\Delta t \to 0} \frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}.$$

Graphically, plot $[A]$ (or $[B]$) versus t; the **instantaneous rate at any point equals the (negative of the) slope of the line tangent to the curve at that point**, while the average rate over an interval equals the slope of the *secant* line connecting the two endpoints of that interval. The **initial rate** is simply the instantaneous rate at $t = 0$, the slope of the tangent at the very start of the reaction — this is the quantity used in the method of initial rates (Section 5.2).



Concentration-versus-time curve for a reactant A. The dashed line is the tangent at $t = 30$ s; its slope is the instantaneous rate of disappearance of A at that moment. The tangent's slope becomes shallower at longer times because the curve flattens as $[A]$ is depleted, so instantaneous rate decreases over the course of the reaction.

Instantaneous rate from a tangent line

A tangent line drawn to a $[A]$-versus-t curve at $t = 20$ s passes through the points $(10\text{ s},\ 0.620\text{ M})$ and $(40\text{ s},\ 0.485\text{ M})$. Find the instantaneous rate of disappearance of A at $t = 20$ s.

Slope of the tangent line:

$$\text{slope} = \frac{0.485 - 0.620}{40 - 10} = \frac{-0.135}{30} = -0.00450\text{ M/s}.$$

The instantaneous rate is the negative of this slope (so that rate is reported as a positive quantity): rate $= 0.00450$ M/s $= 4.50 \times 10^{-3}$ M/s at $t = 20$ s.

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Tốc độ tức thời tại một thời điểm chính là độ dốc (âm) của tiếp tuyến với đường cong nồng độ theo thời gian tại điểm đó, khác với tốc độ trung bình (độ dốc của đường thẳng nối hai điểm — dây cung/secant) trên một khoảng thời gian. **Tốc độ đầu** (initial rate) là tốc độ tức thời tại $t = 0$, được dùng trong phương pháp tốc độ đầu ở Section 5.2. Vì nồng độ chất phản ứng giảm dần nên đường cong thoải dần theo thời gian, do đó tốc độ tức thời giảm dần trong suốt phản ứng (trừ trường hợp bậc 0).

5.2 Introduction to rate law

The **rate law** (or differential rate law) expresses how the instantaneous rate of a reaction depends on the concentrations of the species that affect it. For a reaction with reactants A and B, the general form is

$$\text{rate} = k[A]^m[B]^n,$$

where k is the **rate constant** (a proportionality constant, independent of concentration, that depends only on temperature and the identity of the reaction), and m and n are the **reaction orders** with respect to A and B. The **overall reaction order** is the sum $m + n$. Orders are almost always small integers (0, 1, 2; occasionally 3) but can in principle be fractional or negative for complex mechanisms.

Reaction orders and k must be determined experimentally — they cannot be read off from the coefficients of the balanced overall equation. The balanced equation only fixes the stoichiometric ratios of reactants consumed and products formed; it carries no information about the mechanism by which the reaction actually proceeds, and it is the mechanism (specifically, the slowest step — see Section 5.6) that dictates the rate law. The one exception is an *elementary* step considered by itself (Section 5.4).

VN **GIẢI THÍCH TIẾNG VIỆT**

Định luật tốc độ (rate law) có dạng rate $= k[A]^m[B]^n$, trong đó m, n là bậc phản ứng riêng phần theo từng chất, $m + n$ là bậc phản ứng toàn phần, và k là hằng số tốc độ (chỉ phụ thuộc nhiệt độ, không phụ thuộc nồng độ). Điều quan trọng nhất cần nhớ: bậc phản ứng **không** được suy ra từ hệ số cân bằng của phương trình tổng — phải xác định bằng thực nghiệm.

5.2.1 The method of initial rates

The most common experimental technique for determining reaction orders is the **method of initial rates**: run the reaction several times with different starting concentrations of each reactant (holding the others fixed where possible), and measure the initial rate (the instantaneous rate at $t = 0$, before any significant product buildup or reactant depletion) in each trial. Comparing two trials in which only one reactant's concentration changes isolates the effect of that reactant:

$$\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

lets you solve for m directly, since only the exponent is unknown once the concentration ratio and rate ratio are known.

Determining a rate law from initial-rates data

For the reaction $A + 2B \rightarrow$ products, the following initial-rate data were collected:

Trial	$[A]_0$ (M)	$[B]_0$ (M)	Initial rate (M/s)
1	0.10	0.10	2.0×10^{-3}
2	0.20	0.10	8.0×10^{-3}
3	0.20	0.20	1.6×10^{-2}

Determine the rate law and the value of k (with units).

Order in A (compare trials 1 and 2, $[B]$ constant): $[A]$ doubles and rate increases by a factor $8.0 \times 10^{-3}/2.0 \times 10^{-3} = 4.0 = 2^2$, so the order in A is $m = 2$.

Order in B (compare trials 2 and 3, $[A]$ constant): $[B]$ doubles and rate increases by a factor $1.6 \times 10^{-2}/8.0 \times 10^{-3} = 2.0 = 2^1$, so the order in B is $n = 1$.

Rate law: rate $= k[A]^2[B]$, overall order $= 3$.

Solve for k using trial 1: $2.0 \times 10^{-3} = k(0.10)^2(0.10) = k(1.0 \times 10^{-3})$, so $k = 2.0\ \text{M}^{-2}\text{s}^{-1}$. Check with trial 3: $k(0.20)^2(0.20) = 2.0(0.04)(0.20) = 0.016 = 1.6 \times 10^{-2}$ M/s ✓.

The units of k depend on the overall order $n = m + n_B + \cdots$ so that both sides of rate $= k[\text{conc}]^{\text{order}}$ balance to M/s:

Overall order	Units of k	Example
0	M s^{-1}	rate independent of concentration
1	s^{-1}	
2	$\text{M}^{-1}\text{s}^{-1}$	
3	$\text{M}^{-2}\text{s}^{-1}$	
n (general)	$\text{M}^{1-n}\text{s}^{-1}$	

Reporting a numeric value of k without units, or with the wrong units for the order found, is treated as an incomplete answer.

(!) Lỗi thường gặp: Do not assume that a reactant with a coefficient in the balanced equation must appear in the rate law, or that its order equals its coefficient. It is entirely possible for a reactant to have order 0 (rate independent of its concentration, as with B in a table where doubling $[B]$ leaves the rate unchanged) or for a species not written as a reactant at all (a catalyst) to appear in the rate law. Only for an *elementary* reaction step is the order in each species guaranteed to equal its coefficient in that step — never assume this for an overall, multistep reaction unless told the step shown *is* elementary.

5.3 Concentration changes over time and $t_{1/2}$

The differential rate law (Section 5.2) gives the instantaneous rate as a function of concentration, but does not directly say what the concentration will be after a specific elapsed time. Integrating the differential rate law with respect to time produces an **integrated rate law**: an explicit equation for $[A]$ as a function of t, distinct for each reaction order. Integrated rate laws are used to (i) calculate concentration at any later time, (ii) determine reaction order graphically from experimental concentration-time data, and (iii) define the **half-life**, $t_{1/2}$, the time required for the concentration of a reactant to fall to half its initial value.

5.3.1 Zero-order reactions

For a reaction $A \rightarrow$ products that is zero order in A (rate $= k$, independent of $[A]$), integration gives a *linear* decrease of concentration with time:

$$[A]_t = [A]_0 - kt, \qquad t_{1/2} = \frac{[A]_0}{2k}.$$

A plot of $[A]$ versus t is a straight line of slope $-k$ and y-intercept $[A]_0$. Because the half-life formula contains $[A]_0$, the half-life of a zero-order reaction is *not* constant — it shortens as the reaction proceeds and $[A]_0$ (the concentration remaining at the start of each successive half-life interval) decreases.

5.3.2 First-order reactions

For a reaction first order in A (rate $= k[A]$), integration gives exponential decay:

$$\ln[A]_t = \ln[A]_0 - kt \quad \Longleftrightarrow \quad [A]_t = [A]_0 e^{-kt}, \qquad t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}.$$

A plot of $\ln[A]$ versus t is a straight line of slope $-k$ and y-intercept $\ln[A]_0$. The first-order half-life formula contains *no* concentration term: $t_{1/2}$ is **constant**, independent of $[A]_0$, and is the unmistakable experimental signature of a first-order process — after each successive half-life, exactly half of whatever concentration remained is consumed, regardless of how much that was.

5.3.3 Second-order reactions

For a reaction second order in a single reactant A (rate $= k[A]^2$), integration gives

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt, \qquad t_{1/2} = \frac{1}{k[A]_0}.$$

A plot of $1/[A]$ versus t is a straight line of slope $+k$ and y-intercept $1/[A]_0$. The second-order half-life *depends inversely* on $[A]_0$: unlike zero order (where $t_{1/2}$ shrinks as $[A]_0$ falls, since $t_{1/2} \propto [A]_0$), the second-order half-life *grows longer* as the reaction proceeds and $[A]_0$ falls, since $t_{1/2} \propto 1/[A]_0$.

Graphical order determination. Plot $[A]$, $\ln[A]$, and $1/[A]$ each against t using the same concentration-time data set; whichever plot comes out as a straight line reveals the order. Only one of the three will be linear (barring a reaction that happens to be pseudo-linear over a very narrow concentration range).

Order	Integrated rate law	Linear plot	Slope of line
0	$[A]_t = [A]_0 - kt$	$[A]$ vs t	$-k$
1	$\ln[A]_t = \ln[A]_0 - kt$	$\ln[A]$ vs t	$-k$
2	$1/[A]_t = 1/[A]_0 + kt$	$1/[A]$ vs t	$+k$

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Ba định luật tốc độ tích phân: bậc 0 ($[A]_t = [A]_0 - kt$, đồ thị $[A]$ theo t là đường thẳng), bậc 1 ($\ln[A]_t = \ln[A]_0 - kt$, đồ thị $\ln[A]$ theo t là đường thẳng), bậc 2 ($1/[A]_t = 1/[A]_0 + kt$, đồ thị $1/[A]$ theo t là đường thẳng). Chu kỳ bán rã: bậc 0 giảm dần theo thời gian ($t_{1/2} = [A]_0/2k$), bậc 1 **không đổi** ($t_{1/2} = \ln 2/k$, đặc trưng riêng của bậc 1), bậc 2 tăng dần theo thời gian ($t_{1/2} = 1/(k[A]_0)$). Muốn xác định bậc phản ứng bằng đồ thị, vẽ cả ba đồ thị từ cùng bộ số liệu và xem đồ thị nào là đường thẳng.

Half-life of a first-order reaction

A first-order reaction has rate constant $k = 0.0231\ \text{s}^{-1}$. Find its half-life.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{0.0231} = 30.0\ \text{s}.$$

Concentration after elapsed time — first order

Using the same reaction ($k = 0.0231\ \text{s}^{-1}$, first order, $t_{1/2} = 30.0$ s), if $[A]_0 = 0.400$ M, find $[A]$ after $t = 60.0$ s.

$$\ln[A]_t = \ln(0.400) - (0.0231)(60.0) = -0.9163 - 1.386 = -2.302.$$

$$[A]_t = e^{-2.302} = 0.100\ \text{M}.$$

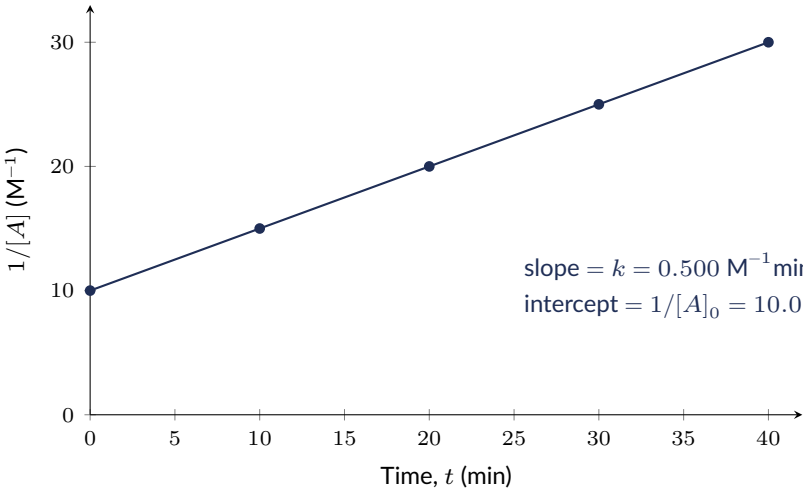
This is a useful check: 60.0 s is exactly two half-lives (2×30.0 s), so $[A]$ should fall $0.400 \to 0.200 \to 0.100$ M — matching the integrated-rate-law result exactly.

Concentration after elapsed time — second order

A reaction is second order in A with $k = 0.250\ \text{M}^{-1}\text{s}^{-1}$. If $[A]_0 = 0.0500$ M, find $[A]$ after $t = 120$ s.

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt = \frac{1}{0.0500} + (0.250)(120) = 20.0 + 30.0 = 50.0\ \text{M}^{-1}.$$

$$[A]_t = \frac{1}{50.0} = 0.0200\ \text{M}.$$



$1/[A]$ plotted against t for the data set in the next example. The perfectly linear trend confirms second-order kinetics; the slope equals k and the intercept equals $1/[A]_0$.

Determining order from a linearized graph

A reactant's concentration was measured over time:

t (min)	0	10	20	30	40
$[A]$ (M)	0.1000	0.0667	0.0500	0.0400	0.0333

Determine the reaction order and the rate constant.

Computing $1/[A]$ at each time gives $10.0,\ 15.0,\ 20.0,\ 25.0,\ 30.0\ \text{M}^{-1}$ — these increase by exactly $5.0\ \text{M}^{-1}$ every 10 min, i.e. $1/[A]$ is a perfectly linear function of t (shown in the figure above). Since $1/[A]$ vs t is the linear plot that diagnoses second order, the reaction is **second order** in A. The slope of the line is

$$k = \frac{30.0 - 10.0}{40 - 0} = \frac{20.0}{40} = 0.500\ \text{M}^{-1}\text{min}^{-1},$$

consistent with the y-intercept $1/[A]_0 = 10.0\ \text{M}^{-1}$, i.e. $[A]_0 = 0.100$ M, matching the data. (By contrast, computing $\ln[A]$ at each time — $-2.303,\ -2.708,\ -2.996,\ -3.219,\ -3.401$ — shows successive differences of decreasing magnitude, $-0.405, -0.288, -0.223, -0.182$; this curve is *not* linear, confirming the reaction is not first order.)

(!) Lỗi thường gặp: The single most tested fact in this unit: only the *first-order* half-life is a constant, concentration-independent number. Do not apply $t_{1/2} = 0.693/k$ to a reaction that

is zero or second order — each order has its own half-life formula, and for zero- and second-order reactions the half-life explicitly depends on $[A]_0$ and changes as the reaction proceeds (shrinking for zero order, growing for second order).

5.4 Elementary reactions

An **elementary reaction** (or elementary step) is a single mechanistic event — one collision or one bond-breaking/bond-forming act — that occurs exactly as written, with no intermediate species or hidden steps. Elementary steps are the building blocks from which a multistep **mechanism** (Section 5.6) is assembled; the overall balanced equation for a reaction is rarely elementary itself.

Khái niệm cốt lõi

The **molecularity** of an elementary step is the number of reactant particles (molecules, atoms, or ions) that must come together for that step to occur:

- **Unimolecular** ($A \rightarrow$ products): a single molecule undergoes rearrangement or decomposition (e.g. isomerization, or a bond simply breaking apart). Rate $= k[A]$ — first order.
- **Bimolecular** ($A + B \rightarrow$ products, or $2A \rightarrow$ products): two particles collide and react. This is by far the most common type of elementary step, since two-body collisions are far more probable than higher-order collisions. Rate $= k[A][B]$ or $k[A]^2$ — second order overall.
- **Termolecular** ($2A + B \rightarrow$ products, etc.): three particles must collide *simultaneously*. This is very rare, because the probability of three particles meeting at exactly the same instant, with the correct energy and orientation, is far lower than for a two-body collision. Genuinely termolecular elementary steps are unusual; reactions that appear to require three-body collisions overall are almost always the sum of two or more bimolecular/unimolecular elementary steps (see the pre-equilibrium example in Section 5.7).

For an elementary step only, the rate law can be written *directly* from its stoichiometry — the order in each species equals its coefficient in that step, because the step's molecularity literally tells you how many particles of each kind must collide. This is the one situation in kinetics where the rate law can be read off an equation without experimental data — but it applies only to a single elementary step, never to an overall, multistep balanced equation.

Rate law of an elementary step

The reaction of nitric oxide with ozone, $NO + O_3 \rightarrow NO_2 + O_2$, occurs as a single elementary, bimolecular step. Write its rate law and state its molecularity.

Because this step is elementary, the rate law follows directly from the coefficients: rate $= k[NO][O_3]$ — first order in each reactant, second order overall. The step is **bimolecular** (two reactant particles, NO and O_3, collide).

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Phản ứng đơn giản (elementary reaction/step) là một bước phản ứng xảy ra đúng như phương trình viết ra, không qua giai đoạn trung gian ẩn nào. **Độ phân tử** (molecularity) đếm số hạt phản ứng va chạm cùng lúc: đơn phân tử (unimolecular, 1 hạt), lưỡng phân tử (bimolecular, 2 hạt — phổ biến nhất), tam phân tử (termolecular, 3 hạt — rất hiếm vì xác suất ba hạt va chạm đồng thời cực thấp). **Chỉ với bước đơn giản (elementary)**, ta mới được viết định luật tốc độ trực tiếp từ hệ số phương trình — quy tắc này KHÔNG áp dụng cho phương trình tổng của phản ứng nhiều bước.

5.5 Collision model

The **collision model** explains, at the molecular level, why reactions have rate constants that depend on temperature and why not every collision between reactant particles leads to product formation.

Khái niệm cốt lõi

For a collision between reactant particles to be successful (to actually produce product), two conditions must both be satisfied:

- **Sufficient energy**: the collision must supply at least the **activation energy**, E_a — the minimum kinetic energy, concentrated into the colliding bond(s), needed to distort and break existing bonds so that new ones can form. Collisions with total kinetic energy below E_a simply bounce apart unreacted, however favorably oriented they are.
- **Proper orientation**: the particles must collide in a geometric arrangement that brings the reactive atoms/groups together correctly. Even a collision with more than enough energy fails if the molecules strike each other in a geometry that cannot lead to the required bond reorganization (e.g. the wrong ends of two molecules colliding).

Only the (typically small) fraction of collisions satisfying both conditions simultaneously result in reaction; this is why measured rate constants are almost always far smaller than the theoretical total collision frequency.

5.5.1 The Maxwell–Boltzmann distribution and temperature

At any given temperature, molecules in a sample do not all have the same kinetic energy — their energies are spread over a continuous **Maxwell–Boltzmann distribution**. The fraction of molecules possessing kinetic energy at or above E_a can be approximated by the Boltzmann factor

$$f \approx e^{-E_a/RT},$$

which is exactly the exponential term that appears in the Arrhenius equation below. As temperature increases, the entire Maxwell–Boltzmann curve broadens and its peak shifts to higher energy; critically, the *area under the curve beyond* E_a — the fraction of sufficiently energetic collisions — grows sharply, even though the total number of molecules and the average collision frequency change only modestly. This is the fundamental molecular-level reason that reaction rate increases so strongly with temperature: raising T only slightly increases the collision frequency, but it can multiply the fraction of collisions with $E \geq E_a$ many times over, because that fraction sits on the exponentially decaying tail of the distribution.

Effect of temperature on the fraction of sufficiently energetic collisions

For a reaction with $E_a = 50.0$ kJ/mol, estimate the fraction of collisions with energy $\geq E_a$ at 298 K and at 308 K using $f = e^{-E_a/RT}$, and compare.

At $T = 298$ K: $\dfrac{E_a}{RT} = \dfrac{50{,}000}{(8.314)(298)} = 20.18$, so $f_{298} = e^{-20.18} = 1.72 \times 10^{-9}$.

At $T = 308$ K: $\dfrac{E_a}{RT} = \dfrac{50{,}000}{(8.314)(308)} = 19.53$, so $f_{308} = e^{-19.53} = 3.31 \times 10^{-9}$.

Ratio: $f_{308}/f_{298} = 1.93$ — raising the temperature by just 10 K (about 3%) very nearly *doubles* the fraction of molecules energetic enough to react, even though f itself remains a tiny fraction of all molecules. This is the molecular-level origin of the familiar rule of thumb that reaction rate roughly doubles for every $10\ ^\circ$C rise near room temperature.

VN GIẢI THÍCH TIẾNG VIỆT

Theo thuyết va chạm, một va chạm chỉ dẫn đến phản ứng khi thoả **đồng thời hai điều kiện**: (1) năng lượng va chạm $\geq E_a$ (năng lượng hoạt hoá) và (2) định hướng va chạm phù hợp về mặt hình học. Phân bố Maxwell–Boltzmann cho thấy khi tăng nhiệt độ, phần diện tích dưới đường cong ứng với $E \geq E_a$ tăng mạnh (dù tần suất va chạm tổng thể chỉ tăng nhẹ) — đây là lý do gốc rễ khiến tốc độ phản ứng tăng nhanh theo nhiệt độ.

5.5.2 The Arrhenius equation

The Swedish chemist Svante Arrhenius formalized the temperature dependence of the rate constant in the **Arrhenius equation**:

$$k = Ae^{-E_a/RT},$$

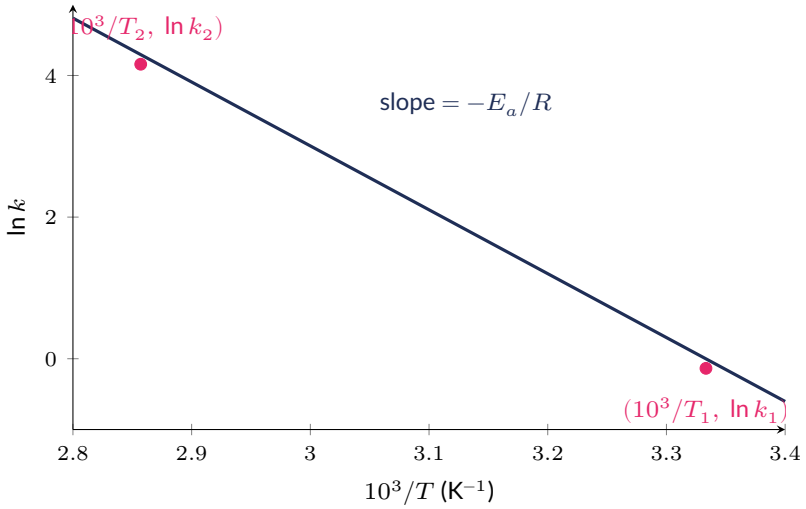
where A is the **pre-exponential factor** (or frequency factor, related to collision frequency and orientation probability, roughly constant over modest temperature ranges), E_a is the activation energy in J/mol, $R = 8.314\ \text{J mol}^{-1}\text{K}^{-1}$, and T is absolute temperature in kelvin. Taking the natural log of both sides linearizes the equation:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A,$$

so a plot of $\ln k$ (vertical axis) against $1/T$ (horizontal axis) is a straight line of slope $-E_a/R$ and y-intercept $\ln A$ — this is the standard experimental method for extracting E_a from rate constants measured at several temperatures. When only two (T, k) data points are available, subtracting the two log forms eliminates $\ln A$ and gives the convenient **two-point form**:

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

(!) Lỗi thường gặp: Activation energies are usually quoted in kJ/mol, but $R = 8.314\ \text{J mol}^{-1}\text{K}^{-1}$ uses joules. Forgetting to convert E_a to J/mol (multiply the kJ/mol value by 1000) before dividing by R is one of the most common arithmetic errors in this topic, and it throws the final exponent off by a factor of 1000. Always check units before evaluating E_a/R or $E_a/(RT)$.



Arrhenius plot for the worked example below: $T_1 = 300$ K, $k_1 = 0.873\ \text{s}^{-1}$; $T_2 = 350$ K, $k_2 = 64.0\ \text{s}^{-1}$. The line's slope, $-E_a/R$ (expressed here per unit of $10^3/T$), gives $E_a \approx 75.0$ kJ/mol.

Finding E_a from two (T, k) data points

A first-order reaction has $k_1 = 0.873\ \text{s}^{-1}$ at $T_1 = 300$ K and $k_2 = 64.0\ \text{s}^{-1}$ at $T_2 = 350$ K. Find E_a.

$$\ln\frac{k_2}{k_1} = \ln\frac{64.0}{0.873} = \ln(73.3) = 4.295.$$

$$\frac{1}{T_2} - \frac{1}{T_1} = \frac{1}{350} - \frac{1}{300} = 0.0028571 - 0.0033333 = -4.762 \times 10^{-4}\ \text{K}^{-1}.$$

Solving the two-point Arrhenius equation for E_a:

$$E_a = -R\,\frac{\ln(k_2/k_1)}{(1/T_2 - 1/T_1)} = -(8.314)\frac{4.295}{-4.762 \times 10^{-4}} = 74{,}980\ \text{J/mol} \approx 75.0\ \text{kJ/mol}.$$

Predicting k at a new temperature

Using $E_a = 75.0$ kJ/mol and $k_1 = 0.873\ \text{s}^{-1}$ at $T_1 = 300$ K (from the previous example), predict k at $T_3 = 340$ K.

$$\frac{1}{T_3} - \frac{1}{T_1} = \frac{1}{340} - \frac{1}{300} = 0.0029412 - 0.0033333 = -3.922 \times 10^{-4}\ \text{K}^{-1}.$$

$$\ln\frac{k_3}{k_1} = -\frac{75{,}000}{8.314}\left(-3.922 \times 10^{-4}\right) = 3.538.$$

$$k_3 = k_1\, e^{3.538} = (0.873)(34.4) = 30.0\ \text{s}^{-1}.$$

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Phương trình Arrhenius $k = Ae^{-E_a/RT}$ (hoặc dạng logarit $\ln k = -\frac{E_a}{R}\cdot\frac{1}{T} + \ln A$) mô tả sự phụ thuộc của hằng số tốc độ vào nhiệt độ. Đồ thị $\ln k$ theo $1/T$ là đường thẳng có độ dốc $-E_a/R$. Với hai cặp số liệu (T_1, k_1) và (T_2, k_2), dùng công thức hai điểm để tính E_a hoặc dự đoán k ở nhiệt độ khác. **Lưu ý đơn vị**: nếu E_a cho theo kJ/mol, phải đổi sang J/mol trước khi chia cho $R = 8.314\ \text{J mol}^{-1}\text{K}^{-1}$.

5.6 Reaction mechanism and rate law

A **reaction mechanism** is the sequence of elementary steps that, taken together, describes how an overall reaction actually occurs at the molecular level. Each elementary step in a mechanism is written and interpreted according to the rules of Section 5.4 (molecularity, direct rate law from stoichiometry).

Khái niệm cốt lõi

A valid mechanism must satisfy two requirements:

- **The elementary steps must sum to the overall balanced equation.** Any species produced in one step and entirely consumed in a later step (never appearing in the overall equation) is a **reaction intermediate**.
- **The rate law predicted by the mechanism must match the experimentally observed rate law.** A mechanism is only a proposed explanation until this consistency is verified; several different mechanisms may be consistent with the same overall equation, but only one (or a small set of kinetically indistinguishable ones) matches the actual measured rate law.

5.6.1 The rate-determining step

When a mechanism has one elementary step that is much slower than the others, that step acts as a bottleneck: the overall reaction can proceed no faster than this slowest step allows, no matter how fast the other steps are. This slow step is called the **rate-determining step (RDS)**, and — when the RDS is the *first* step of the mechanism — the overall rate law is simply the rate law of that elementary step, written directly from its stoichiometry.

> If the rate-determining step is the first step, species that appear only in later, faster steps do *not* appear in the overall rate law at all, even though they are reactants in the overall balanced equation — because the RDS alone controls the observed kinetics.

Deriving a rate law from a mechanism — slow step first

The reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is proposed to occur by the mechanism

$$\text{Step 1 (slow): } 2NO_2 \rightarrow NO_3 + NO$$

$$\text{Step 2 (fast): } NO_3 + CO \rightarrow NO_2 + CO_2$$

Verify the steps sum to the overall equation, identify any intermediate, and predict the rate law.

Summing the steps: adding the two equations, $2NO_2 + NO_3 + CO \rightarrow NO_3 + NO + NO_2 + CO_2$; canceling NO_3 (appears on both sides) and one NO_2 from each side gives $NO_2 + CO \rightarrow NO + CO_2$ — matches the overall equation ✓. NO_3 is produced in Step 1 and entirely consumed in Step 2, so it is a **reaction intermediate** (it never appears in the overall equation).

Rate law: since Step 1 is both elementary and rate-determining, the overall rate law is simply Step 1's rate law: rate $= k[NO_2]^2$. Note that CO, although a reactant in the overall equation, does not appear in the rate law at all — it only participates in the fast step *after* the bottleneck, so its concentration has no effect on the observed rate. (This matches the rate law actually measured for this reaction at low temperature.)

VN **GIẢI THÍCH TIẾNG VIỆT**

Cơ chế phản ứng (mechanism) là chuỗi các bước đơn giản (elementary steps) cộng lại đúng bằng phương trình tổng. Chất sinh ra ở một bước rồi bị tiêu thụ hết ở bước sau (không xuất hiện trong phương trình tổng) gọi là **chất trung gian** (intermediate). Nếu bước chậm nhất — **bước quyết định tốc độ** (rate-determining step, RDS) — là bước đầu tiên, thì định luật tốc độ của toàn phản ứng chính là định luật tốc độ của bước đó, viết trực tiếp từ hệ số của nó; các chất chỉ xuất hiện ở bước nhanh phía sau sẽ không xuất hiện trong định luật tốc độ tổng.

5.7 Pre-equilibrium approximation

The slow-step-first case in Section 5.6 is straightforward, but many real mechanisms instead have a **fast, reversible** step *preceding* the rate-determining step. In that situation the rate law of the slow step usually contains the concentration of a reaction intermediate — and a valid rate law can never be left in terms of an intermediate, since intermediates are not directly measurable/controllable reactant concentrations. The **pre-equilibrium approximation** resolves this: because the first step is fast and reversible, it is assumed to reach equilibrium essentially instantaneously (rapidly compared to the slow step that follows), so its forward and reverse rates are equal and its equilibrium-constant expression can be used to solve for the intermediate's concentration in terms of the actual reactants.

Khái niệm cốt lõi

Procedure. For a mechanism

$$\text{Step 1 (fast, reversible): } A + B \rightleftharpoons I \qquad (\text{rate}_f = k_1[A][B],\ \text{rate}_r = k_{-1}[I])$$

$$\text{Step 2 (slow): } I + C \rightarrow \text{products} \qquad (\text{rate} = k_2[I][C])$$

setting the forward and reverse rates of Step 1 equal (equilibrium) gives $k_1[A][B] = k_{-1}[I]$, so

$$[I] = \frac{k_1}{k_{-1}}[A][B] = K_1[A][B],$$

where $K_1 = k_1/k_{-1}$ is the equilibrium constant of the fast first step. Substituting into the rate law of the slow step eliminates the intermediate:

$$\text{rate} = k_2[I][C] = k_2K_1[A][B][C],$$

an overall rate law expressed entirely in terms of reactants, with an experimentally observed rate constant $k_{\text{obs}} = k_2K_1$.

Deriving a rate law using the pre-equilibrium approximation

The reaction $2\text{NO}(g) + \text{Br}_2(g) \rightarrow 2\text{NOBr}(g)$ is proposed to occur by

$$\text{Step 1 (fast, reversible): NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$$

$$\text{Step 2 (slow): NOBr}_2 + \text{NO} \rightarrow 2\text{NOBr}$$

Verify the mechanism sums correctly and derive the predicted rate law.

Summing: $\text{NO} + \text{Br}_2 + \text{NOBr}_2 + \text{NO} \rightarrow \text{NOBr}_2 + 2\text{NOBr}$; canceling NOBr_2 gives $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$ ✓. NOBr_2 is the intermediate (produced in Step 1, consumed in Step 2).

Naive rate law from Step 2 alone: rate $= k_2[\text{NOBr}_2][\text{NO}]$ — invalid as written because $[\text{NOBr}_2]$, an intermediate, cannot be measured or controlled directly.

Apply pre-equilibrium to Step 1: $k_1[\text{NO}][\text{Br}_2] = k_{-1}[\text{NOBr}_2] \Rightarrow [\text{NOBr}_2] = K_1[\text{NO}][\text{Br}_2]$, with $K_1 = k_1/k_{-1}$.

Substitute:

$$\text{rate} = k_2(K_1[\text{NO}][\text{Br}_2])[\text{NO}] = k_2K_1[\text{NO}]^2[\text{Br}_2] = k_{\text{obs}}[\text{NO}]^2[\text{Br}_2].$$

This third-order rate law (second order in NO, first order in Br_2) matches the rate law actually measured for this reaction — even though no single elementary step in the mechanism is termolecular. This is precisely why the naive assumption of a single termolecular step $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$ (which would also predict rate $= k[\text{NO}]^2[\text{Br}_2]$) is chemically implausible despite matching the same rate law: a two-step mechanism with a fast pre-equilibrium is a far more probable physical pathway than a single three-body collision.

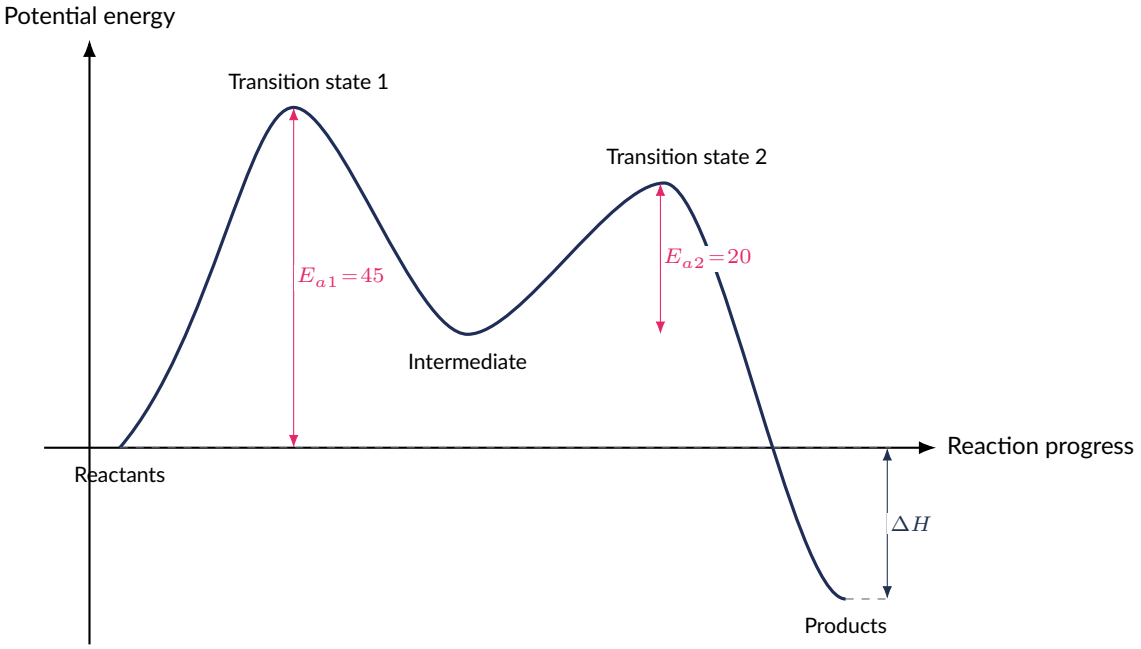
VN **GIẢI THÍCH TIẾNG VIỆT**

Khi bước đầu tiên là bước nhanh, thuận nghịch (fast, reversible), và bước chậm (RDS) xảy ra **sau** nó, định luật tốc độ của bước chậm thường chứa nồng độ chất trung gian — điều này không được phép trong đáp án cuối cùng. **Xấp xỉ tiền cân bằng** (pre-equilibrium approximation) giải quyết vấn đề này: coi bước nhanh đạt cân bằng, dùng biểu thức hằng số cân bằng K_1 của

bước đó để thay thế nồng độ chất trung gian bằng nồng độ của các chất phản ứng ban đầu. Đây là lý do một phản ứng có vẻ bậc ba (ví dụ bậc 2 theo NO, bậc 1 theo Br_2) vẫn có thể xảy ra qua hai bước lưỡng phân tử, thay vì một va chạm tam phân tử hiếm gặp.

5.8 Multistep reaction energy profile

A **reaction-coordinate diagram** (energy profile) plots potential energy against the progress of the reaction. For a multistep mechanism, the diagram shows one "hump" for every elementary step: each hump's peak is a **transition state** (an unstable, fleeting arrangement of partially-formed and partially-broken bonds, a local *maximum* in energy that is never isolated as an actual species), and each valley between two humps is a **reaction intermediate** (an actual, if often short-lived and highly reactive, chemical species — a local *minimum* in energy that in principle could be isolated or detected).



Two-step reaction energy profile (energies in kJ/mol). Reactants (E $= 0$) climb over transition state 1 ($E_{a1} = 45$ kJ/mol) to reach a valley — the intermediate ($E = 15$ kJ/mol, an actual species) — then climb over transition state 2 ($E_{a2} = 20$ kJ/mol, measured from the intermediate) down to products ($E = -20$ kJ/mol). Overall $\Delta H = -20 - 0 = -20$ kJ/mol: exothermic.

Identifying the rate-determining step from a multistep diagram: the RDS corresponds to the step whose transition state sits at the *highest absolute energy in the whole diagram*, measured on a single common energy axis from the reactants. In the figure above, transition state 1 (45 kJ/mol above the reactants) is higher than transition state 2 (35 kJ/mol above the reactants, even though its own local barrier from the intermediate is only 20 kJ/mol) — so **Step 1 is rate-determining**. Comparing each step's local E_a in isolation, without referencing them to the same overall energy axis, can give the wrong step.

Interpreting a multistep energy diagram

Using the diagram above, find (a) ΔH for Step 1 and Step 2 individually, (b) the overall ΔH, and (c) which step is rate-determining.

(a) Step 1: $\Delta H_1 = E_{\text{intermediate}} - E_{\text{reactants}} = 15 - 0 = +15$ kJ/mol (endothermic). Step 2: $\Delta H_2 = E_{\text{products}} - E_{\text{intermediate}} = -20 - 15 = -35$ kJ/mol (exothermic).

(b) Overall $\Delta H = \Delta H_1 + \Delta H_2 = 15 + (-35) = -20$ kJ/mol, matching $E_{\text{products}} - E_{\text{reactants}} = -20 - 0 = -20$ kJ/mol directly — the reaction is exothermic overall even though the first step is endothermic.

(c) Transition state 1 sits at 45 kJ/mol above the reactants, the single highest point on the diagram (transition state 2 sits at only 35 kJ/mol above the reactants); **Step 1 is the rate-determining step**.

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Trên giản đồ năng lượng phản ứng nhiều bước, mỗi "đỉnh" (điểm cực đại cục bộ) là một **trạng thái chuyển tiếp** (transition state) — không phải chất thực sự, chỉ tồn tại trong khoảnh khắc va chạm. Mỗi "đáy" giữa hai đỉnh là một **chất trung gian** (intermediate) — chất thực sự có thể tồn tại (dù thường kém bền, tồn tại ngắn). **Bước quyết định tốc độ** ứng với đỉnh có năng lượng **tuyệt đối cao nhất** trên toàn giản đồ (tính từ mức năng lượng chất đầu), chứ không phải bước có E_a cục bộ (tính từ chất trung gian) lớn nhất.

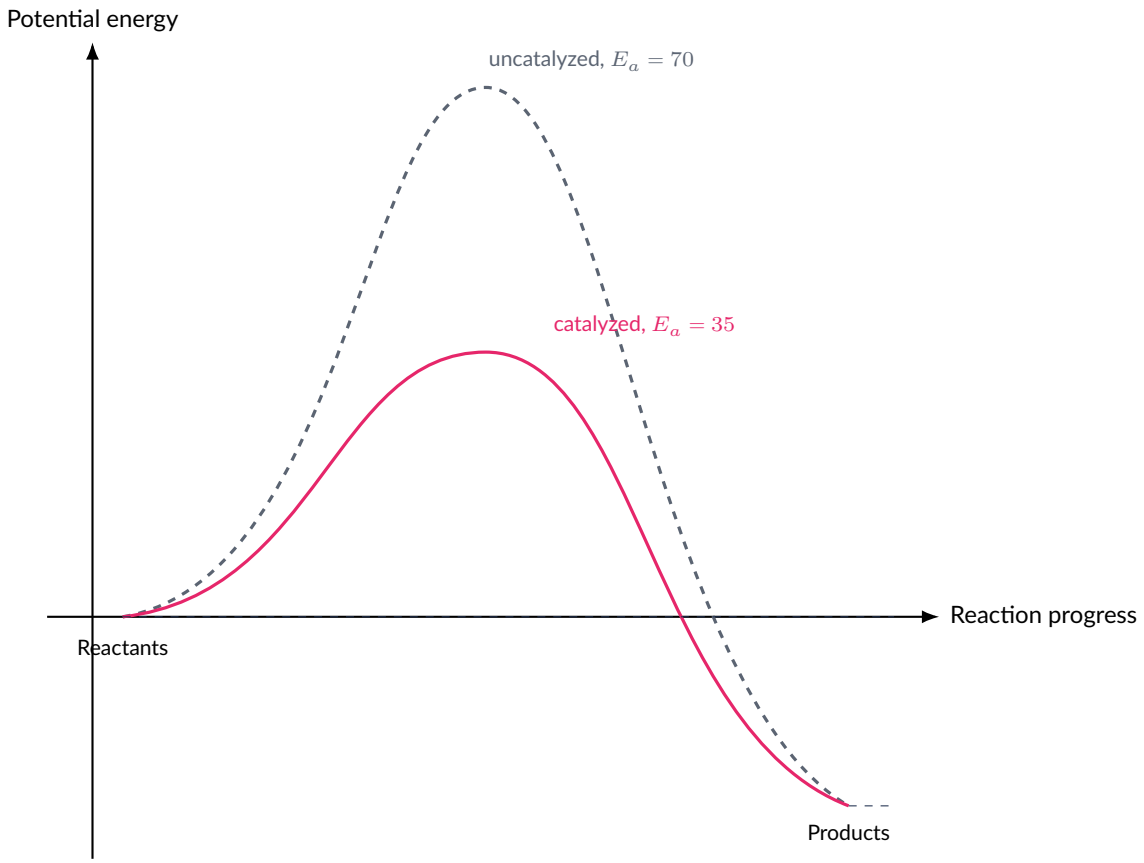
5.9 Catalysis

A **catalyst** is a substance that increases the rate of a reaction without being permanently consumed: it participates in the mechanism (often forming a bond with a reactant or accepting/donating a proton or electron) but is fully regenerated by the end of the overall reaction, so it does not appear in the overall balanced equation. A catalyst works by providing an **alternate reaction pathway with a lower activation energy**, not by supplying energy to the reactants — it changes *how* the reaction gets from reactants to products, not the reactants' or products' energies themselves.

Because a catalyst only lowers E_a along an alternate mechanism, and does not change the energies of the reactants or products themselves, a catalyst:

- **does** increase the rate constant k (both forward and reverse rates increase equally, by the Arrhenius relationship, since E_a drops for both directions of an alternate pathway);
- **does not** change ΔH of the reaction (start and end energies are unchanged — only the pathway between them changes);
- **does not** change the equilibrium constant K (since a catalyst speeds the forward and reverse reactions by exactly the same factor, the equilibrium position — and hence K — is reached faster but is not shifted);
- **does not** appear in the overall balanced equation (though it does appear in the mechanism's elementary steps, being consumed in an early step and regenerated in a later one).

(!) Lỗi thường gặp: Do not confuse a **catalyst** with a **reaction intermediate** — they are, in a sense, mirror images of each other in a mechanism. A catalyst is present *before* the reaction begins, is consumed in an early step, and is regenerated in a later step (net: present at start and end, temporarily "used up" in the middle). An intermediate is *produced* in an early step (it is not present initially) and consumed in a later step (net: absent at start and end, temporarily present in the middle). If a species is consumed then reappears, it is a catalyst; if a species appears then disappears, it is an intermediate.



Catalyzed (pink) versus uncatalyzed (grey, dashed) pathway for the same reaction, energies in kJ/mol. Both curves share the same start and end points, so ΔH is identical for both pathways (-25 kJ/mol here); the catalyst only lowers the height of the barrier that must be crossed, from $E_a = 70$ to $E_a = 35$ kJ/mol.

5.9.1 Homogeneous versus heterogeneous catalysis

A **homogeneous catalyst** is present in the same phase as the reactants (e.g. an aqueous acid or dissolved metal ion catalyzing a reaction in aqueous solution). A **heterogeneous catalyst** is present in a different phase from the reactants — most commonly a solid catalyzing a gas- or liquid-phase reaction, as in a car's catalytic converter (solid platinum/palladium/rhodium catalyzing gas-phase combustion of exhaust pollutants). Heterogeneous catalysis typically proceeds by **adsorption** of reactant molecules onto active sites on the catalyst's surface, which weakens their internal bonds and holds them in favorable orientation for reaction, followed by **desorption** of the product once formed.

Enzymes are highly specific biological catalysts, almost always proteins, that accelerate biochemical reactions (often by factors of 10^6 or more) by binding a substrate at a precisely shaped **active site**, stabilizing the transition state and thereby lowering E_a for a specific reaction — the same fundamental mechanism as any other catalyst, applied with extraordinary molecular specificity.

Identifying catalyst versus intermediate in a mechanism

Hydrogen peroxide decomposition, $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$, can be catalyzed by iodide ion via the mechanism

$$\text{Step 1: } H_2O_2 + I^- \rightarrow H_2O + IO^-$$

$$\text{Step 2: } H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$$

Identify the catalyst and the intermediate, and verify the mechanism sums to the overall equation.

Summing: $2H_2O_2 + I^- + IO^- \rightarrow 2H_2O + O_2 + IO^- + I^-$; canceling I^- and IO^- (each appears

on both sides) gives $2H_2O_2 \rightarrow 2H_2O + O_2$ ✓, matching the overall equation.

I^- is *consumed* in Step 1 and *regenerated* in Step 2 — present at the start, absent in the middle, present again at the end: I^- is the **catalyst**. IO^- is *produced* in Step 1 and *consumed* in Step 2 — absent at the start, present in the middle, absent at the end: IO^- is the **intermediate**. Note that neither species appears in the overall balanced equation.

Quantifying the rate increase from a lower activation energy

A catalyst lowers the activation energy of a reaction from 80.0 kJ/mol to 50.0 kJ/mol at $T = 298$ K, with the pre-exponential factor A assumed unchanged. By what factor does the rate constant increase?

Since $k = Ae^{-E_a/RT}$ with the same A and T for both pathways,

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{Ae^{-E_{a,\text{cat}}/RT}}{Ae^{-E_{a,\text{uncat}}/RT}} = e^{(E_{a,\text{uncat}} - E_{a,\text{cat}})/RT} = \exp\left(\frac{80{,}000 - 50{,}000}{(8.314)(298)}\right) = e^{12.11}.$$

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = 1.81 \times 10^5.$$

A 30 kJ/mol reduction in activation energy increases the rate constant by roughly $180{,}000$-fold at room temperature — a striking illustration of how exponentially sensitive rate is to E_a, and why even modest changes in barrier height (as achieved by enzymes and industrial catalysts) can have an enormous practical effect on reaction rate.

VN **GIẢI THÍCH TIẾNG VIỆT**

Chất xúc tác (catalyst) làm tăng tốc độ phản ứng bằng cách mở ra một **con đường phản ứng khác có E_a thấp hơn**, chứ không cung cấp năng lượng cho chất phản ứng. Xúc tác **không** làm thay đổi ΔH hay hằng số cân bằng K (vì nó tăng tốc độ thuận và nghịch như nhau). Phân biệt xúc tác với chất trung gian: xúc tác bị tiêu thụ ở bước đầu rồi **tái sinh** ở bước sau (có mặt lúc đầu và lúc cuối); chất trung gian được **sinh ra** ở bước đầu rồi bị tiêu thụ ở bước sau (không có mặt lúc đầu, không có mặt lúc cuối). Xúc tác **đồng thể** (homogeneous) cùng pha với chất phản ứng; xúc tác **dị thể** (heterogeneous) khác pha (thường là chất rắn xúc tác cho phản ứng khí/lỏng, ví dụ bộ chuyển đổi xúc tác ô tô). Enzyme là xúc tác sinh học đặc hiệu cao, hoạt động theo cùng nguyên lý hạ thấp E_a tại vị trí hoạt động (active site).

5.10 Practice problems

Bài tập luyện tập

For the reaction $aA + bB \rightarrow cC$, which expression correctly gives the rate of reaction in terms of the rate of formation of C?

(A) $-\frac{1}{c}\frac{\Delta[C]}{\Delta t}$

(B) $+\frac{1}{c}\frac{\Delta[C]}{\Delta t}$

(C) $+c\frac{\Delta[C]}{\Delta t}$

(D) $-c\frac{\Delta[C]}{\Delta t}$

Lời giải chi tiết

C is a product, so its concentration increases with time and no sign change is needed; dividing by its coefficient c converts the species rate into the single, shared rate of reaction. **(B)**.

Bài tập luyện tập

In the reaction $2A + B \rightarrow C$, the rate of disappearance of A is measured to be 0.020 M/s at a given instant. What is the rate of disappearance of B and the rate of formation of C at that instant?

Lời giải chi tiết

Rate of reaction $= \frac{1}{2}(0.020) = 0.010$ M/s. Since B and C each have coefficient 1, the rate of disappearance of B is 0.010 M/s and the rate of formation of C is 0.010 M/s.

Bài tập luyện tập

For the reaction $A + B \rightarrow C$, the following data were obtained:

Trial	$[A]_0$ (M)	$[B]_0$ (M)	Initial rate (M/s)
1	0.050	0.050	6.0×10^{-4}
2	0.100	0.050	1.2×10^{-3}
3	0.100	0.100	1.2×10^{-3}

Determine the rate law, the value and units of k, and predict the initial rate when $[A]_0 = 0.200$ M and $[B]_0 = 0.400$ M.

Lời giải chi tiết

Trials 1→2: $[A]$ doubles, $[B]$ fixed, rate doubles ($6.0 \times 10^{-4} \rightarrow 1.2 \times 10^{-3}$) $\Rightarrow$ order in $A = 1$. Trials 2→3: $[B]$ doubles, $[A]$ fixed, rate unchanged $\Rightarrow$ order in $B = 0$. Rate law: rate $= k[A]$ (first order overall). Using trial 1: $k = \dfrac{6.0 \times 10^{-4}}{0.050} = 0.0120$ s^{-1}. Predicted rate at $[A]_0 = 0.200$ M (independent of $[B]$): rate $= (0.0120)(0.200) = 2.40 \times 10^{-3}$ M/s.

Bài tập luyện tập

For the reaction $A + B + C \rightarrow$ products:

Trial	$[A]_0$ (M)	$[B]_0$ (M)	$[C]_0$ (M)	Initial rate (M/s)
1	0.10	0.10	0.10	4.0×10^{-3}
2	0.20	0.10	0.10	1.6×10^{-2}
3	0.20	0.20	0.10	1.6×10^{-2}
4	0.20	0.20	0.20	3.2×10^{-2}

(a) Determine the order in each reactant and the overall order. (b) Find k with correct units. (c) Predict the initial rate when $[A]_0 = 0.30$ M, $[B]_0 = 0.50$ M, $[C]_0 = 0.40$ M.

Lời giải chi tiết

(a) Trials 1→2: $[A] \times 2$, rate $\times 4 = 2^2 \Rightarrow$ order in $A = 2$. Trials 2→3: $[B] \times 2$, rate unchanged $\Rightarrow$ order in $B = 0$. Trials 3→4: $[C] \times 2$, rate $\times 2 = 2^1 \Rightarrow$ order in $C = 1$. Rate law: rate $= k[A]^2[C]$; overall order $= 3$ (B does not appear).

(b) Using trial 1: $4.0 \times 10^{-3} = k(0.10)^2(0.10) = k(1.0 \times 10^{-3}) \Rightarrow k = 4.0\ \text{M}^{-2}\text{s}^{-1}$. Check trial 4: $4.0(0.20)^2(0.20) = 4.0(0.008) = 0.032 = 3.2 \times 10^{-2}$ M/s ✓.

(c) rate $= 4.0(0.30)^2(0.40) = 4.0(0.09)(0.40) = 0.144 = 1.44 \times 10^{-1}$ M/s ($[B]_0$ is irrelevant since order in B is 0).

Bài tập luyện tập

A reaction obeys the rate law rate $= k[A]^2[B]$. What are the units of k?

(A) $\text{M}^{-1}\text{s}^{-1}$

(B) $\text{M}^{-2}\text{s}^{-1}$

(C) s^{-1}

(D) M s^{-1}

Lời giải chi tiết

Overall order $= 2 + 1 = 3$; units of $k = \text{M}^{1-n}\text{s}^{-1} = \text{M}^{1-3}\text{s}^{-1} = \text{M}^{-2}\text{s}^{-1}$. **(B)**.

Bài tập luyện tập

A first-order reaction has $k = 0.0347\ \text{min}^{-1}$. Find its half-life.

Lời giải chi tiết

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{0.0347} = 20.0\ \text{min}.$$

Bài tập luyện tập

A first-order reaction has $t_{1/2} = 15$ min. What fraction of the original reactant remains after 45 minutes?

Lời giải chi tiết

45 min $= 3$ half-lives. Fraction remaining $= (1/2)^3 = 1/8 = 0.125$, i.e. 12.5% of the original concentration remains.

Bài tập luyện tập

A reaction is second order in A with $k = 0.150\ \text{M}^{-1}\text{min}^{-1}$. Starting from $[A]_0 = 0.220$ M, how long does it take for $[A]$ to fall to 0.100 M?

Lời giải chi tiết

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \ \Rightarrow\ \frac{1}{0.100} - \frac{1}{0.220} = 10.0 - 4.545 = 5.455 = (0.150)t.$$

$$t = \frac{5.455}{0.150} = 36.4\ \text{min}.$$

Bài tập luyện tập

A zero-order reaction has $k = 0.0250$ M/s and $[A]_0 = 0.500$ M. (a) Find $[A]$ after $t = 15.0$ s. (b) Find the half-life.

Lời giải chi tiết

(a) $[A]_t = [A]_0 - kt = 0.500 - (0.0250)(15.0) = 0.500 - 0.375 = 0.125$ M.

(b) $t_{1/2} = \dfrac{[A]_0}{2k} = \dfrac{0.500}{2(0.0250)} = \dfrac{0.500}{0.0500} = 10.0$ s.

Bài tập luyện tập

Concentration-time data for a reactant A:

t (min)	0	5	10	15	20
$[A]$ (M)	0.200	0.1558	0.1213	0.0945	0.0736

Determine the reaction order and the rate constant.

Lời giải chi tiết

Computing $\ln[A]$ at each time: -1.609, -1.859, -2.109, -2.359, -2.609. These decrease by exactly 0.250 every 5 min — a perfectly linear function of t — so the reaction is **first order**. Slope $= -k = \dfrac{-2.609 - (-1.609)}{20 - 0} = \dfrac{-1.000}{20} = -0.0500$ min^{-1}, so $k = 0.0500$ min^{-1}. (Plotting $1/[A]$ instead would *not* give a straight line, confirming the order is not second.)

Bài tập luyện tập

For a reaction known to be second order in a single reactant A, which graph will be linear?

(A) $[A]$ vs t

(B) $\ln[A]$ vs t

(C) $1/[A]$ vs t

(D) $[A]^2$ vs t

Lời giải chi tiết

The second-order integrated rate law $1/[A]_t = 1/[A]_0 + kt$ is linear in $1/[A]$ versus t, with slope k. **(C).**

Bài tập luyện tập

A reaction has $k_1 = 3.20$ s^{-1} at $T_1 = 280$ K and $k_2 = 80.3$ s^{-1} at $T_2 = 320$ K. Find E_a.

Lời giải chi tiết

$$\ln\frac{k_2}{k_1} = \ln\frac{80.3}{3.20} = \ln(25.09) = 3.222.$$

$$\frac{1}{T_2} - \frac{1}{T_1} = \frac{1}{320} - \frac{1}{280} = 0.0031250 - 0.0035714 = -4.464 \times 10^{-4}\ \text{K}^{-1}.$$

$$E_a = -R\frac{\ln(k_2/k_1)}{1/T_2 - 1/T_1} = -(8.314)\frac{3.222}{-4.464 \times 10^{-4}} = 60{,}000\ \text{J/mol} = 60.0\ \text{kJ/mol}.$$

Bài tập luyện tập

A reaction has $E_a = 88.0$ kJ/mol and pre-exponential factor $A = 2.50 \times 10^{12}$ s^{-1}. Find k at $T = 350$ K.

Lời giải chi tiết

$$\frac{E_a}{RT} = \frac{88{,}000}{(8.314)(350)} = 30.25.$$

$$k = Ae^{-E_a/RT} = (2.50 \times 10^{12})e^{-30.25} = (2.50 \times 10^{12})(7.35 \times 10^{-14}) = 0.184\ s^{-1}.$$

Bài tập luyện tập

A reaction has $E_a = 100.0$ kJ/mol. At $T = 310$ K, the measured rate constant is $k = 4.50 \times 10^{-3}$ s^{-1}. Find the pre-exponential factor A.

Lời giải chi tiết

$$\frac{E_a}{RT} = \frac{100{,}000}{(8.314)(310)} = 38.79, \qquad e^{-38.79} = 1.41 \times 10^{-17}.$$

$$A = \frac{k}{e^{-E_a/RT}} = \frac{4.50 \times 10^{-3}}{1.41 \times 10^{-17}} = 3.19 \times 10^{14}\ s^{-1}.$$

Bài tập luyện tập

Which of the following best describes a termolecular elementary step?

(A) One molecule rearranges into an isomer

(B) Two particles collide and react

(C) Three particles must collide simultaneously; rare due to low collision probability

(D) A catalyst regenerates after the step

Lời giải chi tiết

Termolecular means three reactant particles must collide at once; because the probability of a precisely-timed three-body collision with sufficient energy and orientation is very low, genuinely termolecular elementary steps are uncommon. **(C)**.

Bài tập luyện tập

If the overall reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ were assumed (incorrectly, as a simplification) to occur as a single termolecular elementary step, what rate law would that assumption predict? Is this necessarily the true, experimentally observed rate law?

Lời giải chi tiết

If the step were elementary as written, the rate law follows directly from the coefficients: rate $= k[NO]^2[O_2]$. However, this cannot simply be assumed — a single termolecular collision of three separate gas molecules is physically improbable. The same overall rate law can, and in reality does, arise instead from a two-step mechanism with a fast pre-equilibrium step followed by a bimolecular slow step (see the next problem), which is a far more plausible physical pathway even though it predicts an identical rate law.

Bài tập luyện tập

The reaction $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ is proposed to occur by:

$$\text{Step 1 (fast, reversible): } \text{NO} + \text{O}_2 \rightleftharpoons \text{NO}_3$$

$$\text{Step 2 (slow): } \text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$$

Verify the mechanism is consistent with the overall equation and derive the rate law predicted by this mechanism.

Lời giải chi tiết

Summing: $\text{NO} + \text{O}_2 + \text{NO}_3 + \text{NO} \rightarrow \text{NO}_3 + 2\text{NO}_2$; canceling NO_3 gives $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ ✓. NO_3 is the intermediate. Naive rate law from Step 2: rate $= k_2[\text{NO}_3][\text{NO}]$ (invalid, contains an intermediate). Apply pre-equilibrium to Step 1: $k_1[\text{NO}][\text{O}_2] = k_{-1}[\text{NO}_3] \Rightarrow [\text{NO}_3] = K_1[\text{NO}][\text{O}_2]$. Substituting: rate $= k_2K_1[\text{NO}][\text{O}_2][\text{NO}] = k_{\text{obs}}[\text{NO}]^2[\text{O}_2]$ — second order in NO, first order in O_2, matching the previous problem's naive termolecular prediction, but derived from a physically realistic two-step pathway.

Bài tập luyện tập

Stratospheric ozone destruction is catalyzed by chlorine atoms via:

$$\text{Step 1: } \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$$

$$\text{Step 2: } \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$$

Write the overall equation, and identify the catalyst and the intermediate.

Lời giải chi tiết

Summing: $\text{Cl} + \text{O}_3 + \text{ClO} + \text{O} \rightarrow \text{ClO} + \text{O}_2 + \text{Cl} + \text{O}_2$; canceling Cl and ClO gives the overall equation $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$. Cl is consumed in Step 1 and regenerated in Step 2 (present at start and end) $\Rightarrow$ **catalyst**. ClO is produced in Step 1 and consumed in Step 2 (absent at start and end) $\Rightarrow$ **intermediate**.

Bài tập luyện tập

A two-step mechanism has the energy profile: reactants at $E = 0$, transition state 1 at $E = +60$ kJ/mol, an intermediate at $E = +25$ kJ/mol, transition state 2 at $E = +40$ kJ/mol, and products at $E = +10$ kJ/mol (all relative to reactants). Find E_{a1}, E_{a2} (each measured from the start of its own step), ΔH_1, ΔH_2, the overall ΔH, and identify the rate-determining step.

Lời giải chi tiết

$E_{a1} = 60 - 0 = 60$ kJ/mol (TS1 measured from reactants). $E_{a2} = 40 - 25 = 15$ kJ/mol (TS2 measured from the intermediate). $\Delta H_1 = 25 - 0 = +25$ kJ/mol (endothermic). $\Delta H_2 = 10 - 25 = -15$ kJ/mol (exothermic). Overall $\Delta H = \Delta H_1 + \Delta H_2 = 25 - 15 = +10$ kJ/mol (matches $10 - 0$ directly) — the reaction is endothermic overall. Comparing absolute transition-state energies on the same axis, TS1 (60 kJ/mol) is higher than TS2 (40 kJ/mol), so **Step 1 is rate-determining**.

Bài tập luyện tập

On a multistep reaction energy diagram with two humps and one valley between them, the valley represents:

(A) A transition state
(B) A reaction intermediate
(C) The activation energy of the slow step
(D) The overall ΔH

Lời giải chi tiết

A valley (local energy minimum) between two humps corresponds to a species that has actually formed and briefly persists before reacting further — a reaction intermediate. Peaks (local maxima) are transition states, not valleys. **(B)**.

Bài tập luyện tập

A solid platinum surface catalyzes the hydrogenation of an alkene gas. This is an example of:

(A) Homogeneous catalysis
(B) Heterogeneous catalysis
(C) Enzyme catalysis
(D) Autocatalysis

Lời giải chi tiết

The catalyst (solid Pt) is in a different phase from the reactants (gases), which is the definition of heterogeneous catalysis. **(B)**.

Bài tập luyện tập

Briefly explain, using the collision model and the Maxwell–Boltzmann distribution, why increasing temperature increases reaction rate even though the increase in average collision frequency with temperature is comparatively modest.

Lời giải chi tiết

Rate depends on the fraction of collisions that are both properly oriented and energetic enough ($E \geq E_a$) to react. Raising T broadens the Maxwell–Boltzmann energy distribution and shifts it toward higher energies; because the fraction of molecules with $E \geq E_a$ lies on the exponentially decaying high-energy tail of this distribution, even a modest rise in T produces a disproportionately large increase in that fraction (captured quantitatively by the exponential factor $e^{-E_a/RT}$ in the Arrhenius equation). This exponential sensitivity, not the comparatively small increase in raw collision frequency, is what drives the strong observed temperature dependence of rate.

Bài tập luyện tập

For a reaction with $E_a = 65.0$ kJ/mol, estimate the ratio f_{320}/f_{300} of the fraction of collisions with energy $\geq E_a$ at 320 K compared to 300 K, using $f = e^{-E_a/RT}$.

Lời giải chi tiết

$$\left.\frac{E_a}{RT}\right|_{300} = \frac{65{,}000}{(8.314)(300)} = 26.06, \qquad \left.\frac{E_a}{RT}\right|_{320} = \frac{65{,}000}{(8.314)(320)} = 24.43.$$

$$\frac{f_{320}}{f_{300}} = e^{26.06-24.43} = e^{1.63} = 5.10.$$

Raising the temperature by 20 K roughly quintuples the fraction of sufficiently energetic collisions.

Bài tập luyện tập

True or false, with justification: "Adding a catalyst shifts the equilibrium of a reversible reaction toward more product, increasing the equilibrium constant K."

Lời giải chi tiết

False. A catalyst lowers E_a for both the forward and reverse reactions by the same amount (since both directions share the same alternate, lower-energy pathway), so both k_{forward} and k_{reverse} increase by the same factor. Equilibrium is reached faster, but the equilibrium position — and therefore $K = k_{\text{forward}}/k_{\text{reverse}}$ — is unchanged.

Bài tập luyện tập

A zero-order reaction has $[A]_0 = 0.800$ M and $k = 0.0400$ M/s. Find the time required for $[A]$ to fall from 0.800 M to 0.400 M, and separately the time required to then fall from 0.400 M to 0.200 M. Comment on whether these two "half-life" intervals are equal.

Lời giải chi tiết

First interval ($0.800 \to 0.400$ M): using $[A]_t = [A]_0 - kt$, $0.400 = 0.800 - (0.0400)t_1 \Rightarrow t_1 = \dfrac{0.400}{0.0400} = 10.0$ s. Second interval ($0.400 \to 0.200$ M): treating 0.400 M as the new starting concentration, $0.200 = 0.400 - (0.0400)t_2 \Rightarrow t_2 = \dfrac{0.200}{0.0400} = 5.0$ s. The two half-life intervals are *not* equal (10.0 s versus 5.0 s) — for a zero-order reaction the half-life shortens as the reaction proceeds, since $t_{1/2} = [A]_0/(2k)$ depends directly on the concentration remaining at the start of the interval, unlike the constant half-life of a first-order reaction.

Bài tập luyện tập

A reaction is second order in A with rate constant $k = 0.200$ M^{-1}s^{-1}. Compare its half-life starting from $[A]_0 = 0.500$ M to its half-life starting from $[A]_0 = 0.250$ M.

Lời giải chi tiết

$$t_{1/2}(0.500\text{ M}) = \frac{1}{k[A]_0} = \frac{1}{(0.200)(0.500)} = 10.0\text{ s}.$$

$$t_{1/2}(0.250\text{ M}) = \frac{1}{(0.200)(0.250)} = 20.0\text{ s}.$$

Halving the starting concentration *doubles* the second-order half-life, the opposite trend from a zero-order reaction (where halving $[A]_0$ halves $t_{1/2}$) and in contrast with first order, where

$t_{1/2}$ does not depend on $[A]_0$ at all.

Bài tập luyện tập

For the single-reactant reaction $A \rightarrow$ products, initial-rate data show: at $[A]_0 = 0.100$ M, initial rate $= 5.00\times10^{-3}$ M/s; at $[A]_0 = 0.200$ M, initial rate $= 2.00\times10^{-2}$ M/s. (a) Determine the order in A and the value of k (with units). (b) Starting from $[A]_0 = 0.100$ M, find the time required for $[A]$ to drop to 0.0400 M. (c) Find the half-life of the reaction starting from $[A]_0 = 0.100$ M.

Lời giải chi tiết

(a) $[A]$ doubles and rate increases by a factor $2.00 \times 10^{-2}/5.00 \times 10^{-3} = 4.0 = 2^2$, so the reaction is **second order** in A. $k = \dfrac{\text{rate}}{[A]^2} = \dfrac{5.00 \times 10^{-3}}{(0.100)^2} = \dfrac{5.00 \times 10^{-3}}{0.0100} = 0.500\ \text{M}^{-1}\text{s}^{-1}$. Check: $0.500(0.200)^2 = 0.500(0.0400) = 0.0200$ M/s ✓.

(b)

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \ \Rightarrow\ \frac{1}{0.0400} - \frac{1}{0.100} = 25.0 - 10.0 = 15.0 = (0.500)t \ \Rightarrow\ t = 30.0\ \text{s}.$$

(c)

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(0.500)(0.100)} = 20.0\ \text{s}.$$

Bài tập luyện tập

A student proposes that, because the overall equation for a reaction is $2X + Y \rightarrow Z$, the rate law must be rate $= k[X]^2[Y]$. Explain the flaw in this reasoning, and describe the only circumstance under which this reasoning would be valid.

Lời giải chi tiết

Reaction orders cannot be inferred from the coefficients of an overall, balanced equation — the overall equation only reflects the net stoichiometry, not the mechanism by which the reaction actually proceeds; orders must be determined experimentally (e.g. by the method of initial rates). This reasoning would only be valid if the overall equation itself represented a single *elementary* step (i.e. the reaction genuinely occurs in one collision event exactly as written, with no intermediates) — in that special case alone, the rate law follows directly from the coefficients.

Bài tập luyện tập

In a multistep mechanism, the second (and final) step is rate-determining, and the first step is fast and reversible. Which of the following is true of the overall rate law?

(A) It is simply the rate law of the first step

(B) It may require the pre-equilibrium approximation to eliminate an intermediate

(C) It always equals k[reactants] to the power of their overall stoichiometric coefficients

(D) It cannot be determined from the mechanism

Lời giải chi tiết

When the slow step is not first, the rate law written directly from the slow step often contains the concentration of an intermediate produced in the preceding fast step; the pre-equilibrium approximation (setting the fast step's forward and reverse rates equal) is used to re-express that intermediate's concentration in terms of true reactants. **(B)**.

Bài tập luyện tập

Explain why enzymes, despite following the same fundamental catalytic principle as any other catalyst, are able to achieve extremely large rate enhancements and high selectivity for one specific reaction.

Lời giải chi tiết

An enzyme's active site has a precise three-dimensional shape and array of functional groups that bind one specific substrate (or a small family of closely related substrates) with high geometric and electronic complementarity. This binding stabilizes the transition state of the reaction being catalyzed far more effectively than a simpler catalyst could, lowering E_a substantially for that one reaction pathway while providing essentially no stabilization (and hence no rate enhancement) for unrelated reactions — giving enzymes both very large rate accelerations (often 10^6-fold or more) and very high substrate/reaction selectivity.

Bài tập luyện tập

A reaction's rate constant is measured at three temperatures and $\ln k$ is plotted against $1/T$. The resulting line has slope -8400 K. What is E_a?

(A) 8.40 kJ/mol
(B) 8.4 J/mol
(C) 69.8 kJ/mol
(D) 698 kJ/mol

Lời giải chi tiết

Slope $= -E_a/R \Rightarrow E_a = (8400)(8.314) = 69{,}838$ J/mol $= 69.8$ kJ/mol. **(C)**.

Bài tập luyện tập

Which statement correctly distinguishes the role of a transition state from that of a reaction intermediate on a multistep energy diagram?

(A) Both are isolable chemical species that differ only in energy
(B) A transition state is a local energy maximum and cannot be isolated; an intermediate is a local energy minimum and is, in principle, an actual species
(C) A transition state has lower energy than the reactants; an intermediate has higher energy than the products
(D) They are two names for the same feature of the diagram

Lời giải chi tiết

A transition state sits at a peak (local maximum) and represents a fleeting, partially-bonded arrangement that is never isolated; an intermediate sits in a valley (local minimum) and is a genuine, if often short-lived, chemical species. **(B)**.

Bài tập luyện tập

For the elementary step $2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$ (assume this step is elementary as written), state its molecularity and write its rate law.

Lời giải chi tiết

Two molecules of NOCl must collide (or one NOCl molecule collides with another simultaneously undergoing the same transformation) — this is a **bimolecular** step. Since it is elementary, the rate law follows directly from stoichiometry: rate $= k[\text{NOCl}]^2$ (second order in NOCl, second order overall).

Bài tập luyện tập

A reaction has $\Delta H_{\text{overall}} = -40$ kJ/mol and, uncatalyzed, $E_{a,\text{forward}} = 90$ kJ/mol. A catalyst lowers the forward activation energy to $E_{a,\text{forward}} = 55$ kJ/mol. Find the catalyzed and uncatalyzed reverse activation energies, and state what (if anything) changes between the catalyzed and uncatalyzed pathways.

Lời giải chi tiết

For any pathway, $E_{a,\text{reverse}} = E_{a,\text{forward}} - \Delta H$ (energy from products back up to the shared transition state). Uncatalyzed: $E_{a,\text{reverse}} = 90 - (-40) = 130$ kJ/mol. Catalyzed: $E_{a,\text{reverse}} = 55 - (-40) = 95$ kJ/mol. Both the forward and reverse activation energies drop by the same amount (35 kJ/mol) on the catalyzed pathway, so their difference — which equals ΔH — stays fixed at -40 kJ/mol in both cases: only the pathway's barrier heights change; the thermodynamics (ΔH, and therefore also K) do not.

Bài tập luyện tập

A proposed mechanism for $\text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g)$ is a single elementary bimolecular step. A rival proposal is: Step 1 (fast, reversible) $\text{I}_2 \rightleftharpoons 2\text{I}$; Step 2 (slow) $\text{H}_2 + 2\text{I} \rightarrow 2\text{HI}$. Derive the rate law predicted by the rival two-step mechanism and compare its form to the single-step proposal's rate law.

Lời giải chi tiết

Single elementary step: rate $= k[\text{H}_2][\text{I}_2]$ directly from stoichiometry.

Two-step mechanism: Step 2 alone gives rate $= k_2[\text{H}_2][\text{I}]^2$, containing the intermediate I. Applying pre-equilibrium to Step 1: $k_1[\text{I}_2] = k_{-1}[\text{I}]^2 \Rightarrow [\text{I}]^2 = \dfrac{k_1}{k_{-1}}[\text{I}_2] = K_1[\text{I}_2]$. Substituting: rate $= k_2[\text{H}_2](K_1[\text{I}_2]) = k_2K_1[\text{H}_2][\text{I}_2] = k_{\text{obs}}[\text{H}_2][\text{I}_2]$.

Both proposed pathways predict the identical rate law, rate $= k[\text{H}_2][\text{I}_2]$ — first order in each reactant, second order overall. This is a classic illustration that matching the experimentally observed rate law does not, by itself, prove a particular mechanism; kinetically indistinguishable mechanisms must be ruled out by other evidence (e.g. direct spectroscopic detection of the iodine-atom intermediate).

Bài tập luyện tập

The reaction $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ has $[\text{NO}_2]_0 = 0.0500$ M and is second order in NO_2 with $k = 0.640$ $\text{M}^{-1}\text{s}^{-1}$. Find $[\text{NO}_2]$ after 8.00 s.

Lời giải chi tiết

$$\frac{1}{[\mathrm{NO_2}]_t} = \frac{1}{[\mathrm{NO_2}]_0} + kt = \frac{1}{0.0500} + (0.640)(8.00) = 20.0 + 5.12 = 25.12\ \mathrm{M}^{-1}.$$

$$[\mathrm{NO_2}]_t = \frac{1}{25.12} = 0.0398\ \mathrm{M}.$$

Bài tập luyện tập

Explain why measuring the *initial* rate (rather than the rate at some arbitrary later time) is the preferred experimental strategy for determining reaction order by the method of initial rates.

Lời giải chi tiết

At $t = 0$, the concentrations of all reactants are known precisely (they are the amounts weighed/measured out to start the trial), and no products have yet accumulated to potentially interfere via a reverse reaction or competing pathway. At any later time, reactant concentrations have already changed by an amount that must itself be calculated from the (as yet undetermined) rate law, introducing circularity, and products may begin to affect the rate. Measuring the tangent slope at $t = 0$ avoids both complications, giving a rate that can be directly and unambiguously tied to the initial, precisely known concentrations.

Thermodynamics

Mục tiêu Unit: Phân biệt hệ (system) và môi trường (surroundings); nắm vững quy ước dấu của nhiệt q và enthalpy ΔH cho quá trình toả nhiệt/thu nhiệt; đọc và phân tích giản đồ năng lượng phản ứng (năng lượng hoạt hoá thuận/nghịch E_a, ΔH); hiểu nguyên lý truyền nhiệt và cân bằng nhiệt ($q_{\text{mất}} = -q_{\text{nhận}}$); tính nhiệt lượng bằng nhiệt dung riêng ($q = mc\Delta T$) và phân tích số liệu nhiệt lượng kế (coffee-cup đo ΔH, bomb calorimeter đo ΔE); tính năng lượng cho quá trình chuyển pha qua đường cong gia nhiệt (heating curve); xác định ΔH phản ứng bằng bốn phương pháp: số liệu nhiệt lượng kế, năng lượng liên kết trung bình, enthalpy tạo thành chuẩn ΔH_f°, và định luật Hess.

6.1 Endothermic and exothermic processes

Thermochemistry studies the heat absorbed or released as chemical and physical processes occur. Every analysis begins by drawing a boundary between the **system** — the specific collection of matter under study (the reactants and products of a reaction, the contents of a beaker, the sample inside a calorimeter) — and the **surroundings** — literally everything else, including the container, the solvent, the air, and the room. Energy can cross the boundary between system and surroundings as **heat** (q) or as **work** (w), and thermochemistry is fundamentally the bookkeeping of that energy flow.

System and surroundings

- An **exothermic** process releases energy from the system to the surroundings, usually sensed as the surroundings warming up (a beaker feels hot). The system loses potential energy (stored in chemical bonds or intermolecular arrangement) and that energy is transferred outward as heat.
- An **endothermic** process absorbs energy from the surroundings into the system, usually sensed as the surroundings cooling down (a beaker feels cold, sometimes cold enough to frost over). The system gains potential energy, drawing it from the thermal energy of the surroundings.

Everyday examples: combustion, neutralization of a strong acid with a strong base, and the setting of concrete are exothermic. Melting ice, the dissolution of ammonium nitrate (NH_4NO_3) in water (the basis of instant cold packs), and photosynthesis are endothermic.

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Hệ (system) là phần vật chất đang được nghiên cứu (thường là các chất phản ứng và sản phẩm); **môi trường** (surroundings) là tất cả phần còn lại (bình chứa, dung môi, không khí xung quanh). Quá trình **toả nhiệt** (exothermic) giải phóng năng lượng từ hệ ra môi trường — môi trường ấm lên. Quá trình **thu nhiệt** (endothermic) hấp thụ năng lượng từ môi trường vào hệ — môi trường lạnh đi. Túi chườm lạnh dùng NH_4NO_3 hoà tan trong nước là ví dụ kinh điển của quá trình thu nhiệt.

6.1.1 Sign convention for q and ΔH

Both heat (q) and enthalpy change (ΔH) are reported *from the perspective of the system*, and the two quantities share the same sign for a process occurring at constant pressure (where $q_p = \Delta H$; this equivalence is developed further in Section 6.4).

Exothermic: energy leaves the system $\Rightarrow q < 0$ and $\Delta H < 0$ (heat content of the system decreases).
Endothermic: energy enters the system $\Rightarrow q > 0$ and $\Delta H > 0$ (heat content of the system increases).
The surroundings always experience the *opposite* sign: if the system releases 500 J ($q_{\text{sys}} = -500$ J), the surroundings absorb exactly 500 J ($q_{\text{surr}} = +500$ J). This is a direct statement of **conservation of energy**: energy is neither created nor destroyed, only transferred between system and surroundings (the qualitative content of the **first law of thermodynamics**, $\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$).

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Dấu của q và ΔH luôn được xét **từ góc nhìn của hệ**: hệ toả nhiệt thì $q < 0, \Delta H < 0$; hệ thu nhiệt thì $q > 0, \Delta H > 0$. Môi trường luôn có dấu **ngược lại** với hệ — đây chính là định luật bảo toàn năng lượng (nội dung định tính của định luật 1 nhiệt động lực học): năng lượng hệ mất đi đúng bằng năng lượng môi trường nhận được, và ngược lại. Lỗi phổ biến nhất của học sinh là gán nhầm dấu q theo góc nhìn môi trường thay vì hệ.

Classifying processes and assigning signs

For each process, state whether it is exothermic or endothermic and give the sign of q_{system}: (a) methane burning in a furnace; (b) solid NH_4NO_3 dissolving in water inside an instant cold pack; (c) water vapor condensing on a cold window.

(a) Combustion releases energy as light and heat to the surroundings: **exothermic**, $q < 0$.
(b) The cold pack becomes cold, meaning the surroundings (the pack's outer surface, and the hand touching it) lose thermal energy to the dissolution process: **endothermic**, $q > 0$.
(c) Condensation releases the energy that was absorbed during vaporization; the window (part of the surroundings, if the system is defined as the water) warms slightly: **exothermic**, $q < 0$.

(!) Lỗi thường gặp: Students frequently report the sign of q or ΔH from the surroundings' point of view instead of the system's. A reaction that makes the beaker feel *hot* is exothermic *for the system* ($q_{\text{sys}} < 0$) even though the surroundings gained heat ($q_{\text{surr}} > 0$) — the surroundings warming up is the *evidence* of an exothermic system, not a contradiction of the sign convention. Always ask, "did the chemical/physical process itself release or absorb energy?" before assigning the sign.

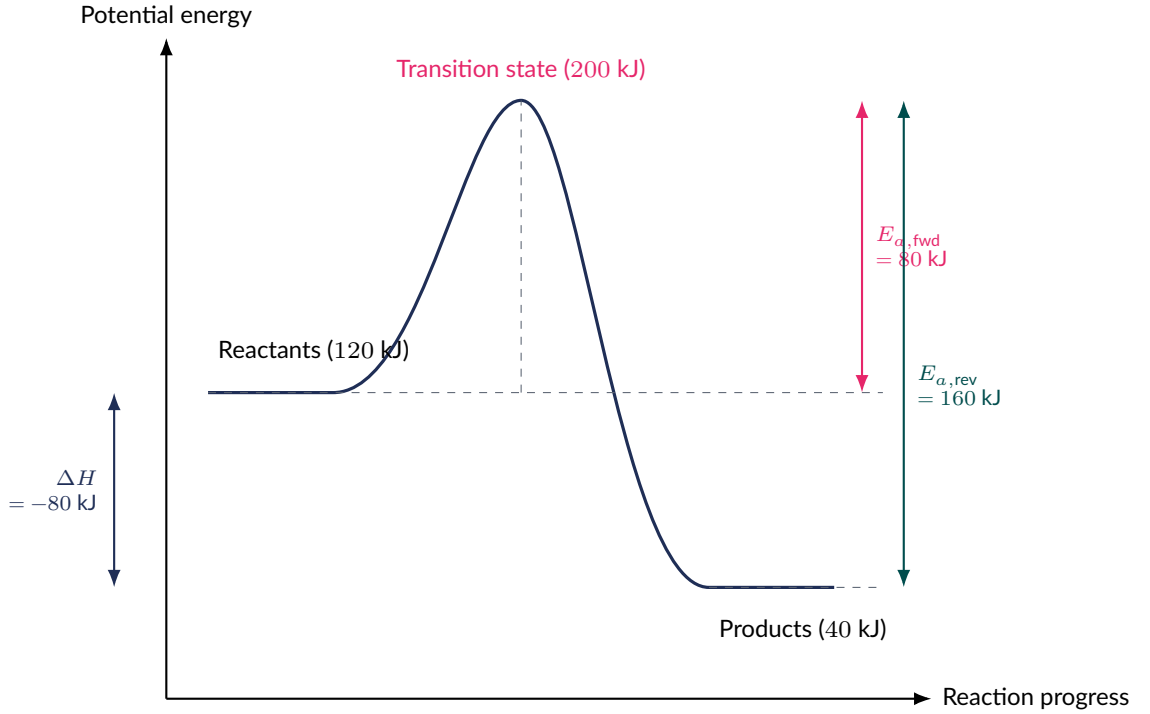
6.2 Energy diagrams

A **reaction-coordinate diagram** (also called a potential-energy diagram) plots the potential energy of the reacting system (vertical axis) against the **reaction progress** — an abstract coordinate tracking the reaction from reactants (left) to products (right) as bonds break and form. Every elementary reaction step passes through a high-energy, unstable arrangement of partially broken and partially formed bonds called the **transition state** (or activated complex), which sits at the single peak of the curve.

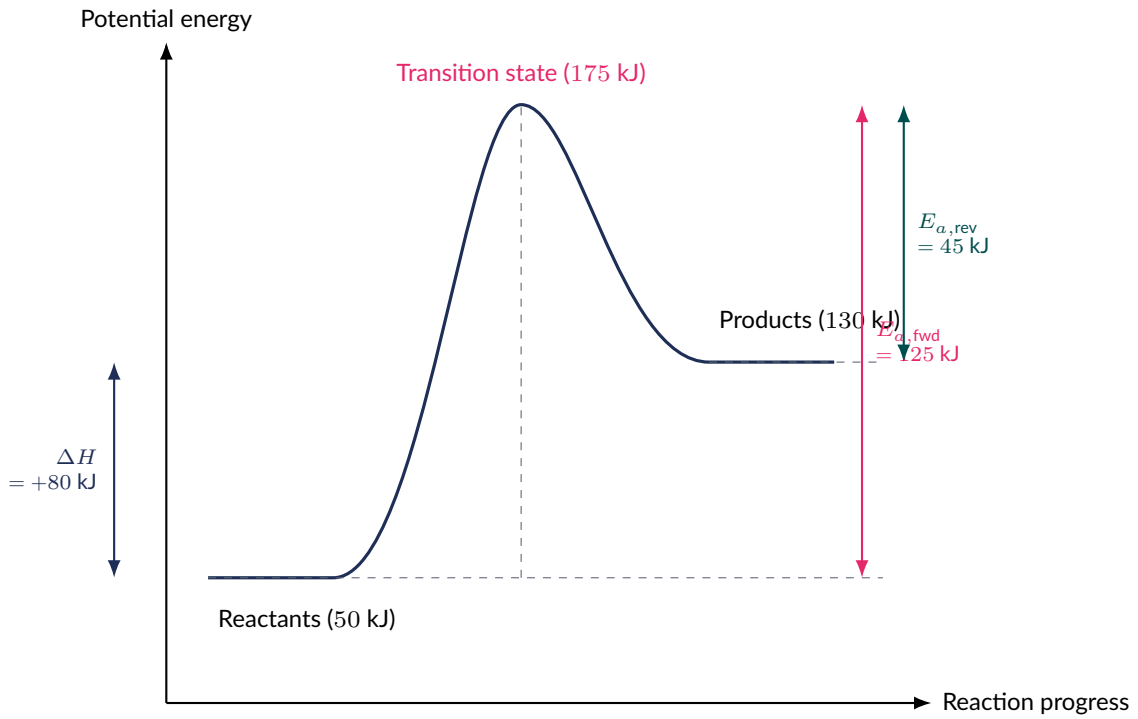
Reading a reaction-coordinate diagram

- The **reactant energy level** is the potential energy of the flat plateau on the left; the **product energy level** is the flat plateau on the right.
- The **activation energy of the forward reaction**, $E_{a,\text{fwd}}$, is the energy gap between the reactant level and the peak (transition state) — the minimum kinetic energy colliding reactant particles must supply to reach the transition state.
- The **activation energy of the reverse reaction**, $E_{a,\text{rev}}$, is the energy gap between the *product* level and the same peak.
- The **enthalpy change of the reaction**, ΔH, is the difference between product and reactant energy levels: $\Delta H = E_{\text{products}} - E_{\text{reactants}} = E_{a,\text{fwd}} - E_{a,\text{rev}}$.

A reaction is **exothermic** when the product plateau sits *below* the reactant plateau ($\Delta H < 0$; equivalently $E_{a,\text{fwd}} < E_{a,\text{rev}}$) and **endothermic** when the product plateau sits *above* the reactant plateau ($\Delta H > 0$; equivalently $E_{a,\text{fwd}} > E_{a,\text{rev}}$).



Reaction-coordinate diagram for an **exothermic** reaction: the product plateau (40 kJ) lies below the reactant plateau (120 kJ), so $\Delta H = 40 - 120 = -80$ kJ. Equivalently, $E_{a,\text{fwd}} - E_{a,\text{rev}} = 80 - 160 = -80$ kJ.



Reaction-coordinate diagram for an **endothermic** reaction: the product plateau (130 kJ) lies above the reactant plateau (50 kJ), so $\Delta H = 130 - 50 = +80$ kJ. Equivalently, $E_{a,\text{fwd}} - E_{a,\text{rev}} = 125 - 45 = +80$ kJ.

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Giản đồ năng lượng phản ứng biểu diễn thế năng theo tiến trình phản ứng. Đỉnh của đường cong là **trạng thái chuyển tiếp** (transition state), tại đó liên kết cũ chưa đứt hẳn và liên kết mới chưa hình thành hẳn. E_a thuận là khoảng cách từ mức chất phản ứng lên đỉnh; E_a nghịch là khoảng cách từ mức sản phẩm lên đỉnh. ΔH chính là hiệu năng lượng sản phẩm trừ chất phản ứng, và cũng bằng $E_{a,\text{thuận}} - E_{a,\text{nghịch}}$. Phản ứng toả nhiệt có sản phẩm thấp hơn chất đầu ($\Delta H < 0$); phản ứng thu nhiệt có sản phẩm cao hơn chất đầu ($\Delta H > 0$). Lưu ý: E_a luôn dương dù phản ứng toả hay thu nhiệt.

Reading a reaction-coordinate diagram

An energy diagram shows the reactant plateau at 50 kJ, the transition-state peak at 175 kJ, and the product plateau at 130 kJ (this is the endothermic diagram above). Find $E_{a,\text{fwd}}$, $E_{a,\text{rev}}$, and ΔH, and state whether the reaction is endothermic or exothermic.

$$E_{a,\text{fwd}} = 175 - 50 = 125 \text{ kJ}, \qquad E_{a,\text{rev}} = 175 - 130 = 45 \text{ kJ}.$$

$$\Delta H = E_{\text{products}} - E_{\text{reactants}} = 130 - 50 = +80 \text{ kJ}.$$

Check: $E_{a,\text{fwd}} - E_{a,\text{rev}} = 125 - 45 = +80$ kJ, consistent. Since $\Delta H > 0$, the reaction is **endothermic**.

Catalysts and energy diagrams

A **catalyst** provides an alternative reaction pathway with a *lower* transition-state peak, decreasing both $E_{a,\text{fwd}}$ and $E_{a,\text{rev}}$ by the same amount. Because the catalyst changes only the pathway (and hence the kinetics/rate) and not the identity or relative energy of the reactants and products themselves, ΔH is completely unchanged by a catalyst.

6.3 Heat transfer and thermal equilibrium

When two objects or samples at different temperatures are placed in contact, heat flows spontaneously from the **hotter** object to the **colder** object — never the reverse — until both reach a common final temperature called **thermal equilibrium**. At thermal equilibrium, no net heat flows because there is no longer a temperature difference to drive it.

Conservation of heat in an isolated system

If two substances exchange heat only with each other (an **isolated system**, with no heat escaping to or entering from the outside), conservation of energy requires that the heat lost by the hotter substance exactly equals the heat gained by the colder substance:

$$q_{\text{lost}} = -q_{\text{gained}}, \qquad \text{equivalently} \qquad q_{\text{hot}} + q_{\text{cold}} = 0.$$

The negative sign reflects the opposite-sign convention: the hot object's q is negative (it releases heat, its temperature falls), the cold object's q is positive (it absorbs heat, its temperature rises), and the two magnitudes are equal.

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Nhiệt luôn truyền từ vật **nóng hơn** sang vật **lạnh hơn** cho đến khi đạt **cân bằng nhiệt** (hai vật có cùng nhiệt độ cuối). Trong hệ cô lập (không trao đổi nhiệt với bên ngoài), nhiệt lượng vật nóng mất đi đúng bằng nhiệt lượng vật lạnh nhận được: $q_{\text{mất}} = -q_{\text{nhận}}$, hay $q_{\text{nóng}} + q_{\text{lạnh}} = 0$. Đây là nguyên lý nền tảng của mọi bài toán nhiệt lượng kế (calorimetry).

6.4 Heat capacity and calorimetry

6.4.1 Specific heat capacity and $q = mc\Delta T$

The **specific heat capacity** c of a substance is the quantity of heat required to raise the temperature of 1 gram of that substance by 1°C (equivalently, by 1 K, since a temperature *change* of 1°C equals a change of 1 K). Liquid water has an unusually high specific heat, $c_{\text{water}} = 4.18\,\text{J}/(\text{g}\cdot{}^\circ\text{C})$, meaning water resists temperature change more than most common substances — this is why large bodies of water moderate coastal climates. For a sample of mass m undergoing a temperature change $\Delta T = T_{\text{final}} - T_{\text{initial}}$:

$$q = mc\Delta T.$$

When a substance is *heated* ($\Delta T > 0$), $q > 0$ (heat flows into the substance); when a substance is *cooled* ($\Delta T < 0$), $q < 0$ (heat flows out).

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Nhiệt dung riêng c là nhiệt lượng cần để làm tăng 1 gam chất đó lên 1°C. Nước có $c = 4.18$ J/(g·°C) — khá cao so với hầu hết các chất, nên nước hấp thụ/toả nhiệt rất "chậm" (nhiệt độ thay đổi ít dù nhận nhiều nhiệt). Công thức $q = mc\Delta T$ với $\Delta T = T_{\text{cuối}} - T_{\text{đầu}}$: nếu chất được làm nóng thì $q > 0$, nếu bị làm lạnh thì $q < 0$.

Basic $q = mc\Delta T$ calculation

Find the heat required to warm 150.0 g of liquid water from 20.0°C to 95.0°C.

$$q = mc\Delta T = (150.0\ \text{g})(4.18\ \text{J/(g}\cdot{}^\circ\text{C)})(95.0 - 20.0)^\circ\text{C}$$
$$= (150.0)(4.18)(75.0) = 47{,}025\ \text{J} = \boxed{47.0\ \text{kJ}}.$$

Since the water was heated, $q > 0$ as expected.

6.4.2 Calorimetry: coffee-cup vs. bomb calorimeters

Calorimetry is the experimental measurement of heat flow using a device called a **calorimeter**. AP Chemistry uses two idealized calorimeter types that measure two different thermodynamic quantities.

Coffee-cup vs. bomb calorimetry

- A **coffee-cup calorimeter** (a nested pair of insulated foam cups, open to the atmosphere) holds a reaction in solution at constant, ambient **pressure**. Because the only work possible is atmospheric expansion/compression work, the heat exchanged at constant pressure equals the enthalpy change: $q_p = \Delta H$. Coffee-cup calorimetry directly measures ΔH.
- A **bomb calorimeter** is a rigid, sealed steel vessel submerged in a water bath, used mainly for combustion reactions. Because the vessel's **volume** cannot change, no expansion work is done ($w = 0$), and the heat exchanged at constant volume equals the change in internal energy: $q_v = \Delta E$ (also written ΔU). Bomb calorimetry directly measures ΔE, not ΔH.

For most reactions involving only solids, liquids, and dissolved species (negligible change in gas moles), $\Delta H \approx \Delta E$ and the distinction is small. When a reaction changes the number of moles of gas significantly, ΔH and ΔE can differ measurably (Example K below).

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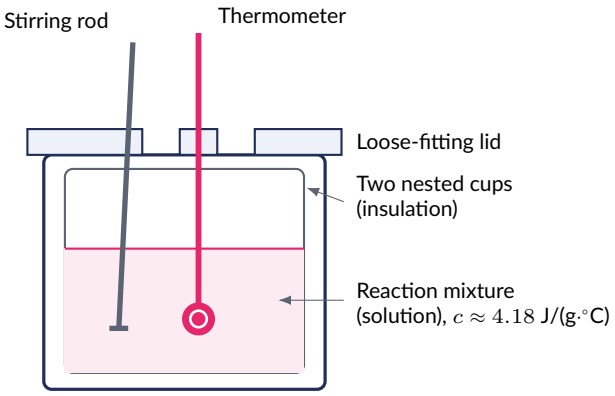
Coffee-cup calorimeter đo ở áp suất không đổi (constant P), cho trực tiếp ΔH vì $q_p = \Delta H$. **Bomb calorimeter** là bình thép kín, thể tích không đổi (constant V), không có công giãn nở nên $q_v = \Delta E$ (biến thiên nội năng), KHÔNG phải ΔH trực tiếp. Với phản ứng không làm thay đổi nhiều số mol khí, $\Delta H \approx \Delta E$; nhưng với phản ứng thay đổi đáng kể số mol khí, hai đại lượng này có thể lệch nhau vài kJ.



A coffee-cup calorimeter: two nested foam cups minimize heat exchange with the outside room, so essentially all the heat released or absorbed by the reaction is exchanged with the solution inside, whose temperature change is monitored by the thermometer.

Determining an unknown specific heat

A 100.0 g sample of a metal, initially at 95.0°C, is dropped into 150.0 g of water initially at 22.0°C inside an insulated (coffee-cup) calorimeter. The system reaches a final temperature of 31.5°C. Find the specific heat of the metal.

By conservation of energy, $q_{\text{metal}} = -q_{\text{water}}$. First find the heat gained by the water:

$$q_{\text{water}} = m_w c_w \Delta T_w = (150.0)(4.18)(31.5 - 22.0) = (150.0)(4.18)(9.5) = 5956.5 \text{ J}.$$

So $q_{\text{metal}} = -5956.5$ J. Solve for c_{metal} using $\Delta T_{\text{metal}} = 31.5 - 95.0 = -63.5^\circ$C:

$$c_{\text{metal}} = \frac{q_{\text{metal}}}{m_{\text{metal}}\Delta T_{\text{metal}}} = \frac{-5956.5}{(100.0)(-63.5)} = \boxed{0.938 \text{ J/(g}\cdot^\circ\text{C)}}.$$

Determining a calorimeter's own heat capacity

100.0 g of hot water at 80.0°C is added to 100.0 g of cold water at 20.0°C inside a calorimeter. If the calorimeter itself absorbed no heat, the final temperature would be the simple average, 50.0°C; instead, the measured final temperature is 48.0°C, showing that the calorimeter itself absorbed some of the heat. Find the calorimeter's heat capacity C_{cal} (in J/°C; note this is a *total* heat capacity for the whole apparatus, not a per-gram specific heat).

Heat released by the hot water:

$$q_{\text{hot}} = (100.0)(4.18)(48.0 - 80.0) = (100.0)(4.18)(-32.0) = -13{,}376 \text{ J}.$$

Heat absorbed by the cold water:

$$q_{\text{cold}} = (100.0)(4.18)(48.0 - 20.0) = (100.0)(4.18)(28.0) = 11{,}704 \text{ J}.$$

Energy conservation: heat released by the hot water is shared between the cold water and the calorimeter itself, $-q_{\text{hot}} = q_{\text{cold}} + q_{\text{cal}}$:

$$q_{\text{cal}} = 13{,}376 - 11{,}704 = 1672 \text{ J}.$$

The calorimeter warmed from 20.0°C to 48.0°C along with the cold-water portion, so $\Delta T_{\text{cal}} = 28.0^\circ$C:

$$C_{\text{cal}} = \frac{q_{\text{cal}}}{\Delta T_{\text{cal}}} = \frac{1672}{28.0} = \boxed{59.7 \text{ J/}^\circ\text{C}}.$$

Once known, C_{cal} can be included as an extra "mc" term (using $C_{\text{cal}}\Delta T$ directly, since it is already a total heat capacity) in future experiments with the same calorimeter, correcting for the heat it absorbs.

Bomb calorimetry: combustion of benzoic acid

Benzoic acid ($C_7H_6O_2$, $M = 122.1$ g/mol) is a standard used to calibrate and test bomb calorimeters. A 1.200 g sample is burned completely in a bomb calorimeter with heat capacity $C_{\text{cal}} = 9.50$ kJ/°C. The temperature of the water bath rises from 24.00°C to 27.34°C. Find q_v for the combustion of the sample, and express the result as ΔE per mole of benzoic acid.

$$\Delta T = 27.34 - 24.00 = 3.34^\circ\text{C}, \qquad q_{\text{absorbed by calorimeter}} = C_{\text{cal}}\Delta T = (9.50)(3.34) = 31.73 \text{ kJ}.$$

The combustion reaction released this heat, so from the reaction's perspective $q_{\text{rxn}} = -31.73$ kJ for 1.200 g:

$$\frac{-31.73 \text{ kJ}}{1.200 \text{ g}} = -26.44 \text{ kJ/g}, \qquad (-26.44 \text{ kJ/g})(122.1 \text{ g/mol}) = \boxed{\Delta E \approx -3229 \text{ kJ/mol}}.$$

Since a bomb calorimeter operates at constant volume, this is ΔE (equivalently ΔU), not ΔH, for the combustion of benzoic acid — consistent with the accepted literature value near -3227 kJ/mol.

Constant-P vs. constant-V: a numeric comparison

For the synthesis of ammonia, $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$, using $\Delta H_f^\circ(NH_3) = -45.9$ kJ/mol (Section 6.8), the enthalpy change (what a constant-pressure, "coffee-cup-style" measurement would report) is

$$\Delta H = 2(-45.9) - 0 = -91.8 \text{ kJ}.$$

This reaction consumes 4 mol of gas and produces 2 mol of gas, so $\Delta n_{gas} = 2 - 4 = -2$ mol. The relationship between ΔH (constant-P heat) and ΔE (constant-V heat, what a bomb-style measurement would report) is $\Delta H = \Delta E + \Delta n_{gas} RT$, so at $T = 298$ K ($R = 8.314$ J/(mol·K)$= 0.008314$ kJ/(mol·K)):

$$\Delta n_{gas} RT = (-2)(0.008314)(298) = -4.96 \text{ kJ}.$$

$$\Delta E = \Delta H - \Delta n_{gas} RT = -91.8 - (-4.96) = \boxed{-86.8 \text{ kJ}}.$$

The constant-pressure value (-91.8 kJ) and constant-volume value (-86.8 kJ) differ by about 5 kJ — small but non-negligible, because this reaction consumes a large *net* number of gas moles. For a reaction with $\Delta n_{gas} = 0$, the two measurements would agree exactly.

(!) Lỗi thường gặp: When combining $q_{lost} = -q_{gained}$, remember that ΔT itself is always $T_{final} - T_{initial}$ for *each* substance separately (using that substance's own initial temperature), not the overall change in the mixture. A common error is to compute $|T_f - T_i|$ generically and then guess the sign, rather than tracking each substance's own algebraic ΔT (negative for the object that cools, positive for the object that warms) and letting the arithmetic produce the correct opposite signs automatically.

6.5 Energy of phase changes

Supplying heat to a pure substance does not always raise its temperature. A **heating curve** plots temperature (vertical axis) against cumulative heat added (horizontal axis) and reveals two alternating kinds of segments:

Sloped segments vs. plateaus

- **Sloped segments**: within a single phase (all solid, all liquid, or all gas), added heat raises the temperature according to $q = mc\Delta T$, using the specific heat of *that phase*. Water's three phases have different specific heats: $c_{ice} \approx 2.09\,J/(g\cdot{}^\circ C)$, $c_{liquid} = 4.18\,J/(g\cdot{}^\circ C)$, $c_{steam} \approx 2.01\,J/(g\cdot{}^\circ C)$.
- **Flat plateaus**: while two phases coexist (melting or boiling), all added heat goes into overcoming intermolecular attractions to convert one phase into the other, and the temperature stays perfectly constant until the phase change is complete. On a plateau, $q = n\Delta H_{fus}$ (melting/freezing plateau, at 0°C for water) or $q = n\Delta H_{vap}$ (boiling/condensing plateau, at 100°C for water), where n is the amount in moles.

For water: $\Delta H_{fus} = +6.01$ kJ/mol and $\Delta H_{vap} = +40.7$ kJ/mol. Because $\Delta H_{vap} \gg \Delta H_{fus}$ (roughly 6.8 times larger), the boiling plateau is much wider on the heating curve than the melting plateau — vaporization requires far more energy than fusion, since it must fully separate molecules against the entire intermolecular attraction, whereas melting only needs to loosen a rigid lattice into a mobile but still-touching liquid.

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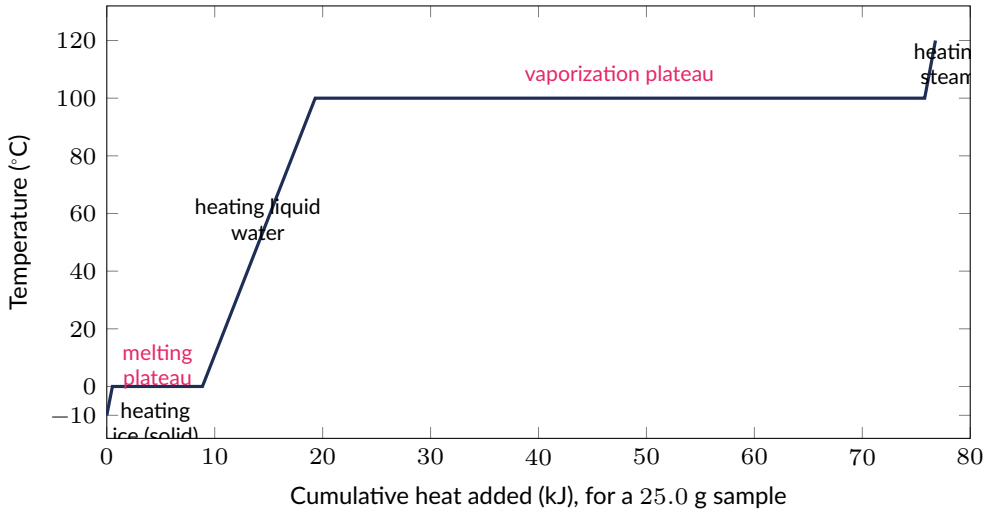
VN Đường cong gia nhiệt (heating curve) có hai loại đoạn xen kẽ: **đoạn dốc** (trong một pha duy nhất, nhiệt độ tăng theo $q = mc\Delta T$) và **đoạn phẳng** (tại điểm chuyển pha, nhiệt độ không đổi, toàn bộ nhiệt dùng để phá vỡ lực liên phân tử: $q = n\Delta H_{\text{nc}}$ khi nóng chảy, $q = n\Delta H_{\text{hh}}$ khi hoá hơi). Vì $\Delta H_{\text{hh}} = 40.7$ kJ/mol lớn hơn nhiều so với $\Delta H_{\text{nc}} = 6.01$ kJ/mol (gấp khoảng 6.8 lần), đoạn phẳng ứng với hoá hơi luôn **rộng hơn nhiều** so với đoạn phẳng nóng chảy trên đồ thị.



Heating curve for 25.0 g of water, from ice at -10.0°C to steam at 120.0°C (drawn to scale on both axes; see the worked example below for the numeric breakdown of each segment).

Multi-step calculation: ice to steam

Find the total heat required to convert 25.0 g of ice at -10.0°C to steam at 120.0°C. Use $c_{\text{ice}} = 2.09$, $c_{\text{water}} = 4.18$, $c_{\text{steam}} = 2.01$ J/(g·°C); $\Delta H_{\text{fus}} = 6.01$ kJ/mol; $\Delta H_{\text{vap}} = 40.7$ kJ/mol; $M(\text{H}_2\text{O}) = 18.02$ g/mol.

Moles of water: $n = \dfrac{25.0}{18.02} = 1.387$ mol. There are five steps:

1. **Heat ice from** -10.0°C **to** 0°C: $q_1 = mc_{\text{ice}}\Delta T = (25.0)(2.09)(10.0) = 522.5$ J $= 0.5225$ kJ.
2. **Melt the ice at** 0°C: $q_2 = n\Delta H_{\text{fus}} = (1.387)(6.01) = 8.338$ kJ.
3. **Heat liquid water from** 0°C **to** 100°C: $q_3 = mc_{\text{water}}\Delta T = (25.0)(4.18)(100.0) = 10{,}450$ J $= 10.450$ kJ.
4. **Vaporize the water at** 100°C: $q_4 = n\Delta H_{\text{vap}} = (1.387)(40.7) = 56.47$ kJ.
5. **Heat steam from** 100°C **to** 120°C: $q_5 = mc_{\text{steam}}\Delta T = (25.0)(2.01)(20.0) = 1005$ J $= 1.005$ kJ.

$$q_{\text{total}} = 0.5225 + 8.338 + 10.450 + 56.47 + 1.005 = \boxed{76.8 \text{ kJ}}.$$

Notice that step 4 (vaporization) alone accounts for nearly 74% of the total energy — a direct consequence of ΔH_{vap} being so much larger than ΔH_{fus} or any single heating segment.

6.6 Introduction to enthalpy of reaction

The **enthalpy of reaction**, ΔH_{rxn}, is the heat exchanged with the surroundings when a chemical reaction occurs at constant pressure, exactly as written in the balanced equation (with the given stoichiometric coefficients and states of matter). As established in Section 6.4, coffee-cup calorimetry measures ΔH_{rxn} directly via $q_p = \Delta H$.

Properties of ΔH_{rxn}

- ΔH is an **extensive** property: it scales directly with the amount of substance reacting. If a reaction as written (for n moles of a given reactant) has enthalpy ΔH, then reacting $2n$ moles releases/absorbs $2\Delta H$, reacting $n/2$ moles releases/absorbs $\Delta H/2$, and so on.
- **Reversing a reaction reverses the sign of** ΔH: if the forward reaction A $\rightarrow$ B has ΔH_{fwd}, the reverse reaction B $\rightarrow$ A has $\Delta H_{\text{rev}} = -\Delta H_{\text{fwd}}$. This follows because the transition state and bond energies are identical in both directions; only the starting and ending reference points swap.

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ΔH_{rxn} là nhiệt trao đổi ở áp suất không đổi ứng đúng với phương trình đã cân bằng. ΔH là đại lượng **tỉ lệ với lượng chất**: phản ứng gấp đôi lượng chất thì ΔH cũng gấp đôi. **Đảo chiều phản ứng thì đổi dấu** ΔH: $\Delta H_{\text{nghịch}} = -\Delta H_{\text{thuận}}$. Đây là hai quy tắc nền tảng sẽ được dùng liên tục trong định luật Hess (mục 6.9).

Coffee-cup calorimetry: neutralization

50.0 mL of 1.00 M HCl and 50.0 mL of 1.00 M NaOH, both initially at 22.5°C, are mixed in a coffee-cup calorimeter. The combined solution reaches a maximum temperature of 29.3°C. Assume the combined solution has mass 100.0 g, density 1.00 g/mL, and specific heat 4.18 J/(g·°C), and that the calorimeter itself absorbs negligible heat. Find ΔH per mole of water formed for $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$.

Moles of each reactant: $(0.0500\ \text{L})(1.00\ \text{mol/L}) = 0.0500$ mol; since they react in a $1{:}1$ ratio with no excess, 0.0500 mol of H_2O forms. Heat absorbed by the solution:

$$q_{\text{soln}} = mc\Delta T = (100.0)(4.18)(29.3 - 22.5) = (100.0)(4.18)(6.8) = 2842\ \text{J} = 2.842\ \text{kJ}.$$

The reaction released this heat ($q_{\text{rxn}} = -q_{\text{soln}} = -2.842$ kJ), so per mole of water formed:

$$\Delta H = \frac{-2.842\ \text{kJ}}{0.0500\ \text{mol}} = \boxed{-56.8\ \text{kJ/mol}}.$$

This is close to the accepted value for strong acid–strong base neutralization (≈ -57.3 kJ/mol), reflecting that the net ionic reaction is the same in every strong-acid/strong-base pair: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$.

6.7 Bond enthalpy

A **bond enthalpy** (bond dissociation energy) is the energy required to break one mole of a specific covalent bond in the gas phase, always a *positive* quantity (breaking bonds always costs energy). Because the exact bond enthalpy depends slightly on the surrounding molecular environment, tabulated values are **average bond enthalpies**, averaged across many different molecules containing that bond.

Estimating ΔH_{rxn} from bond enthalpies

Any gas-phase reaction can be conceptually decomposed into two stages: first, completely atomize the reactants by breaking every bond (this always *costs* energy, $+$); second, reassemble the atoms into products by forming every new bond (this always *releases* energy, so it

contributes with a $-$ sign relative to the breaking step):

$$\Delta H_{\text{rxn}} \approx \sum(\text{bonds broken, reactants}) - \sum(\text{bonds formed, products}).$$

This method gives only an *estimate*, because it uses average bond enthalpies rather than the exact values for the specific molecules involved, and it applies strictly only to gas-phase species (breaking bonds in a solid or liquid also requires overcoming intermolecular/lattice forces, which bond enthalpies do not account for).

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Năng lượng liên kết (bond enthalpy) luôn **dương** (phá vỡ liên kết luôn cần năng lượng). Công thức ước lượng: $\Delta H_{\text{rxn}} \approx \Sigma(\text{liên kết bị phá, chất đầu}) - \Sigma(\text{liên kết hình thành, sản phẩm})$ — nghĩa là "năng lượng phá vỡ trừ năng lượng tạo thành". Đây chỉ là giá trị **ước lượng** (dùng năng lượng liên kết trung bình), và chỉ áp dụng chính xác cho phản ứng ở **pha khí**.

Bond	Avg. (kJ/mol)	Bond	Avg. (kJ/mol)
C–H	413	Cl–Cl	243
C–C	347	H–Cl	431
C=C	614	C–O	358
C≡C	839	C=O (in CO_2)	799
O–H	467	N≡N	941
O=O	495	N–H	391
H–H	436	C–Cl	339

Average bond enthalpies (kJ/mol) used throughout this chapter; all values are positive (energy required to break the bond).

ΔH_{rxn} from bond enthalpies, cross-checked against ΔH_f°

Estimate ΔH_{rxn} for the gas-phase combustion of methane, $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$, using bond enthalpies.

Bonds broken (reactants): CH_4 has 4 C–H bonds; $2\,O_2$ has 2 O=O bonds.

$$\sum(\text{broken}) = 4(413) + 2(495) = 1652 + 990 = 2642 \text{ kJ}.$$

Bonds formed (products): CO_2 has 2 C=O bonds (using the CO_2-specific value); $2\,H_2O$ has 4 O–H bonds total.

$$\sum(\text{formed}) = 2(799) + 4(467) = 1598 + 1868 = 3466 \text{ kJ}.$$

$$\Delta H_{\text{rxn}} \approx 2642 - 3466 = \boxed{-824 \text{ kJ/mol}}.$$

Cross-check: using ΔH_f° values (Section 6.8), the same reaction (with gaseous water) gives $\Delta H_{\text{rxn}}^\circ = [-393.5 + 2(-241.8)] - [-74.8] = -802.3$ kJ/mol. The bond-enthalpy estimate (-824 kJ/mol) and the ΔH_f°-based value (-802.3 kJ/mol) agree to within about 22 kJ, or roughly 3% — a typical level of agreement for the bond-enthalpy method, which is reliable for order-of-magnitude and sign predictions but less precise than a calculation built from measured ΔH_f° data.

6.8 Enthalpy of formation

The **standard enthalpy of formation**, ΔH_f°, of a compound is the enthalpy change when **exactly** 1 **mole** of that compound is formed directly from its constituent **elements**, with every substance (elements and compound) in its **standard state** (most stable physical form at 1 atm and, conventionally, 25°C).

Key properties of ΔH_f°

- By definition, ΔH_f° of any **element in its standard state** is exactly **zero** — no formation reaction is needed because the element already exists in that reference form. Examples: $\Delta H_f^\circ(\mathrm{O_2(g)}) = 0$, $\Delta H_f^\circ(\mathrm{C(graphite)}) = 0$, $\Delta H_f^\circ(\mathrm{Br_2(l)}) = 0$ (bromine's standard state at room temperature is the *liquid*, not the gas), $\Delta H_f^\circ(\mathrm{H_2(g)}) = 0$.
- Because ΔH_f° describes a *formation* reaction, the balanced equation defining it must produce exactly 1 mole of the compound, which sometimes requires fractional coefficients on the elemental reactants (e.g., $\frac{1}{2}\,\mathrm{N_2(g)} + \frac{3}{2}\,\mathrm{H_2(g)} \rightarrow \mathrm{NH_3(g)}$).

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ΔH_f° (enthalpy tạo thành chuẩn) là nhiệt tạo thành **đúng** 1 **mol** hợp chất từ các **nguyên tố** ở trạng thái chuẩn (bền nhất ở 1 atm, 25°C). Nguyên tố ở trạng thái chuẩn luôn có $\Delta H_f^\circ = 0$ — kể cả những trường hợp dễ nhầm như $\mathrm{Br_2}$ (trạng thái chuẩn là **lỏng**, không phải khí) hay carbon (trạng thái chuẩn là **than chì/graphite**, không phải kim cương). Vì cần tạo đúng 1 mol sản phẩm, hệ số của nguyên tố phản ứng đôi khi là phân số.

Species	ΔH_f° (kJ/mol)	Species	ΔH_f° (kJ/mol)
$\mathrm{CO_2(g)}$	-393.5	$\mathrm{CO(g)}$	-110.5
$\mathrm{H_2O(l)}$	-285.8	$\mathrm{NO_2(g)}$	$+33.2$
$\mathrm{H_2O(g)}$	-241.8	$\mathrm{NO(g)}$	$+90.2$
$\mathrm{CH_4(g)}$	-74.8	$\mathrm{CaCO_3(s)}$	-1206.9
$\mathrm{C_2H_2(g)}$	$+226.7$	$\mathrm{CaO(s)}$	-635.1
$\mathrm{C_2H_4(g)}$	$+52.4$	$\mathrm{NaCl(s)}$	-411.2
$\mathrm{C_2H_6(g)}$	-84.7	$\mathrm{HCl(g)}$	-92.3
$\mathrm{NH_3(g)}$	-45.9		

Standard enthalpies of formation used throughout this chapter (elements in their standard states: $\Delta H_f^\circ = 0$).

Formation-enthalpy shortcut (a direct consequence of Hess's law, Section 6.9): for any reaction,

$$\Delta H^\circ_{\text{rxn}} = \sum n_p\,\Delta H_f^\circ(\text{products}) - \sum n_r\,\Delta H_f^\circ(\text{reactants}),$$

where n_p and n_r are the stoichiometric coefficients from the balanced equation. Elements appearing in their standard state contribute zero to the sum.

$\Delta H^\circ_{\text{rxn}}$ from ΔH_f°: combustion of ethane

Find $\Delta H^\circ_{\text{rxn}}$ for $\mathrm{C_2H_6(g)} + \frac{7}{2}\,\mathrm{O_2(g)} \rightarrow 2\,\mathrm{CO_2(g)} + 3\,\mathrm{H_2O(l)}$.

$$\Delta H^\circ_{\text{rxn}} = \left[2\,\Delta H_f^\circ(\mathrm{CO_2}) + 3\,\Delta H_f^\circ(\mathrm{H_2O}, l)\right] - \left[\Delta H_f^\circ(\mathrm{C_2H_6}) + \tfrac{7}{2}(0)\right]$$
$$= \left[2(-393.5) + 3(-285.8)\right] - \left[-84.7\right] = \left[-787.0 - 857.4\right] + 84.7$$

$$= -1644.4 + 84.7 = \boxed{-1559.7 \text{ kJ/mol}}.$$

The large negative value is typical of combustion reactions — strongly exothermic, consistent with hydrocarbons being used as fuels.

6.9 Hess's law

Enthalpy is a **state function**: ΔH for a process depends only on the initial and final states (the identity, amount, phase, and temperature of reactants and products), not on the path or number of steps taken to get from one to the other. **Hess's law** is the direct consequence of this property: *if a target reaction can be written as the sum of two or more other reactions (each possibly reversed and/or scaled by a coefficient), then ΔH of the target equals the sum of the (correspondingly reversed and/or scaled) ΔH values of those reactions.*

Rules for combining reactions

- **Reversing** a given reaction flips the sign of its ΔH.
- **Multiplying** a given reaction's coefficients by a factor k multiplies its ΔH by that same factor k.
- **Adding** reactions together (after any needed reversal/scaling) adds their ΔH values; species that appear identically on both sides of the combined equation **cancel out** and must not appear in the final target equation.
- The goal is always to choose reversals/multipliers for the given reactions so that, after cancellation, the sum reproduces the target equation exactly (same species, same coefficients, same physical states, on the correct sides).

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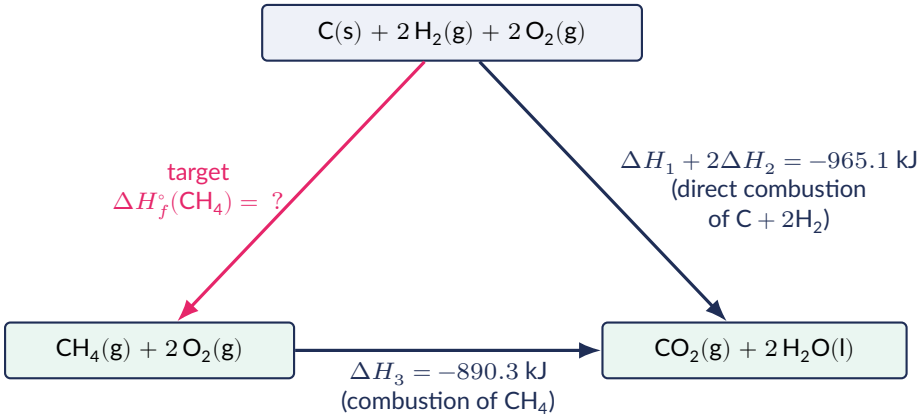
Enthalpy là **hàm trạng thái** (state function): ΔH chỉ phụ thuộc trạng thái đầu và trạng thái cuối, không phụ thuộc "con đường" đi qua bao nhiêu bước. Định luật Hess khai thác tính chất này: nếu phản ứng đích có thể viết thành tổng của các phản ứng đã cho (sau khi đảo chiều và/hoặc nhân hệ số phù hợp), thì ΔH đích bằng tổng các ΔH đã đảo/nhân tương ứng. **Đảo chiều** $\Rightarrow$ đổi dấu ΔH; **nhân hệ số** $k \Rightarrow$ nhân ΔH với k; **cộng phản ứng** $\Rightarrow$ cộng ΔH, và các chất giống nhau xuất hiện hai bên phải bị triệt tiêu.



Hess's-law cycle for the formation of methane. Both paths from node A to node C must give the same total ΔH (state-function property), so $\Delta H_f^\circ(\text{CH}_4) + \Delta H_3 = \Delta H_1 + 2\Delta H_2$, giving $\Delta H_f^\circ(\text{CH}_4) = -965.1 - (-890.3) = -74.8$ kJ/mol.

Hess's law: combining three given reactions

Given the following data,

$$\text{(1)}\quad \mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}, \quad \Delta H_1 = -393.5\ \text{kJ}$$

$$\text{(2)}\quad \mathrm{H_2(g)} + \tfrac{1}{2}\,\mathrm{O_2(g)} \rightarrow \mathrm{H_2O(l)}, \quad \Delta H_2 = -285.8\ \text{kJ}$$

$$\text{(3)}\quad \mathrm{CH_4(g)} + 2\,\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} + 2\,\mathrm{H_2O(l)}, \quad \Delta H_3 = -890.3\ \text{kJ}$$

find ΔH for the target reaction $\mathrm{C(s)} + 2\,\mathrm{H_2(g)} \rightarrow \mathrm{CH_4(g)}$.

Take reaction (1) as written, **double** reaction (2) (to supply $2\,\mathrm{H_2}$), and **reverse** reaction (3) (to place $\mathrm{CH_4}$ on the product side):

$$\text{(1)}\quad \mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2}, \qquad \Delta H_1 = -393.5\ \text{kJ}$$

$$2\times\text{(2)}\quad 2\,\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\,\mathrm{H_2O}, \qquad 2\Delta H_2 = 2(-285.8) = -571.6\ \text{kJ}$$

$$-\text{(3)}\quad \mathrm{CO_2} + 2\,\mathrm{H_2O} \rightarrow \mathrm{CH_4} + 2\,\mathrm{O_2}, \qquad -\Delta H_3 = +890.3\ \text{kJ}$$

Adding all three left sides and all three right sides: $\mathrm{C} + 2\,\mathrm{H_2} + 2\,\mathrm{O_2} + \mathrm{CO_2} + 2\,\mathrm{H_2O} \rightarrow \mathrm{CO_2} + 2\,\mathrm{H_2O} + \mathrm{CH_4} + 2\,\mathrm{O_2}$. Cancel $\mathrm{CO_2}$, $2\,\mathrm{H_2O}$, and $2\,\mathrm{O_2}$ from both sides, leaving exactly the target: $\mathrm{C(s)} + 2\,\mathrm{H_2(g)} \rightarrow \mathrm{CH_4(g)}$.

$$\Delta H_{\text{target}} = \Delta H_1 + 2\Delta H_2 + (-\Delta H_3) = -393.5 - 571.6 + 890.3 = \boxed{-74.8\ \text{kJ}}.$$

This matches the tabulated $\Delta H_f^\circ(\mathrm{CH_4}) = -74.8$ kJ/mol exactly, as it must: the target reaction *is* the formation reaction of methane, and Hess's law guarantees any valid combination of correct data reproduces the same answer.

(!) Lỗi thường gặp: The single most common Hess's-law error is combining the given ΔH values **without correctly flipping the sign** when a reaction must be reversed to match the target. If a given reaction must run backward relative to how it is written to fit into the target equation, its ΔH contribution must be written as $-\Delta H_{\text{given}}$, not $+\Delta H_{\text{given}}$. Always physically rewrite each reaction in the orientation and scale it will actually take in the sum *before* adding the enthalpies — never try to track sign flips "in your head" while only writing the final arithmetic.

(!) Lỗi thường gặp: A closely related error is scaling the *reaction* (doubling or halving its coefficients) without scaling its ΔH by the same factor. If reaction (2) above is doubled to supply $2\,\mathrm{H_2}$ instead of $1\,\mathrm{H_2}$, its enthalpy contribution must also double, from -285.8 kJ to -571.6 kJ — forgetting this step is a very common source of numeric error even when the sign logic is otherwise correct.

6.10 Practice Problems

Bài tập luyện tập

Which statement correctly describes an exothermic process, using the sign convention for the system?

(A) $q > 0$ and the surroundings cool down

(B) $q < 0$ and the surroundings warm up

(C) $q > 0$ and the surroundings warm up

(D) $q < 0$ and the surroundings cool down

Lời giải chi tiết

An exothermic process releases energy *from* the system *to* the surroundings: $q_{\text{system}} < 0$, and since the surroundings receive that energy, they warm up. **(B)**.

Bài tập luyện tập

Which of the following species has $\Delta H_f^\circ = 0$?

(A) $O_3(g)$
(B) $Br_2(g)$
(C) $Br_2(l)$
(D) $C(\text{diamond})$

Lời giải chi tiết

$\Delta H_f^\circ = 0$ only for an element in its standard (most stable) state at 25°C and 1 atm. Ozone (O_3) is not the standard state of oxygen (that is O_2); gaseous bromine is not its standard state (liquid bromine is); diamond is not carbon's standard state (graphite is). Liquid bromine, $Br_2(l)$, is the standard state of elemental bromine. **(C)**.

Bài tập luyện tập

Solid ammonium nitrate is dissolved in water inside a test tube held in a gloved hand. The outside of the test tube quickly becomes noticeably cold. Taking the dissolving salt as the system, state the sign of q_{system} and identify whether the process is endothermic or exothermic, explaining your reasoning in terms of energy flow between system and surroundings.

Lời giải chi tiết

The hand and test tube (surroundings) lose thermal energy, evidenced by the cooling sensation; that energy is drawn *into* the dissolving salt (the system) to break apart the ionic lattice and separate the ions into solution. Since the system gains energy, $q_{\text{system}} > 0$, and the process is **endothermic**. (The surroundings feeling cold is the observable evidence of an endothermic system, not evidence of a negative system q.)

Bài tập luyện tập

On a reaction-coordinate diagram for an exothermic reaction, the product energy plateau is _____ the reactant energy plateau, and $E_{a,\text{fwd}}$ is _____ $E_{a,\text{rev}}$.

(A) above; greater than
(B) above; less than
(C) below; less than
(D) below; greater than

Lời giải chi tiết

Exothermic means $\Delta H < 0$, so products must sit *below* reactants in energy. Since $\Delta H = E_{a,\text{fwd}} - E_{a,\text{rev}} < 0$, it follows that $E_{a,\text{fwd}}$ is *less than* $E_{a,\text{rev}}$. **(C)**.

Bài tập luyện tập

An energy diagram shows $E_{a,\text{fwd}} = 68$ kJ and $E_{a,\text{rev}} = 112$ kJ. Find ΔH for the reaction and state whether it is endothermic or exothermic.

Lời giải chi tiết

$$\Delta H = E_{a,\text{fwd}} - E_{a,\text{rev}} = 68 - 112 = \boxed{-44\ \text{kJ}}.$$

Since $\Delta H < 0$, the reaction is **exothermic**.

Bài tập luyện tập

Two metal blocks, one at 80°C and one at 20°C, are pressed together and isolated from the rest of the room. Which statement correctly describes what happens?

(A) Heat flows from the cold block to the hot block until both reach 50°C

(B) Heat flows from the hot block to the cold block until both reach the same final temperature (not necessarily 50°C)

(C) No heat flows because metals do not conduct heat well

(D) Heat flows until the cold block is colder and the hot block is hotter

Lời giải chi tiết

Heat always flows spontaneously from higher to lower temperature until thermal equilibrium (a common final temperature) is reached. The final temperature equals the simple average (50°C) only if the two blocks have identical mass *and* identical specific heat — in general it depends on both mc products. **(B)**.

Bài tập luyện tập

An 80.0 g sample of aluminum ($c = 0.900$ J/(g·°C)) at 150.0°C is dropped into 200.0 g of water ($c = 4.18$ J/(g·°C)) at 20.0°C in an insulated container. Find the final equilibrium temperature.

Lời giải chi tiết

Set $q_{\text{Al}} + q_{\text{water}} = 0$:

$$(80.0)(0.900)(T_f - 150.0) + (200.0)(4.18)(T_f - 20.0) = 0$$

$$72.0(T_f - 150.0) + 836(T_f - 20.0) = 0 \;\Rightarrow\; 908\,T_f = 72.0(150.0) + 836(20.0)$$

$$908\,T_f = 10{,}800 + 16{,}720 = 27{,}520$$

$$T_f = \frac{27{,}520}{908} = \boxed{30.3^\circ\text{C}}.$$

The large mass and specific heat of the water dominate, pulling the final temperature much closer to the water's initial temperature than to the aluminum's.

Bài tập luyện tập

Sample X (100.0 g, $c = 0.50$ J/(g·°C)) and Sample Y (50.0 g, $c = 2.00$ J/(g·°C)) both start at the same temperature and are heated by the same amount of heat, q. Which sample undergoes the larger temperature change?

(A) Sample X, because it has greater mass

(B) Sample Y, because mc for Y (100 J/°C) is greater than mc for X (50 J/°C)

(C) Sample X, because mc for X (50 J/°C) is less than mc for Y (100 J/°C)

(D) They undergo the same ΔT because q is identical

Lời giải chi tiết

For fixed q, $\Delta T = q/(mc)$, so the sample with the *smaller* mc product undergoes the *larger* temperature change. $mc(\text{X}) = (100.0)(0.50) = 50$ J/°C; $mc(\text{Y}) = (50.0)(2.00) = 100$ J/°C. Since X has the smaller mc, X undergoes the larger ΔT. **(C)**.

Bài tập luyện tập

500.0 g of water at 15.0°C absorbs 62.5 kJ of heat. Find the final temperature.

(A) 29.9°C

(B) 44.9°C

(C) 59.9°C

(D) 74.9°C

Lời giải chi tiết

$$\Delta T = \frac{q}{mc} = \frac{62{,}500}{(500.0)(4.18)} = \frac{62{,}500}{2090} = 29.9^\circ\text{C}.$$

$$T_f = 15.0 + 29.9 = \boxed{44.9^\circ\text{C}}. \quad \textbf{(B)}.$$

Bài tập luyện tập

A 65.0 g sample of an unknown metal, initially at 99.0°C, is placed in 120.0 g of water at 24.0°C inside a coffee-cup calorimeter (assume no heat loss to the calorimeter itself). The final temperature is 28.1°C. Determine the specific heat of the metal, and identify the metal given: Al $= 0.900$, Fe $= 0.449$, Cu $= 0.385$, Pb $= 0.129$ J/(g·°C).

Lời giải chi tiết

$$q_{\text{water}} = (120.0)(4.18)(28.1 - 24.0) = (120.0)(4.18)(4.1) = 2056.6 \text{ J}.$$

$$q_{\text{metal}} = -2056.6 \text{ J}, \qquad \Delta T_{\text{metal}} = 28.1 - 99.0 = -70.9^\circ\text{C}.$$

$$c_{\text{metal}} = \frac{-2056.6}{(65.0)(-70.9)} = \boxed{0.446 \text{ J/(g} \cdot {}^\circ\text{C)}}.$$

Comparing to the table, this value matches **iron** (0.449 J/(g·°C)) far more closely than any of the other candidates, so the unknown metal is identified as iron.

Bài tập luyện tập

Coffee-cup calorimetry directly measures which thermodynamic quantity, and why?

(A) ΔE, because no work of any kind occurs

(B) ΔH, because $q_p = \Delta H$ at constant pressure

(C) ΔH, because the volume is fixed

(D) ΔE, because $q_v = \Delta E$ at constant volume

Lời giải chi tiết

A coffee-cup calorimeter is open to the atmosphere and held at constant (ambient) pressure. Heat exchanged at constant pressure equals the enthalpy change, $q_p = \Delta H$. **(B)**.

Bài tập luyện tập

A 0.800 g sample of sucrose ($C_{12}H_{22}O_{11}$, $M = 342.3$ g/mol) is burned completely in a bomb calorimeter with heat capacity $C_{\text{cal}} = 5.00$ kJ/°C. The temperature rises by 2.640°C. Find ΔE of combustion per gram and per mole of sucrose.

Lời giải chi tiết

$$q_{\text{absorbed by calorimeter}} = C_{\text{cal}}\Delta T = (5.00)(2.640) = 13.20 \text{ kJ}, \qquad q_{\text{rxn}} = -13.20 \text{ kJ (for } 0.800 \text{ g)}.$$

Per gram: $\dfrac{-13.20}{0.800} = \boxed{-16.5 \text{ kJ/g}}$. Per mole: $(-16.5)(342.3) = \boxed{-5648 \text{ kJ/mol}}$.

Since the bomb calorimeter operates at constant volume, both results are ΔE (equivalently ΔU) values, not ΔH.

Bài tập luyện tập

80.0 g of hot water at 75.0°C is mixed with 120.0 g of cold water at 18.0°C inside a calorimeter. The measured final temperature is 38.5°C. Find the calorimeter's heat capacity C_{cal}.

Lời giải chi tiết

$$q_{\text{hot}} = (80.0)(4.18)(38.5 - 75.0) = (80.0)(4.18)(-36.5) = -12{,}206 \text{ J}.$$
$$q_{\text{cold}} = (120.0)(4.18)(38.5 - 18.0) = (120.0)(4.18)(20.5) = 10{,}283 \text{ J}.$$
$$q_{\text{cal}} = -(q_{\text{hot}} + q_{\text{cold}}) = -(-12{,}206 + 10{,}283) = 1923 \text{ J}.$$
$$C_{\text{cal}} = \frac{q_{\text{cal}}}{\Delta T_{\text{cal}}} = \frac{1923}{38.5 - 18.0} = \frac{1923}{20.5} = \boxed{93.8 \text{ J/°C}}.$$

Bài tập luyện tập

On a heating curve for a pure substance, the flat (constant-temperature) segment at the substance's boiling point corresponds to which process?

(A) The liquid and gas phases coexisting while $q = mc\Delta T$ applies

(B) The liquid warming toward its boiling point

(C) The liquid and gas phases coexisting while $q = n\Delta H_{\text{vap}}$ applies

(D) The gas warming above the boiling point

Lời giải chi tiết

On a plateau, temperature is constant and the substance exists as a mixture of two coexisting phases (here, liquid and gas); all heat added goes toward converting liquid to gas, so $q = n\Delta H_{\text{vap}}$ applies rather than $q = mc\Delta T$ (which applies only within a single phase). **(C)**.

Bài tập luyện tập

Find the total heat required to raise 40.0 g of liquid water from 10.0°C to its boiling point and then completely vaporize it at 100.0°C. Use $M(\text{H}_2\text{O}) = 18.02$ g/mol, $\Delta H_{\text{vap}} = 40.7$ kJ/mol.

Lời giải chi tiết

Heating step: $q_1 = mc\Delta T = (40.0)(4.18)(100.0-10.0) = (40.0)(4.18)(90.0) = 15{,}048$ J $= 15.05$ kJ.
Vaporization step: $n = \dfrac{40.0}{18.02} = 2.220$ mol; $q_2 = n\Delta H_{\text{vap}} = (2.220)(40.7) = 90.34$ kJ.

$$q_{\text{total}} = 15.05 + 90.34 = \boxed{105.4 \text{ kJ}}.$$

Bài tập luyện tập

How many grams of ice at 0°C can be melted by 15.0 kJ of heat? ($\Delta H_{\text{fus}} = 6.01$ kJ/mol, $M(\text{H}_2\text{O}) = 18.02$ g/mol.)

Lời giải chi tiết

$$n = \frac{q}{\Delta H_{\text{fus}}} = \frac{15.0}{6.01} = 2.496 \text{ mol}.$$

$$m = n \times M = (2.496)(18.02) = \boxed{45.0 \text{ g}}.$$

Bài tập luyện tập

Approximately how many times more energy is needed to vaporize 1 mole of liquid water at 100°C than to melt 1 mole of ice at 0°C?

(A) $0.15\times$
(B) $1\times$
(C) $6.8\times$
(D) $40.7\times$

Lời giải chi tiết

$$\frac{\Delta H_{\text{vap}}}{\Delta H_{\text{fus}}} = \frac{40.7}{6.01} = 6.77.$$

(C). This large ratio reflects that vaporization must fully separate molecules against the entire intermolecular attraction, while melting only loosens a rigid lattice into a still-touching liquid.

Bài tập luyện tập

For the reaction $2\,\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\,\text{SO}_3(\text{g})$, $\Delta H_{\text{rxn}} = -198$ kJ (as written). Calculate the heat released when 5.00 mol of SO_2 reacts completely with excess oxygen.

Lời giải chi tiết

The given $\Delta H = -198$ kJ corresponds to 2 mol SO_2 reacting, so per mole of SO_2:

$$\frac{-198 \text{ kJ}}{2 \text{ mol}} = -99.0 \text{ kJ/mol SO}_2.$$

$$\Delta H = (5.00\ \text{mol})(-99.0\ \text{kJ/mol}) = \boxed{-495\ \text{kJ}}.$$

Bài tập luyện tập

If the forward reaction A → B has $\Delta H = +65$ kJ, what is ΔH for the reverse reaction B → A?

(A) $+65$ kJ
(B) -65 kJ
(C) 0 kJ
(D) Cannot be determined without more data

Lời giải chi tiết

Reversing a reaction reverses the sign of ΔH (the transition state and all bond energies are unchanged; only the reference starting/ending points swap). $\Delta H_{\text{rev}} = -65$ kJ. **(B)**.

Bài tập luyện tập

Given $N_2(g) + O_2(g) \rightarrow 2\,NO(g)$, $\Delta H = +180.4$ kJ, find ΔH for $2\,NO(g) \rightarrow N_2(g) + O_2(g)$.

Lời giải chi tiết

This is the exact reverse of the given reaction, so its ΔH has the opposite sign:

$$\Delta H = \boxed{-180.4\ \text{kJ}}.$$

Bài tập luyện tập

Use bond enthalpies to estimate ΔH_{rxn} for $H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$, then check your value against the value obtained from $\Delta H_f^\circ(\text{HCl}) = -92.3$ kJ/mol.

Lời giải chi tiết

Bond enthalpy method: bonds broken = H–H + Cl–Cl $= 436 + 243 = 679$ kJ; bonds formed $= 2\times$H–Cl$= 2(431) = 862$ kJ.

$$\Delta H_{\text{rxn}} \approx 679 - 862 = \boxed{-183\ \text{kJ}}.$$

ΔH_f° **check:** $\Delta H_{\text{rxn}}^\circ = 2(-92.3) - 0 = -184.6$ kJ. The two methods agree closely (within 2 kJ), because HCl's bond enthalpy is well represented by the tabulated average.

Bài tập luyện tập

Use bond enthalpies to estimate ΔH for the hydrogenation of ethylene, $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$. (Ethylene has 4 C–H bonds and 1 C=C bond; ethane has 6 C–H bonds and 1 C–C bond.)

Lời giải chi tiết

Bonds broken (reactants): 4 C–H $+1$ C=C (in C_2H_4) $+1$ H–H (in H_2):

$$4(413) + 614 + 436 = 1652 + 614 + 436 = 2702\ \text{kJ}.$$

Bonds formed (products): 6 C–H $+1$ C–C (in C_2H_6):

$$6(413) + 347 = 2478 + 347 = 2825 \text{ kJ}.$$

$$\Delta H_{\text{rxn}} \approx 2702 - 2825 = \boxed{-123 \text{ kJ}}.$$

(Compare with the more precise ΔH_f°-based value of -137.1 kJ found in Problem 26 below — the two estimates agree to within about 14 kJ, typical accuracy for the bond-enthalpy method.)

Bài tập luyện tập

Find $\Delta H^\circ_{\text{rxn}}$ for the combustion of acetylene, $2\,C_2H_2(g) + 5\,O_2(g) \rightarrow 4\,CO_2(g) + 2\,H_2O(l)$, and express the answer per mole of C_2H_2.

Lời giải chi tiết

$$\Delta H^\circ_{\text{rxn}} = [4(-393.5) + 2(-285.8)] - [2(226.7) + 0] = [-1574.0 - 571.6] - [453.4]$$

$$= -2145.6 - 453.4 = \boxed{-2599.0 \text{ kJ (for 2 mol } C_2H_2)}.$$

$$\text{Per mole: } \frac{-2599.0}{2} = \boxed{-1299.5 \text{ kJ/mol}}.$$

This matches the well-known, strongly exothermic combustion of acetylene used in oxy-acetylene welding torches.

Bài tập luyện tập

Find $\Delta H^\circ_{\text{rxn}}$ for the thermal decomposition of limestone, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$.

Lời giải chi tiết

$$\Delta H^\circ_{\text{rxn}} = [\Delta H_f^\circ(CaO) + \Delta H_f^\circ(CO_2)] - \Delta H_f^\circ(CaCO_3) = [-635.1 + (-393.5)] - (-1206.9)$$

$$= -1028.6 + 1206.9 = \boxed{+178.3 \text{ kJ}}.$$

The positive sign confirms this decomposition is endothermic, consistent with the industrial process (lime kilns) requiring continuous, intense heating to drive the reaction forward.

Bài tập luyện tập

Given $N_2(g) + O_2(g) \rightarrow 2\,NO(g)$, $\Delta H_1 = +180.4$ kJ, and $N_2(g) + 2\,O_2(g) \rightarrow 2\,NO_2(g)$, $\Delta H_2 = +66.4$ kJ, use Hess's law to find ΔH for $2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$.

Lời giải chi tiết

Take reaction (2) as written and **reverse** reaction (1):

$$\text{(2)} \quad N_2 + 2\,O_2 \rightarrow 2\,NO_2, \qquad \Delta H_2 = +66.4 \text{ kJ}$$

$$-\text{(1)} \quad 2\,NO \rightarrow N_2 + O_2, \qquad -\Delta H_1 = -180.4 \text{ kJ}$$

Adding: $N_2 + 2\,O_2 + 2\,NO \rightarrow 2\,NO_2 + N_2 + O_2$; cancel N_2 and one O_2 from both sides, leaving

$2\,NO + O_2 \rightarrow 2\,NO_2$ — exactly the target.

$$\Delta H_{\text{target}} = \Delta H_2 - \Delta H_1 = 66.4 - 180.4 = \boxed{-114.0\ \text{kJ}}.$$

(This also equals the ΔH_f°-shortcut result, $2(33.2) - 2(90.2) = -114.0$ kJ — a useful cross-check.)

Bài tập luyện tập

Given the following three combustion reactions,

$$C_2H_4(g) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(l), \quad \Delta H_1 = -1411.0\ \text{kJ}$$

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \rightarrow H_2O(l), \quad \Delta H_2 = -285.8\ \text{kJ}$$

$$C_2H_6(g) + \tfrac{7}{2}\,O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(l), \quad \Delta H_3 = -1559.7\ \text{kJ}$$

use Hess's law to find ΔH for the hydrogenation of ethylene, $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$.

Lời giải chi tiết

Add reactions (1) and (2), then **reverse** reaction (3):

$$(1) + (2): \quad C_2H_4 + H_2 + 3.5\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$$

$$\Delta H_1 + \Delta H_2 = -1411.0 - 285.8 = -1696.8\ \text{kJ}$$

$$-(3): \quad 2\,CO_2 + 3\,H_2O \rightarrow C_2H_6 + 3.5\,O_2, \qquad -\Delta H_3 = +1559.7\ \text{kJ}$$

Adding: $C_2H_4 + H_2 + 3.5\,O_2 + 2\,CO_2 + 3\,H_2O \rightarrow 2\,CO_2 + 3\,H_2O + C_2H_6 + 3.5\,O_2$; cancel $2\,CO_2$, $3\,H_2O$, and $3.5\,O_2$ from both sides, leaving $C_2H_4 + H_2 \rightarrow C_2H_6$ — the target.

$$\Delta H_{\text{target}} = (\Delta H_1 + \Delta H_2) + (-\Delta H_3) = -1696.8 + 1559.7 = \boxed{-137.1\ \text{kJ}}.$$

This matches the ΔH_f°-shortcut result, $\Delta H_f^\circ(C_2H_6) - \Delta H_f^\circ(C_2H_4) = -84.7 - 52.4 = -137.1$ kJ, and is close to the bond-enthalpy estimate of -123 kJ from Problem 22 — three independent methods converging on essentially the same answer.

Bài tập luyện tập

A student combines two given reactions to find a target reaction's ΔH. Reaction (1) must be reversed and its coefficients doubled to fit the target. Which operation correctly transforms ΔH_1 for use in the sum?

(A) Use $+\Delta H_1$ unchanged

(B) Use $+2\Delta H_1$

(C) Use $-2\Delta H_1$

(D) Use $-\frac{1}{2}\Delta H_1$

Lời giải chi tiết

Reversing flips the sign; doubling the coefficients doubles the magnitude. Both operations must be applied together: $-2\Delta H_1$. **(C)**.

Bài tập luyện tập

A comprehensive problem: 45.0 g of ice at 0.00°C is added to 200.0 g of liquid water at 35.0°C in a well-insulated, isolated container. (a) Show that all of the ice melts. (b) Find the final equilibrium temperature of the resulting liquid water. Use $\Delta H_{\text{fus}} = 6.01$ kJ/mol, $M(\text{H}_2\text{O}) = 18.02$ g/mol, $c_{\text{water}} = 4.18$ J/(g·°C).

Lời giải chi tiết

(a) Maximum heat available if the 200.0 g of warm water cooled all the way down to 0.00°C:

$$q_{\text{available}} = (200.0)(4.18)(35.0 - 0.00) = 29{,}260 \text{ J} = 29.26 \text{ kJ}.$$

Heat required to melt all 45.0 g of ice: $n = \dfrac{45.0}{18.02} = 2.497$ mol,

$$q_{\text{melt}} = n\Delta H_{\text{fus}} = (2.497)(6.01) = 15.01 \text{ kJ}.$$

Since $q_{\text{melt}}(15.01 \text{ kJ}) < q_{\text{available}}(29.26 \text{ kJ})$, there is more than enough heat in the warm water to melt all of the ice; **all 45.0 g of ice melts**, and the final state is entirely liquid water above 0°C.

(b) With all ice melted, set up the energy balance: heat lost by the original 200.0 g of water cooling from 35.0°C to the final temperature T_f equals the heat used to melt the ice *plus* the heat used to warm the resulting 45.0 g of meltwater from 0.00°C to T_f:

$$(200.0)(4.18)(35.0 - T_f) = 15{,}010 + (45.0)(4.18)(T_f - 0.00)$$

$$29{,}260 - 836\,T_f = 15{,}010 + 188.1\,T_f \;\Rightarrow\; 14{,}250 = 1024.1\,T_f \;\Rightarrow\; T_f = \boxed{13.9^\circ\text{C}}.$$

Bài tập luyện tập

A bomb calorimeter, by design, holds volume constant so that no expansion work is possible. Which statement correctly relates the measured heat to a thermodynamic state function?

(A) $q_v = \Delta H$, because pressure is held constant

(B) $q_v = \Delta E$, because $w = 0$ at constant volume

(C) $q_v = 0$, because the vessel is sealed

(D) $q_v = \Delta H - \Delta E$

Lời giải chi tiết

At constant volume, no $P\Delta V$ expansion work occurs, so from the first law $\Delta E = q + w = q_v + 0 = q_v$. **(B).**

Bài tập luyện tập

A catalyst is added to a reaction with $\Delta H = -120$ kJ, $E_{a,\text{fwd}} = 95$ kJ, and $E_{a,\text{rev}} = 215$ kJ. The catalyzed pathway lowers $E_{a,\text{fwd}}$ to 60 kJ. Find the new $E_{a,\text{rev}}$ and the new ΔH for the catalyzed pathway.

Lời giải chi tiết

A catalyst lowers the transition-state peak, reducing both activation energies by the *same* amount, but leaves ΔH completely unchanged (reactants and products are the same species at the same energy levels regardless of pathway). The peak dropped by $95 - 60 = 35$ kJ, so:

$$E_{a,\text{rev,new}} = 215 - 35 = \boxed{180 \text{ kJ}}, \qquad \Delta H_{\text{new}} = \boxed{-120 \text{ kJ (unchanged)}}.$$

Check: $E_{a,\text{fwd,new}} - E_{a,\text{rev,new}} = 60 - 180 = -120$ kJ $= \Delta H$, consistent.

Bài tập luyện tập

Which of the following is a valid justification for Hess's law?

(A) q and w are both state functions, so any path gives the same q

(B) Enthalpy is a state function, so ΔH depends only on initial and final states, not on the path/number of steps

(C) Bond enthalpies are always exactly additive

(D) Calorimeters always measure ΔH exactly, regardless of design

Lời giải chi tiết

Hess's law rests specifically on enthalpy (H) being a **state function** — path-independent. (q and w individually are *not* state functions; only their sum, $\Delta E = q + w$, is, and ΔH is likewise path-independent.) **(B)**.

Bài tập luyện tập

75.0 mL of 2.00 M HNO_3 and 75.0 mL of 2.00 M KOH, both initially at 21.4°C, are mixed in a coffee-cup calorimeter. The mixture reaches a maximum temperature of 35.1°C. Assume the combined solution has mass 150.0 g and specific heat 4.18 J/(g·°C), with negligible heat absorbed by the calorimeter. Find ΔH of neutralization per mole of water formed.

Lời giải chi tiết

Moles of each reactant: $(0.0750 \text{ L})(2.00 \text{ mol/L}) = 0.150$ mol, reacting in a $1{:}1$ ratio with no excess, so 0.150 mol of H_2O forms.

$$q_{\text{soln}} = (150.0)(4.18)(35.1 - 21.4) = (150.0)(4.18)(13.7) = 8590 \text{ J} = 8.590 \text{ kJ}.$$

$$q_{\text{rxn}} = -8.590 \text{ kJ}, \qquad \Delta H = \frac{-8.590}{0.150} = \boxed{-57.3 \text{ kJ/mol}}.$$

This agrees closely with the accepted strong acid–strong base neutralization enthalpy near -57 kJ/mol.

Equilibrium

Mục tiêu Unit: Hiểu bản chất **cân bằng động** (dynamic equilibrium) ở cấp độ phân tử; viết đúng biểu thức hằng số cân bằng K (bỏ chất rắn/lỏng nguyên chất), phân biệt K_c và K_p; tính K từ số liệu nồng độ/áp suất tại cân bằng; đánh giá mức độ thuận lợi của phản ứng qua độ lớn của K; áp dụng các quy tắc biến đổi K (đảo chiều, nhân hệ số, cộng phản ứng); lập và giải bảng ICE (kể cả dùng công thức nghiệm phương trình bậc hai và quy tắc gần đúng 5%); đọc hình biểu diễn hạt cân bằng; vận dụng nguyên lý Le Chatelier cho các loại stress (nồng độ, thể tích/áp suất, nhiệt độ) và phân biệt rõ sự dịch chuyển cân bằng với sự thay đổi giá trị K; nắm vững cân bằng tan K_{sp}, độ tan mol, hiệu ứng ion chung, ảnh hưởng của pH lên độ tan muối có anion base, và mối liên hệ định tính giữa năng lượng tự do Gibbs với quá trình hoà tan.

7.1 Introduction to equilibrium

Many chemical reactions do not run to completion in one direction; instead, when reactants are mixed in a closed system, the forward reaction produces products, and as soon as any product exists, the reverse reaction begins converting product back into reactant. **Chemical equilibrium** is the state reached when the rate of the forward reaction exactly equals the rate of the reverse reaction. At that point the concentrations of every species stop changing, even though both reactions continue to occur.

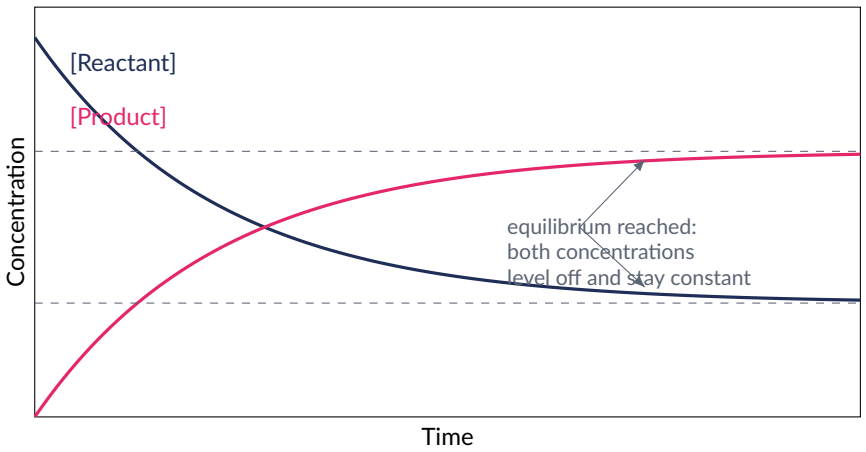
Dynamic equilibrium

Equilibrium is **dynamic**, not static: at the molecular level, forward and reverse reactions never stop. Individual molecules of reactant are constantly converting to product, and individual molecules of product are constantly converting back to reactant, at exactly matched rates. Because these two flows exactly cancel, the *macroscopic*, measurable concentrations of every species remain constant over time — but nothing has actually "stopped happening" at the particle level. This is fundamentally different from a static system in which no reaction occurs at all.

VN **GIẢI THÍCH TIẾNG VIỆT**

Cân bằng hoá học là trạng thái **động** (dynamic), không phải **tĩnh** (static): phản ứng thuận và phản ứng nghịch vẫn diễn ra liên tục ở cấp độ phân tử, nhưng với **tốc độ bằng nhau**, nên nồng độ các chất không đổi theo thời gian ở cấp độ vĩ mô. Đây là điểm học sinh dễ hiểu nhầm nhất: cân bằng **không** có nghĩa là phản ứng đã dừng lại, mà có nghĩa là hai chiều phản ứng triệt tiêu lẫn nhau về mặt tốc độ thay đổi nồng độ quan sát được.

For a generic reversible reaction $a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$, the double-headed arrow ($\rightleftharpoons$) is the standard notation indicating that both the forward and reverse reactions occur. Equilibrium is typically approached from one side (all reactants, all products, or some arbitrary mixture) and, given enough time in a closed system at constant temperature, the system will always settle into the same equilibrium ratio of concentrations, regardless of the starting point.



Concentration-versus-time profile for a reaction A ⇌ B started with only A present. Both curves flatten into horizontal plateaus once equilibrium is reached; the plateau values, not zero, mark where the forward and reverse rates have become equal.

Reaching equilibrium does *not* mean reactants and products are present in equal amounts. It only means the concentrations have stopped changing. The equilibrium mixture can be almost entirely product, almost entirely reactant, or anywhere in between — Section 7.5 connects this composition to the magnitude of the equilibrium constant K.

7.2 Direction of reversible reactions

Whether a reaction net proceeds forward (net formation of products) or in reverse (net formation of reactants) as it moves toward equilibrium depends entirely on the **initial conditions** — what is actually present in the container at the start, and in what amounts.

How initial conditions set the direction

- If a container is charged with **only reactants** (no products present at all), the reaction can only proceed **forward**: some reactant must convert to product before any reverse reaction is even possible.
- If a container is charged with **only products** (no reactants present at all), the reaction can only proceed in **reverse**: net formation of reactants from products.
- If a container is charged with **some mixture of reactants and products**, either direction is possible depending on how that particular mixture compares to the equilibrium ratio. Section 7.3 formalizes this comparison using the **reaction quotient** Q.

In every case, the system evolves toward the *same* equilibrium ratio of concentrations (at a fixed temperature) regardless of which direction it had to travel to get there.

VN **GIẢI THÍCH TIẾNG VIỆT**

Chiều của phản ứng (tiến tới cân bằng theo hướng thuận hay nghịch) phụ thuộc vào **điều kiện ban đầu** trong bình phản ứng. Nếu ban đầu chỉ có chất phản ứng, phản ứng chỉ có thể tiến theo chiều **thuận**. Nếu ban đầu chỉ có sản phẩm, phản ứng chỉ có thể tiến theo chiều **nghịch**. Nếu ban đầu có cả hai, chiều dịch chuyển phụ thuộc vào việc hỗn hợp ban đầu "lệch" về phía nào so với tỉ lệ cân bằng — được định lượng chính xác bằng thương số phản ứng Q ở mục 7.3.

7.3 The reaction quotient Q and equilibrium constant K

For the general reaction $a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$, the **reaction quotient** Q and the **equilibrium constant** K share the identical algebraic form — products raised to their coefficients divided by reactants raised to their coefficients:

$$Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}, \qquad K = \frac{[\mathrm{C}]_{\mathrm{eq}}^c[\mathrm{D}]_{\mathrm{eq}}^d}{[\mathrm{A}]_{\mathrm{eq}}^a[\mathrm{B}]_{\mathrm{eq}}^b}.$$

The difference is purely about *when* the concentrations are measured: Q can be evaluated using concentrations at *any* moment (equilibrium or not), while K is, by definition, Q evaluated using concentrations that are specifically at equilibrium, at a given temperature. Because K depends only on temperature, it is a fixed number for a given reaction at a given T, while Q changes continuously as the reaction proceeds.

7.3.1 Homogeneous versus heterogeneous equilibria

A **homogeneous equilibrium** has every species in the same phase (most commonly, all gases, or all dissolved in one solution). A **heterogeneous equilibrium** involves species in more than one phase — typically a solid or pure liquid together with gases or dissolved species.

Pure solids and pure liquids are omitted from K

The concentration of a pure solid or a pure liquid is an intrinsic physical property (density divided by molar mass) that does *not* change as the amount of that solid or liquid changes, as long as some of it is still present. Because K expressions only make sense in terms of quantities that can actually vary, pure solids and pure liquids are **omitted entirely** from the equilibrium expression (their "concentration" is folded into the constant K itself, effectively treated as 1). Only gases (expressed as concentration or partial pressure) and dissolved (aqueous) species are written into K. Water itself is omitted whenever it appears as the pure liquid solvent, but *is* included if it appears as a gas, $\mathrm{H_2O(g)}$.

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Chất rắn nguyên chất và chất lỏng nguyên chất **KHÔNG** xuất hiện trong biểu thức K, vì nồng độ (mol/thể tích thực) của chúng là hằng số vật lý nội tại, không đổi dù lượng chất rắn/lỏng đó nhiều hay ít (miễn còn tồn tại). Chỉ **chất khí** (theo nồng độ hoặc áp suất riêng phần) và **chất tan trong dung dịch** mới xuất hiện trong K. Nước đóng vai trò dung môi (lỏng nguyên chất) thì bị bỏ qua; nhưng nếu nước ở thể khí $\mathrm{H_2O(g)}$ thì phải đưa vào biểu thức.

Writing equilibrium-constant expressions

Write the K_c expression for each reaction.

1. $\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$ (homogeneous, all gases)
2. $\mathrm{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$ (heterogeneous, two solids and a gas)
3. $\mathrm{C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)}$ (heterogeneous, one solid, two gases)
4. $\mathrm{Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)}$ (homogeneous, all aqueous)

1. All four species are gases, so all four appear:

$$K_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}.$$

2. Both $\mathrm{CaCO_3}$ and CaO are pure solids and are omitted; only the gas remains:

$$K_c = [\mathrm{CO_2}].$$

3. $C(s)$ is a pure solid and is omitted; $H_2O(g)$, $CO(g)$, and $H_2(g)$ are all gases and remain:

$$K_c = \frac{[CO][H_2]}{[H_2O]}.$$

4. All species are dissolved (aqueous), so all three appear:

$$K_c = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}.$$

7.3.2 K_c versus K_p

For gas-phase reactions, the equilibrium constant may be expressed either in terms of molar concentrations (K_c) or in terms of partial pressures in atmospheres (K_p). The two are related through the ideal-gas law, and in general $K_p \neq K_c$ unless $\Delta n_{\text{gas}} = 0$.

$$K_p = K_c\,(RT)^{\Delta n_{\text{gas}}}, \qquad \Delta n_{\text{gas}} = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants}),$$

using the coefficients of the balanced equation, with $R = 0.08206$ L·atm/(mol·K) and T in kelvin. When $\Delta n_{\text{gas}} = 0$, $(RT)^0 = 1$ and $K_p = K_c$ exactly.

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K_p dùng áp suất riêng phần (atm) thay vì nồng độ mol/L. Công thức liên hệ: $K_p = K_c(RT)^{\Delta n_{\text{khí}}}$, với $\Delta n_{\text{khí}}$ là hiệu số mol khí sản phẩm trừ số mol khí chất phản ứng (theo hệ số cân bằng). Nếu $\Delta n_{\text{khí}} = 0$ (số mol khí hai bên bằng nhau) thì $K_p = K_c$ đúng bằng nhau; nếu không, hai giá trị này khác nhau về mặt số học (dù mô tả cùng một cân bằng).

Converting K_c to K_p

For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, $K_c = 0.0434$ at $T = 500$ K. Find K_p.
Moles of gas: 1 reactant $\rightarrow$ 2 products, so $\Delta n_{\text{gas}} = 2 - 1 = +1$.

$$K_p = K_c(RT)^{\Delta n} = (0.0434)\big[(0.08206)(500)\big]^1 = (0.0434)(41.03) = \boxed{1.78}.$$

K_p is larger than K_c here because $\Delta n_{\text{gas}} > 0$ and $RT > 1$; whenever a gas-phase reaction increases the number of gas moles, $K_p > K_c$.

(!) Lỗi thường gặp: The single most common error in writing K expressions is including a pure solid or pure liquid as if it were a normal concentration term. Always scan the balanced equation for the state labels (s) and (l) *other than* the solvent water in an aqueous mixture, and physically cross them out before writing the expression — only (g) and (aq) species (and H_2O when it is itself a gas) belong in K.

7.4 Calculating the equilibrium constant

When a reaction has reached equilibrium and the concentrations (or partial pressures) of every species are measured, K is found simply by substituting those equilibrium values directly into the

equilibrium expression — no algebra beyond arithmetic is required, provided every species' equilibrium value is already known.

Calculating K_c from equilibrium concentration data

At a certain temperature, a 1.00-L flask initially contains 0.0500 mol of $N_2O_4(g)$ and no $NO_2(g)$. The system is allowed to reach equilibrium: $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$. At equilibrium, $[NO_2] = 0.0332$ M. Find K_c.

By the reaction's stoichiometry, every 2 mol of NO_2 formed consumes 1 mol of N_2O_4, so the change in $[N_2O_4]$ is $-\frac{1}{2}(0.0332) = -0.0166$ M:

$$[N_2O_4]_{eq} = 0.0500 - 0.0166 = 0.0334 \text{ M}.$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0332)^2}{0.0334} = \frac{0.0011022}{0.0334} = \boxed{0.0330}.$$

Calculating K_p from equilibrium partial pressures

For $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$, an equilibrium mixture at a fixed temperature has $P_{H_2} = 0.20$ atm, $P_{CO_2} = 0.30$ atm, $P_{H_2O} = 0.55$ atm, $P_{CO} = 0.55$ atm. Find K_p.

$$K_p = \frac{P_{H_2O}\,P_{CO}}{P_{H_2}\,P_{CO_2}} = \frac{(0.55)(0.55)}{(0.20)(0.30)} = \frac{0.3025}{0.060} = \boxed{5.04}.$$

7.5 Magnitude of K

The numeric size of K (at a fixed temperature) reveals, at a glance, whether an equilibrium mixture is dominated by products, dominated by reactants, or contains comparable amounts of both. This follows directly from the definition of K: since K is products divided by reactants (each raised to a coefficient), a large K can only occur if the numerator (products) dominates, and a small K can only occur if the denominator (reactants) dominates.

- $K \gg 1$ (for example, $K > 10^3$): at equilibrium, **products are strongly favored** — the equilibrium mixture is mostly products, with only a small amount of reactant remaining.
- $K \ll 1$ (for example, $K < 10^{-3}$): at equilibrium, **reactants are strongly favored** — the equilibrium mixture is mostly unreacted starting material, with only a small amount of product formed.
- $K \approx 1$ (roughly 10^{-3} to 10^3, and especially close to 1): the equilibrium mixture contains **comparable amounts** of reactants and products, neither side overwhelmingly dominant.

The magnitude of K says nothing about *how fast* equilibrium is reached — that is a kinetics question, entirely independent of the thermodynamic size of K.

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Độ lớn của K cho biết cân bằng nghiêng về phía nào: $K \gg 1$ nghĩa là **sản phẩm chiếm ưu thế**; $K \ll 1$ nghĩa là **chất phản ứng chiếm ưu thế**; $K \approx 1$ nghĩa là hai bên có lượng **tương đương**. Lưu ý quan trọng: độ lớn của K hoàn toàn **không nói lên tốc độ** phản ứng đạt đến cân bằng nhanh hay chậm — đó là vấn đề động học (kinetics), tách biệt hoàn toàn với bản chất nhiệt động học của K.

7.6 Properties of the equilibrium constant

Because K is defined directly from the balanced equation, any manipulation of that equation (reversing it, scaling its coefficients, or combining it with other equations) produces a predictable, calculable change to K.

- **Reversing** a reaction inverts K: if A $\rightleftharpoons$ B has constant K, then B $\rightleftharpoons$ A has constant $K_{\text{rev}} = \dfrac{1}{K}$.
- **Scaling** a reaction's coefficients by a factor n raises K to the n^{th} power: if A $\rightleftharpoons$ B has constant K, then n A $\rightleftharpoons$ n B has constant K^n.
- **Adding** two (or more) reactions together to obtain an overall reaction multiplies their individual K values: if reaction (1) has K_1 and reaction (2) has K_2, then (1)+(2) has constant $K_{\text{overall}} = K_1 \times K_2$.

These three rules can be combined in any order to relate the K of a target reaction to the K values of other, related reactions — directly analogous to the Hess's-law manipulations used for ΔH in Section 6.9, except that K values *multiply* (and are raised to powers) rather than simply adding.

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Ba quy tắc biến đổi K: **đảo chiều** phản ứng $\Rightarrow$ K mới $= 1/K$ cũ; **nhân hệ số** với $n \Rightarrow$ K mới $= K^n$; **cộng hai phản ứng** $\Rightarrow$ K tổng $= K_1 \times K_2$ (nhân, KHÔNG cộng). Đây là điểm khác biệt quan trọng so với ΔH: khi cộng phản ứng, ΔH thì **cộng**, còn K thì **nhân**.

Combining equilibrium constants

Given

$$\text{(1)}\quad 2\,\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\,\text{NO}_2\text{(g)}, \quad K_1 = 25,$$

$$\text{(2)}\quad 2\,\text{NO}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O}_4\text{(g)}, \quad K_2 = 0.40,$$

find (a) K for $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\,\text{NO}_2\text{(g)}$; (b) K for $4\,\text{NO(g)} + 2\,\text{O}_2\text{(g)} \rightleftharpoons 4\,\text{NO}_2\text{(g)}$; (c) K for $2\,\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O}_4\text{(g)}$.

(a) This is reaction (2) reversed: $K = \dfrac{1}{K_2} = \dfrac{1}{0.40} = \boxed{2.5}$.

(b) This is reaction (1) with every coefficient doubled: $K = K_1^2 = 25^2 = \boxed{625}$.

(c) Add reaction (1) as written to reaction (2) as written: the $2\,\text{NO}_2$ produced in (1) is exactly consumed in (2), canceling to leave $2\,\text{NO} + \text{O}_2 \rightleftharpoons \text{N}_2\text{O}_4$, the target.

$$K = K_1 \times K_2 = (25)(0.40) = \boxed{10.0}.$$

7.7 Calculating equilibrium concentrations

Given the initial concentrations of a system and the value of K, the equilibrium concentrations of every species can be found using an **ICE table** — a bookkeeping structure with rows for **I**nitial, **C**hange, and **E**quilibrium concentrations, tied together by the reaction's stoichiometry.

	a A	b B	c C
Initial (M)	$[\text{A}]_0$	$[\text{B}]_0$	$[\text{C}]_0$
Change (M)	$-ax$	$-bx$	$+cx$
Equilibrium (M)	$[\text{A}]_0 - ax$	$[\text{B}]_0 - bx$	$[\text{C}]_0 + cx$

General ICE table skeleton for a A $+ b$ B $\rightleftharpoons c$ C proceeding in the forward direction. The changes are always in the exact ratio of the balanced coefficients, with reactants decreasing and products increasing (signs reverse if the reaction instead runs net in reverse).

Building and solving an ICE table

1. Write the balanced equation and set up the three rows (Initial, Change, Equilibrium) beneath each species.
2. Fill in the known initial concentrations; if a species is not yet present, its initial value is 0.
3. Define the change in one species as x (or a multiple of x matching its coefficient), with the correct sign (reactants decrease, products increase, if the reaction runs forward).
4. Add each column to get the equilibrium row in terms of x.
5. Substitute the equilibrium row into the K expression and solve for x — sometimes by taking a square root directly, sometimes with the quadratic formula, and sometimes using a simplifying approximation (below).
6. Back-substitute x into the equilibrium row to report each numeric equilibrium concentration, and check that all values are physically sensible (none negative).

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Bảng ICE (Initial – Change – Equilibrium) là công cụ chuẩn để giải bài toán cân bằng: hàng **Initial** ghi nồng độ ban đầu, hàng **Change** ghi biến thiên theo đúng tỉ lệ hệ số cân bằng (dùng ẩn x, dấu trừ cho chất phản ứng bị tiêu hao, dấu cộng cho sản phẩm tạo thành), hàng **Equilibrium** là tổng hai hàng trên. Thế hàng Equilibrium vào biểu thức K rồi giải ra x — có thể cần khai căn trực tiếp, dùng công thức nghiệm bậc hai, hoặc áp dụng quy tắc gần đúng khi K rất nhỏ.

7.7.1 Exact solution using the quadratic formula

When the stoichiometry does not reduce to a perfect square (for example, unequal initial concentrations of two reactants, or a K value not small enough to approximate), solving the ICE table's equilibrium expression for x requires expanding into a standard quadratic equation $Ax^2 + Bx + C = 0$ and applying

$$x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A},$$

then rejecting whichever root is physically impossible (typically because it makes an equilibrium concentration negative).

ICE table requiring the quadratic formula

$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_c = 54.3$. A flask is charged with $[H_2]_0 = 0.200$ M and $[I_2]_0 = 0.100$ M, with no HI initially. Find all three equilibrium concentrations.

	H_2	I_2	HI
Initial (M)	0.200	0.100	0
Change (M)	$-x$	$-x$	$+2x$
Equilibrium (M)	$0.200 - x$	$0.100 - x$	$2x$

Because the two reactants start at *unequal* concentrations, the denominator is not a perfect square, and the equation must be solved as a genuine quadratic:

$$K = \frac{(2x)^2}{(0.200 - x)(0.100 - x)} = 54.3.$$

Expand the denominator, $(0.200 - x)(0.100 - x) = 0.0200 - 0.300x + x^2$, and cross-multiply:

$$4x^2 = 54.3(0.0200 - 0.300x + x^2) = 1.086 - 16.29x + 54.3x^2.$$

Collecting all terms on one side with a positive leading coefficient:

$$50.3x^2 - 16.29x + 1.086 = 0.$$

Applying the quadratic formula with $A = 50.3$, $B = -16.29$, $C = 1.086$:

$$x = \frac{16.29 \pm \sqrt{(-16.29)^2 - 4(50.3)(1.086)}}{2(50.3)} = \frac{16.29 \pm \sqrt{265.36 - 218.50}}{100.6} = \frac{16.29 \pm 6.85}{100.6}.$$

This gives $x = 0.230$ or $x = 0.0939$. The root $x = 0.230$ is rejected because it would make $[\mathrm{I_2}] = 0.100 - 0.230 < 0$, which is physically impossible. Using the valid root $x = 0.0939$:

$[\mathrm{H_2}] = 0.200 - 0.0939 = \boxed{0.106\ \mathrm{M}}$, $[\mathrm{I_2}] = 0.100 - 0.0939 = \boxed{0.00612\ \mathrm{M}}$, $[\mathrm{HI}] = 2(0.0939) = \boxed{0.188\ \mathrm{M}}$.

Check: $\dfrac{(0.188)^2}{(0.106)(0.00612)} = \dfrac{0.03534}{0.000649} \approx 54.5$, matching $K = 54.3$ within rounding.

7.7.2 The 5% simplifying approximation

When K is very small compared with the initial concentration (roughly $K \lesssim 10^{-3}$ relative to $[\,]_0$, though the safest test is always the check below), the amount x that reacts is so small that $[\,]_0 - x \approx [\,]_0$. This lets the equilibrium expression be solved by a much simpler direct calculation — provided the approximation is verified afterward.

[The 5% validity rule] After solving for x using the simplified (approximate) expression, always check

$$\frac{x}{[\,]_0} \times 100\% \le 5\%.$$

If this holds, the approximation is valid and the simplified answer may be reported as-is (no further refinement needed). If the ratio exceeds 5%, the approximation has failed and the exact quadratic formula (above) must be used instead — the simplified answer is *not* acceptable.

ICE table using the 5% approximation, with validity check

$\mathrm{A(g)} \rightleftharpoons \mathrm{B(g)} + \mathrm{C(g)}$, $K_c = 1.8 \times 10^{-5}$, with $[\mathrm{A}]_0 = 0.500$ M and no B or C initially. Find the equilibrium concentrations.

	A	B	C
Initial (M)	0.500	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.500 - x$	x	x

$$K = \frac{x^2}{0.500 - x} = 1.8 \times 10^{-5}.$$

Because K is extremely small relative to 0.500, assume $0.500 - x \approx 0.500$:

$$x^2 \approx (1.8 \times 10^{-5})(0.500) = 9.0 \times 10^{-6} \;\Rightarrow\; x \approx \sqrt{9.0 \times 10^{-6}} = 3.0 \times 10^{-3}.$$

Validity check:

$$\frac{x}{[\mathrm{A}]_0} \times 100\% = \frac{3.0 \times 10^{-3}}{0.500} \times 100\% = 0.60\% \;\leq\; 5\% \quad \checkmark$$

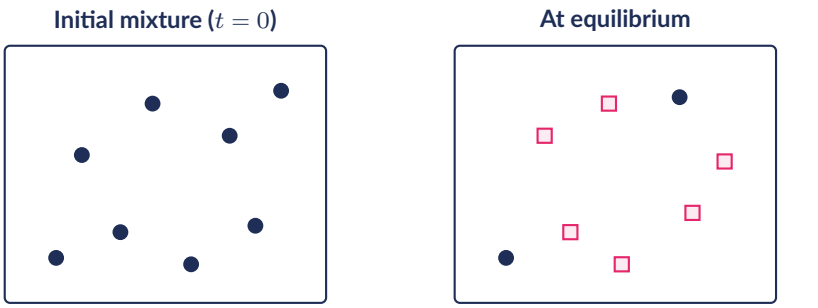
The approximation is valid, so the equilibrium concentrations are

$$[\mathrm{A}] \approx 0.500 - 0.003 = \boxed{0.497\ \mathrm{M}}, \qquad [\mathrm{B}] = [\mathrm{C}] = \boxed{3.0 \times 10^{-3}\ \mathrm{M}}.$$

(!) Lỗi thường gặp: Applying the 5% approximation *without* checking the validity condition afterward is one of the most frequent sources of error on equilibrium problems. A large K, a small initial concentration, or a reaction that consumes a large fraction of the starting material can all push the ratio $x/[\,]_0$ well above 5%, in which case the shortcut answer is simply wrong and the full quadratic formula must be used instead. Never skip the validity check, even when the approximation "feels" safe.

7.8 Representations of equilibrium

Equilibrium mixtures are sometimes shown as **particulate diagrams** — boxes containing a small number of dots or shapes representing individual reactant and product particles, drawn to be roughly proportional to relative concentration (all boxes representing equal volumes). Reading these diagrams correctly, and computing K directly from a particle count, is a core skill tested alongside the algebraic definition of K.



8 A particles (navy •), 0 B particles — 2 A particles (navy •), 6 B particles (pink ■)

Particulate representation of $\mathrm{A(g)} \rightleftharpoons \mathrm{B(g)}$ in a fixed-volume container, from a starting mixture of pure A to the equilibrium mixture. Treating particle count as directly proportional to concentration (equal container volume in both boxes), $K = [\mathrm{B}]/[\mathrm{A}] = 6/2 = 3$: a value of K noticeably greater than 1, consistent with the equilibrium box showing more product particles than reactant particles.

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Hình biểu diễn hạt (particulate diagram) minh hoạ số lượng hạt tương đối của chất phản ứng và sản phẩm tại cân bằng, với giả định các hộp có cùng thể tích nên số hạt tỉ lệ thuận với nồng độ. Từ số hạt đếm được, có thể tính trực tiếp K theo đúng biểu thức đại số — đây là cách kiểm tra trực quan xem giá trị K có phù hợp với hình vẽ hay không (nhiều sản phẩm hơn $\Rightarrow$ K lớn; nhiều chất phản ứng hơn $\Rightarrow$ K nhỏ).

7.9 Introduction to Le Chatelier's principle

Le Chatelier's principle states that if a system at equilibrium is subjected to a **stress** (a change in concentration, volume/pressure, or temperature), the system responds by shifting in whichever direction **partially counteracts** that stress, until a new equilibrium is established.

Types of stress and the qualitative response

- **Adding** a reactant or product shifts the equilibrium *away* from the added species (consuming some of what was added). **Removing** a reactant or product shifts the equilibrium *toward* the removed species (replacing some of what was removed).
- **Decreasing** the container volume (increasing pressure) shifts the equilibrium toward the side with *fewer* moles of gas, since that partially counteracts the pressure increase. **Increasing** the volume (decreasing pressure) shifts the equilibrium toward the side with *more* moles of gas. If both sides have equal moles of gas, volume changes cause no shift at all.
- **Temperature** changes are treated by imagining heat itself as a reactant (in an endothermic reaction) or a product (in an exothermic reaction) — see Section 7.10 for the crucial distinction that temperature is the *only* stress that changes the actual value of K.

VN **GIẢI THÍCH TIẾNG VIỆT**

Nguyên lý Le Chatelier: khi một hệ đang ở cân bằng chịu một **stress** (thay đổi nồng độ, thể tích/áp suất, hoặc nhiệt độ), hệ sẽ dịch chuyển theo chiều làm **giảm bớt một phần** tác động của stress đó, để thiết lập cân bằng mới. Thêm chất $\Rightarrow$ cân bằng dịch chuyển để tiêu hao bớt chất vừa thêm; giảm thể tích (tăng áp suất) $\Rightarrow$ dịch chuyển về phía có **ít mol khí hơn**; tăng thể tích $\Rightarrow$ dịch chuyển về phía **nhiều mol khí hơn**.

Concentration and volume stress on an equilibrium

$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $K_c = 0.500$ at a fixed temperature T. A flask at equilibrium has $[N_2] = 0.500$ M, $[H_2] = 1.00$ M, $[NH_3] = 0.500$ M (verify: $K = (0.500)^2/[(0.500)(1.00)^3] = 0.250/0.500 = 0.500$ ✓). Predict the direction of shift for (a) suddenly adding N_2 until $[N_2] = 1.00$ M (all else unchanged at that instant); (b) suddenly halving the container volume.

(a) Adding N_2: immediately after the addition, before any reaction occurs,

$$Q = \frac{(0.500)^2}{(1.00)(1.00)^3} = \frac{0.250}{1.00} = 0.250.$$

Since $Q(0.250) < K(0.500)$, the reaction shifts **forward** (toward NH_3), consuming some of the added N_2 — consistent with Le Chatelier's qualitative prediction.

(b) Halving the volume: every concentration instantaneously doubles: $[N_2] = 1.00$, $[H_2] = 2.00$, $[NH_3] = 1.00$ M.

$$Q = \frac{(1.00)^2}{(1.00)(2.00)^3} = \frac{1.00}{8.00} = 0.125.$$

Since $Q(0.125) < K(0.500)$, the reaction again shifts **forward**. This matches the mole-counting rule: the reactant side has 4 mol of gas $(1 + 3)$ while the product side has only 2 mol of gas, so compressing the container (raising pressure) favors the side with fewer gas moles, the product side.

7.10 Reaction quotient and Le Chatelier's principle

Every stress can be analyzed rigorously (not just qualitatively) by recomputing Q immediately after the stress is applied and comparing it with K: if $Q < K$, the system must shift **forward** to climb back toward $Q = K$; if $Q > K$, the system must shift in **reverse**; if $Q = K$ already, no net shift occurs (the stress had no effect on that particular equilibrium, or none was actually applied).

$Q < K \Rightarrow$ shifts forward (net reaction produces more products).
$Q > K \Rightarrow$ shifts in reverse (net reaction produces more reactants).
$Q = K \Rightarrow$ already at equilibrium, no net shift.

7.10.1 Temperature: the one stress that changes K itself

Concentration and volume stresses shift the position of equilibrium (the specific concentrations present) but leave the numeric value of K completely unchanged, because K depends only on temperature. **Temperature is different**: changing T genuinely changes the value of K, because it changes the underlying balance between the forward and reverse rate constants.

Direction of K's change with temperature

Treat heat as if it were a chemical species on whichever side of the equation absorbs it:

- For an **exothermic** reaction ($\Delta H < 0$, heat is effectively a "product"), **raising** the temperature acts like adding a product, shifting the equilibrium in **reverse** and **decreasing** K. **Lowering** the temperature shifts it forward and **increases** K.
- For an **endothermic** reaction ($\Delta H > 0$, heat is effectively a "reactant"), **raising** the temperature acts like adding a reactant, shifting the equilibrium **forward** and **increasing** K. **Lowering** the temperature shifts it in reverse and **decreases** K.

For example, ammonia synthesis, $\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$, is exothermic ($\Delta H^\circ_{\text{rxn}} = -91.8$ kJ, Section 6.8). Raising the operating temperature therefore *lowers* the equilibrium constant and, at equilibrium, lowers the fraction of $\mathrm{NH_3}$ present — industrially, this is exactly why the Haber process uses only a moderate temperature (a compromise with the reaction-rate benefits of higher T), rather than the highest temperature possible.

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Thay đổi **nhiệt độ** là stress **duy nhất** thực sự làm thay đổi giá trị K (thay đổi nồng độ hay thể tích chỉ làm dịch chuyển vị trí cân bằng, KHÔNG đổi K). Coi nhiệt như một "chất" ở bên toả nhiệt (nếu phản ứng toả nhiệt, tăng T giống thêm sản phẩm $\Rightarrow$ dịch nghịch, K giảm) hoặc bên thu nhiệt (nếu phản ứng thu nhiệt, tăng T giống thêm chất phản ứng $\Rightarrow$ dịch thuận, K tăng). Đây là lý do công nghiệp tổng hợp $\mathrm{NH_3}$ (phản ứng toả nhiệt) không dùng nhiệt độ quá cao — vì K sẽ giảm mạnh dù tốc độ phản ứng nhanh hơn.

Stress applied	Direction of shift	Effect on K
Add reactant	Shifts forward (toward products)	No change
Add product	Shifts in reverse (toward reactants)	No change
Remove reactant	Shifts in reverse	No change
Remove product	Shifts forward	No change
Decrease volume (increase P)	Shifts toward fewer moles of gas	No change
Increase volume (decrease P)	Shifts toward more moles of gas	No change
Increase T, exothermic rxn	Shifts in reverse	**Decreases**
Increase T, endothermic rxn	Shifts forward	**Increases**
Decrease T, exothermic rxn	Shifts forward	**Increases**
Decrease T, endothermic rxn	Shifts in reverse	**Decreases**
Add inert (nonreacting) gas, constant V	No shift	No change
Add catalyst	No shift (reaches equilibrium faster)	No change

Summary of Le Chatelier's-principle responses to every standard type of stress. Only a temperature change alters K; every other listed stress shifts the position of equilibrium while leaving K exactly the same.

(!) Lỗi thường gặp: A very common conceptual error is describing a concentration or volume stress as "changing K." It does not: adding a reactant, removing a product, or compressing the container all shift the equilibrium *position* (the specific numeric concentrations present at the new equilibrium), but if K were recalculated from those new equilibrium concentrations, it would come out to exactly the same value as before the stress. Only a genuine change in temperature changes K itself.

7.11 Introduction to solubility equilibria

Even substances commonly labeled "insoluble" dissolve to a very small, measurable extent. When an ionic solid $\mathrm{M_pX_q(s)}$ is placed in water and some of it dissolves, the system reaches a heterogeneous equilibrium between the undissolved solid and its dissolved ions:

$$\mathrm{M_pX_q(s)} \rightleftharpoons p\,\mathrm{M^{q+}(aq)} + q\,\mathrm{X^{p-}(aq)}.$$

Because $\mathrm{M_pX_q(s)}$ is a pure solid, it is omitted from the equilibrium expression (Section 7.3), leaving the **solubility-product constant**, K_{sp}:

$$K_{sp} = [\mathrm{M^{q+}}]^p[\mathrm{X^{p-}}]^q.$$

Molar solubility

The **molar solubility**, s, of an ionic solid is the number of moles that dissolve per liter of solution to produce a saturated solution. Because dissolution follows the fixed stoichiometric ratio of the formula, $[\mathrm{M}^{q+}] = ps$ and $[\mathrm{X}^{p-}] = qs$ in a solution formed by dissolving the pure solid in water alone (no other source of either ion), giving

$$K_{sp} = (ps)^p (qs)^q = p^p q^q \, s^{p+q}.$$

For a $1{:}1$ salt (e.g., AgCl), $K_{sp} = s^2$. For a $1{:}2$ salt (e.g., CaF_2 or $Mg(OH)_2$), $K_{sp} = (s)(2s)^2 = 4s^3$.

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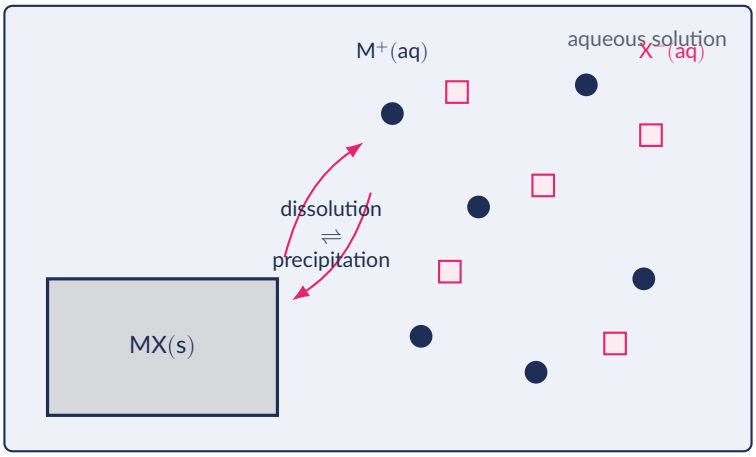
K_{sp} (tích số tan) là hằng số cân bằng cho quá trình hoà tan một muối tan ít, chỉ chứa các ion (bỏ qua chất rắn nguyên chất). **Độ tan mol** s là số mol muối tan trong 1 lít dung dịch bão hoà. Với muối tỉ lệ $1{:}1$ (như AgCl): $K_{sp} = s^2$. Với muối tỉ lệ $1{:}2$ (như CaF_2, $Mg(OH)_2$): $K_{sp} = 4s^3$. Lưu ý: **không thể so sánh trực tiếp** độ tan của hai muối chỉ dựa vào K_{sp} nếu chúng có tỉ lệ ion khác nhau.



Solubility equilibrium for a sparingly soluble salt MX(s): dissolution (solid → dissolved ions) and precipitation (dissolved ions → solid) occur continuously at equal rates once the solution is saturated, exactly analogous to any other dynamic equilibrium.

Salt	Stoichiometry	K_{sp}	Molar solubility s (M)
AgI	$1{:}1$	8.3×10^{-17}	9.11×10^{-9}
$BaSO_4$	$1{:}1$	1.1×10^{-10}	1.05×10^{-5}
AgCl	$1{:}1$	1.8×10^{-10}	1.34×10^{-5}
$CaCO_3$	$1{:}1$	3.3×10^{-9}	5.74×10^{-5}
$Mg(OH)_2$	$1{:}2$	5.6×10^{-12}	1.12×10^{-4}
CaF_2	$1{:}2$	3.9×10^{-11}	2.14×10^{-4}
$PbCl_2$	$1{:}2$	1.7×10^{-5}	1.62×10^{-2}

K_{sp} values (25°C) and the corresponding molar solubility for each salt, computed from the stoichiometry-specific formula. Notice that K_{sp} ranking does *not* match solubility ranking across different stoichiometries: $Mg(OH)_2$ has a smaller K_{sp} than AgCl, yet a *larger* molar solubility, because its $1{:}2$ stoichiometry involves a cube root rather than a square root.

Molar solubility from K_{sp}: a 1:1 salt

Find the molar solubility of AgCl in pure water at 25°C, given $K_{sp} = 1.8 \times 10^{-10}$.

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}, \qquad K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}] = s \cdot s = s^2.$$

$$s = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = \boxed{1.34 \times 10^{-5}\ \mathrm{M}}.$$

K_{sp} from molar solubility: a 1:2 salt

The molar solubility of CaF_2 in water at 25°C is measured to be $s = 2.14 \times 10^{-4}$ M. Calculate K_{sp} and compare with the reference value 3.9×10^{-11}.

$$\mathrm{CaF_2(s)} \rightleftharpoons \mathrm{Ca^{2+}(aq)} + 2\,\mathrm{F^-(aq)}, \qquad [\mathrm{Ca^{2+}}] = s, \quad [\mathrm{F^-}] = 2s.$$

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 = (s)(2s)^2 = 4s^3 = 4(2.14 \times 10^{-4})^3.$$

$$4(2.14 \times 10^{-4})^3 = 4(9.80 \times 10^{-12}) = \boxed{3.92 \times 10^{-11}}.$$

This matches the reference $K_{sp} = 3.9 \times 10^{-11}$ to within rounding, confirming the measured solubility is consistent with the accepted K_{sp}.

7.12 Common-ion effect

If a solution already contains one of the ions produced by a sparingly soluble salt (supplied by a separate, fully soluble source), Le Chatelier's principle predicts that the solubility equilibrium shifts **toward the solid**, and the molar solubility of the salt **decreases** relative to its solubility in pure water. This is the **common-ion effect**.

Solving common-ion-effect solubility problems

Let C be the fixed concentration of the common ion supplied by the other (fully dissociating) source. In the ICE table for the sparingly soluble salt's dissolution, that ion's initial concentration is C (not 0), so its equilibrium concentration is $C +$ (stoichiometric multiple of s) rather than simply a multiple of s. Because the common-ion effect typically suppresses s to a value orders of magnitude below C, it is normally an excellent approximation to treat the common ion's equilibrium concentration as simply C itself (the small contribution from the sparingly soluble salt is negligible next to the large concentration already supplied).

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Hiệu ứng ion chung (common-ion effect): nếu dung dịch đã có sẵn một ion trùng với ion của muối tan ít, cân bằng hoà tan sẽ dịch chuyển **về phía rắn** (theo Le Chatelier), làm **giảm** độ tan mol so với hoà tan trong nước tinh khiết. Vì độ giảm thường rất lớn (vài bậc độ lớn), nồng độ ion chung tại cân bằng gần như bằng đúng nồng độ ion chung ban đầu C — phần đóng góp nhỏ từ muối tan ít có thể bỏ qua.

Common-ion-effect solubility calculation

Find the molar solubility of CaF_2 ($K_{sp} = 3.9 \times 10^{-11}$) in a solution that is already 0.10 M in NaF (a fully soluble source of F^-), and compare with its solubility in pure water.

	$CaF_2(s)$	Ca^{2+}	F^-
Initial (M)	—	0	0.10
Change (M)	—	$+s$	$+2s$
Equilibrium (M)	—	s	$0.10 + 2s \approx 0.10$

$$K_{sp} = [Ca^{2+}][F^-]^2 \approx s(0.10)^2 = 3.9 \times 10^{-11}.$$

$$s = \frac{3.9 \times 10^{-11}}{(0.10)^2} = \frac{3.9 \times 10^{-11}}{0.010} = \boxed{3.9 \times 10^{-9}\ \text{M}}.$$

Check of the approximation: $2s = 7.8 \times 10^{-9}$ M, utterly negligible next to 0.10 M, so treating $[F^-] \approx 0.10$ M is fully justified. Comparing with the pure-water solubility computed earlier, $s_{\text{water}} = 2.14 \times 10^{-4}$ M, the common-ion solubility is smaller by a factor of about $2.14 \times 10^{-4} / 3.9 \times 10^{-9} \approx 5.5 \times 10^4$ — a dramatic suppression, exactly as Le Chatelier's principle predicts.

Predicting precipitation: comparing Q_{sp} with K_{sp}

A solution is prepared by mixing 25.0 mL of 0.0040 M $AgNO_3$ with 75.0 mL of 0.0020 M NaCl. Will a precipitate of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) form?

Mixing dilutes both solutions into a common total volume of $25.0 + 75.0 = 100.0$ mL:

$$[Ag^+]_0 = (0.0040\ \text{M}) \times \frac{25.0}{100.0} = 1.0 \times 10^{-3}\ \text{M}, \qquad [Cl^-]_0 = (0.0020\ \text{M}) \times \frac{75.0}{100.0} = 1.5 \times 10^{-3}\ \text{M}.$$

Compute the reaction quotient for the dissolution equilibrium, Q_{sp}, using these just-mixed (not-yet-equilibrium) concentrations:

$$Q_{sp} = [Ag^+]_0[Cl^-]_0 = (1.0 \times 10^{-3})(1.5 \times 10^{-3}) = 1.5 \times 10^{-6}.$$

Since $Q_{sp}(1.5 \times 10^{-6}) > K_{sp}(1.8 \times 10^{-10})$, the solution is supersaturated with respect to AgCl, and a **precipitate forms** — solid AgCl deposits until the remaining dissolved ion concentrations satisfy $[Ag^+][Cl^-] = K_{sp}$ once more.

(!) Lỗi thường gặp: When comparing K_{sp} values across different salts to judge which is "more soluble," it is only valid to compare K_{sp} directly when the salts share the *same* ion stoichiometry (e.g., two $1{:}1$ salts). For salts with different stoichiometries, the actual molar solubility must be calculated separately for each (using s^2, $4s^3$, or the appropriate general formula) before any comparison is meaningful — a smaller K_{sp} does not automatically mean a smaller molar solubility, as the $Mg(OH)_2$-versus-AgCl comparison in Section 7.11 demonstrates.

7.13 pH and solubility

Some sparingly soluble salts contain an anion that is itself a **base** — one capable of reacting with H^+. Common examples include **hydroxides** (OH^-), **carbonates** (CO_3^{2-}), and **sulfides** (S^{2-}). For these salts, the pH of the surrounding solution has a direct, predictable effect on molar solubility.

Why acidic solution increases solubility of a basic-anion salt

Consider the dissolution equilibrium $M(OH)_2(s) \rightleftharpoons M^{2+}(aq) + 2\,OH^-(aq)$. In an acidic solution, added H^+ reacts with the basic anion, $OH^-(aq) + H^+(aq) \rightleftharpoons H_2O(l)$, continuously removing OH^- from the dissolution equilibrium. By Le Chatelier's principle, removing a product (OH^-) shifts the dissolution equilibrium **forward**, dissolving *more* solid than would dissolve in neutral water. The lower the pH (the more acidic the solution, and the lower $[OH^-]$), the greater the molar solubility. The same reasoning applies to carbonates (whose CO_3^{2-} reacts with H^+ to form HCO_3^- and eventually H_2CO_3) and sulfides (whose S^{2-} reacts with H^+ to form HS^- and H_2S).
By contrast, a salt whose anion is the conjugate base of a *strong* acid (for example, Cl^- in AgCl, or SO_4^{2-}-type salts) shows essentially **no** pH dependence, because that anion has no meaningful tendency to react with H^+.

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Muối chứa anion có tính **base** (như hydroxide OH^-, carbonate CO_3^{2-}, sulfide S^{2-}) sẽ tan **nhiều hơn** trong môi trường **acid**: H^+ phản ứng với anion, làm giảm nồng độ anion đó, theo Le Chatelier cân bằng hoà tan dịch chuyển về phía tạo thêm ion (hoà tan thêm chất rắn). pH càng thấp (càng acid), độ tan càng cao. Ngược lại, muối có anion là base liên hợp của acid **mạnh** (như Cl^- trong AgCl) hầu như **không** bị ảnh hưởng bởi pH.

Numeric effect of pH on the solubility of a metal hydroxide

$Mg(OH)_2$ has $K_{sp} = 5.6 \times 10^{-12}$. Find its molar solubility in a solution buffered at (a) pH $= 9.00$ and (b) pH $= 11.00$, and compare both with its solubility in pure water, $s_{\text{water}} = 1.12 \times 10^{-4}$ M.

When the pH is held fixed by a buffer, $[OH^-]$ is externally fixed rather than being tied to the amount of $Mg(OH)_2$ that dissolves, so $K_{sp} = [Mg^{2+}][OH^-]^2$ can be solved directly for $[Mg^{2+}] = s$:

$$s = \frac{K_{sp}}{[OH^-]^2}.$$

(a) pH $= 9.00$**:** pOH $= 14.00 - 9.00 = 5.00$, so $[OH^-] = 10^{-5.00} = 1.0 \times 10^{-5}$ M.

$$s = \frac{5.6 \times 10^{-12}}{(1.0 \times 10^{-5})^2} = \frac{5.6 \times 10^{-12}}{1.0 \times 10^{-10}} = \boxed{5.6 \times 10^{-2}\ \text{M}}.$$

(b) pH $= 11.00$**:** pOH $= 14.00 - 11.00 = 3.00$, so $[OH^-] = 10^{-3.00} = 1.0 \times 10^{-3}$ M.

$$s = \frac{5.6 \times 10^{-12}}{(1.0 \times 10^{-3})^2} = \frac{5.6 \times 10^{-12}}{1.0 \times 10^{-6}} = \boxed{5.6 \times 10^{-6}\ \text{M}}.$$

At the lower, more acidic pH (9.00), the solubility (5.6×10^{-2} M) is far *greater* than in pure water (1.12×10^{-4} M); at the higher, more basic pH (11.00), the solubility (5.6×10^{-6} M) is far *smaller* than in pure water — a direct numeric confirmation that lowering the pH increases the solubility of a metal hydroxide, and raising the pH (adding a common ion, OH^-) suppresses it.

7.14 Free energy of dissolution

Whether a given amount of a solid dissolves spontaneously under a particular set of conditions is ultimately governed by the **Gibbs free energy of dissolution**, ΔG_{soln}, exactly as any other process's spontaneity is governed by ΔG (developed fully in a later unit). The qualitative connection to K_{sp}, however, can already be stated precisely here.

ΔG° and K_{sp}

The standard free energy change for the dissolution reaction is related to K_{sp} by

$$\Delta G^\circ = -RT \ln K_{sp}.$$

- If $K_{sp} < 1$ (true of essentially every "sparingly soluble" salt), $\ln K_{sp} < 0$, so $\Delta G^\circ > 0$: dissolution to reach standard-state (1 M) ion concentrations is **not** spontaneous. This is entirely consistent with such salts being labeled "insoluble" — only a small amount can dissolve before the process becomes non-favorable.
- A very negative ΔG° would correspond to a very large K_{sp} ($K_{sp} \gg 1$), describing a salt so soluble that essentially all of it dissolves — the everyday case of a "soluble" salt like NaCl.

Qualitatively, dissolution of an ionic solid is driven by two competing thermodynamic effects: breaking the ionic lattice costs energy (unfavorable, tends to make ΔH_{soln} less negative or positive), while dispersing the rigid solid into freely moving, independently hydrated ions in solution is strongly favored entropically (dissolution generally increases the disorder of the ion arrangement, favoring $\Delta S_{\text{soln}} > 0$). Whether dissolution is spontaneous at a given temperature depends on the balance of these two contributions, $\Delta G_{\text{soln}} = \Delta H_{\text{soln}} - T\Delta S_{\text{soln}}$, a relationship developed in full quantitative detail in the thermodynamics unit.

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ΔG° của quá trình hoà tan liên hệ với K_{sp} qua $\Delta G^\circ = -RT \ln K_{sp}$. Vì hầu hết muối "tan ít" có $K_{sp} < 1$, nên $\Delta G^\circ > 0$ — quá trình hoà tan để đạt nồng độ chuẩn (1 M) là **không tự diễn ra**, phù hợp với việc muối đó được coi là "ít tan". Về mặt định tính, phá vỡ mạng tinh thể ion cần năng lượng (bất lợi cho ΔH), nhưng việc phân tán ion thành các ion tự do, hydrat hoá trong dung dịch làm tăng độ hỗn loạn (có lợi cho $\Delta S > 0$) — quá trình hoà tan có tự diễn ra hay không phụ thuộc vào sự cân bằng giữa hai hiệu ứng này, $\Delta G = \Delta H - T\Delta S$ (nội dung định lượng đầy đủ thuộc chương nhiệt động học).

Computing ΔG° of dissolution from K_{sp}

Find ΔG° for the dissolution of AgCl at 25°C (298 K), given $K_{sp} = 1.8 \times 10^{-10}$.

$$\Delta G^\circ = -RT \ln K_{sp} = -(8.314 \text{ J/(mol} \cdot \text{K)})(298 \text{ K}) \ln(1.8 \times 10^{-10}).$$

$$\ln(1.8 \times 10^{-10}) = -22.44.$$

$$\Delta G^\circ = -(8.314)(298)(-22.44) = \boxed{+55{,}600 \text{ J/mol}} = +55.6 \text{ kJ/mol}.$$

The large positive ΔG° confirms that dissolving AgCl to standard-state (1 M) ion concentrations is strongly non-spontaneous, consistent with AgCl's very small K_{sp} and its classification as an insoluble salt.

7.15 Practice Problems

Bài tập luyện tập

Which statement most accurately describes a chemical system at equilibrium?

(A) The forward and reverse reactions have both stopped completely.

(B) The forward and reverse reactions continue to occur, but at equal rates, so concentrations no longer change.

(C) Only the forward reaction occurs, but so slowly that no change is detectable.

(D) The concentrations of reactants and products are always exactly equal.

Lời giải chi tiết

The correct answer is **(B)**. Equilibrium is dynamic: both reactions continue indefinitely, but because their rates are equal, the net (observable) concentrations stop changing. (A) and (C) both incorrectly describe equilibrium as reactions having stopped. (D) confuses "equal rates" with "equal concentrations," which are unrelated — the equilibrium concentrations can be very unequal (Section 7.5) even though the rates are, by definition, equal.

Bài tập luyện tập

A student claims that once a reaction reaches equilibrium, no individual reactant molecule can ever convert into a product molecule again. Explain, in one or two sentences, why this claim is incorrect.

Lời giải chi tiết

The claim is incorrect because equilibrium is a *dynamic* state, not a static one. Individual reactant molecules continue converting into product molecules (the forward reaction), and individual product molecules continue converting back into reactant molecules (the reverse reaction), at all times after equilibrium is reached. What stops changing is only the *net*, macroscopically observable concentration of each species, because the forward and reverse conversions are happening at exactly matched rates and therefore cancel out in their effect on the bulk concentrations.

Bài tập luyện tập

A rigid, sealed container is charged with 2.0 mol of $SO_2(g)$ and 1.0 mol of $O_2(g)$, with no $SO_3(g)$ present, for the reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$. In which direction must the net reaction initially proceed to reach equilibrium, and why?

Lời giải chi tiết

The net reaction must proceed in the **forward** direction. Since SO_3 (the only product) is initially completely absent, $Q = [SO_3]^2/([SO_2]^2[O_2]) = 0$. Because $Q = 0$ is necessarily less than K for any positive equilibrium constant, the reaction can only shift forward (producing SO_3) until equilibrium is established; a reverse shift is physically impossible when the product's concentration cannot go below zero.

Bài tập luyện tập

For $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$, $K_c = 5.10$ at a certain temperature. A flask is charged with $[CO] = 0.0500$ M, $[H_2O] = 0.0500$ M, $[CO_2] = 0.0500$ M, and $[H_2] = 0.100$ M (not yet at equilibrium). Determine the direction the reaction must proceed to reach equilibrium.

Lời giải chi tiết

Compute the reaction quotient using the given (non-equilibrium) concentrations:

$$Q = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0500)(0.100)}{(0.0500)(0.0500)} = \frac{0.00500}{0.00250} = 2.00.$$

Since $Q(2.00) < K(5.10)$, the reaction must proceed **forward** (net production of CO_2 and H_2) to increase Q up to K and reach equilibrium.

Bài tập luyện tập

Which of the following correctly gives the K_c expression for $4\,Fe(s) + 3\,O_2(g) \rightleftharpoons 2\,Fe_2O_3(s)$?

(A) $K_c = \dfrac{[Fe_2O_3]^2}{[Fe]^4[O_2]^3}$

(B) $K_c = [O_2]^3$

(C) $K_c = \dfrac{1}{[O_2]^3}$

(D) $K_c = [Fe]^4[O_2]^3$

Lời giải chi tiết

The correct answer is **(C)**. Both $Fe(s)$ and $Fe_2O_3(s)$ are pure solids and are omitted entirely; only the gas, O_2, remains, and it sits in the *denominator* of the general products-over-reactants form (it is a reactant). Written out fully before cancellation, $K_c = \dfrac{[Fe_2O_3]^2}{[Fe]^4[O_2]^3}$ becomes, after removing the solids, $K_c = \dfrac{1}{[O_2]^3}$.

Bài tập luyện tập

Write the K_c expression for $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$.

Lời giải chi tiết

Water appears here as the pure liquid solvent, so it is omitted; the three aqueous species remain:

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}.$$

Bài tập luyện tập

For $2\,NO_2(g) \rightleftharpoons N_2O_4(g)$, $K_c = 170$ at $25^\circ C$ (298 K). Find K_p.

Lời giải chi tiết

Moles of gas: 2 reactant → 1 product, so $\Delta n_{gas} = 1 - 2 = -1$.

$$K_p = K_c(RT)^{\Delta n} = (170)\big[(0.08206)(298)\big]^{-1} = \frac{170}{24.45} = \boxed{6.95}.$$

Bài tập luyện tập

At equilibrium, a mixture of $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ has $[SO_3] = 0.150$ M, $[SO_2] = 0.0500$ M, and $[O_2] = 0.0250$ M. Calculate K_c.

Lời giải chi tiết

$$K_c = \frac{[\mathrm{SO_2}]^2[\mathrm{O_2}]}{[\mathrm{SO_3}]^2} = \frac{(0.0500)^2(0.0250)}{(0.150)^2} = \frac{(0.00250)(0.0250)}{0.0225} = \frac{6.25 \times 10^{-5}}{0.0225} = \boxed{2.78 \times 10^{-3}}.$$

Bài tập luyện tập

Which of the following units, if any, is correct for a value of K_c reported for a gas-phase reaction?

(A) K is always reported in mol/L.

(B) K is always reported in atm.

(C) K is a unitless number, since it is technically defined using activities relative to a standard state.

(D) The units of K depend on temperature.

Lời giải chi tiết

The correct answer is **(C)**. Although K expressions are written using molar concentrations (or partial pressures), the rigorous thermodynamic definition of K uses dimensionless *activities* (each concentration or pressure divided by its standard-state value of 1 M or 1 atm), so K itself is unitless. In introductory work, K is often reported as a bare number for exactly this reason, even though the intermediate calculation clearly involves concentrations with units.

Bài tập luyện tập

For $\mathrm{H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)}$, an equilibrium mixture has $P_{\mathrm{H_2}} = 0.20$ atm, $P_{\mathrm{CO_2}} = 0.30$ atm, $P_{\mathrm{H_2O}} = 0.55$ atm, and $P_{\mathrm{CO}} = 0.55$ atm. Calculate K_p.

Lời giải chi tiết

$$K_p = \frac{P_{\mathrm{H_2O}} P_{\mathrm{CO}}}{P_{\mathrm{H_2}} P_{\mathrm{CO_2}}} = \frac{(0.55)(0.55)}{(0.20)(0.30)} = \frac{0.3025}{0.060} = \boxed{5.04}.$$

Bài tập luyện tập

A reaction has $K = 4.2 \times 10^{-9}$ at a given temperature. Which best describes the equilibrium mixture?

(A) Almost entirely products

(B) Almost entirely reactants

(C) Roughly equal amounts of reactants and products

(D) Cannot be determined without knowing the initial concentrations

Lời giải chi tiết

The correct answer is **(B)**. A K value this far below 1 ($K \ll 1$) means the denominator (reactants) of the equilibrium expression must dominate over the numerator (products) for the ratio to come out so small — the equilibrium mixture consists almost entirely of unreacted starting material, with only a trace of product formed.

Bài tập luyện tập

Two reactions at the same temperature have $K_1 = 8.5 \times 10^6$ and $K_2 = 3.1$. Without doing any further calculation, state which reaction produces the higher percentage conversion of reactants to products at equilibrium, and justify your answer in one sentence.

Lời giải chi tiết

Reaction 1 (with $K_1 = 8.5 \times 10^6$) produces the higher percentage conversion. Both constants exceed 1 (both are somewhat product-favored), but K_1 is vastly larger, indicating an equilibrium mixture that is overwhelmingly product, whereas $K_2 \approx 3$ (close to 1) indicates comparable, not overwhelming, amounts of both reactants and products at equilibrium.

Bài tập luyện tập

Given $\mathrm{SO_2(g)} + \mathrm{NO_2(g)} \rightleftharpoons \mathrm{SO_3(g)} + \mathrm{NO(g)}$, $K_1 = 3.75$, find K for $\mathrm{SO_3(g)} + \mathrm{NO(g)} \rightleftharpoons \mathrm{SO_2(g)} + \mathrm{NO_2(g)}$.

Lời giải chi tiết

This target reaction is the exact reverse of the given reaction, so

$$K = \frac{1}{K_1} = \frac{1}{3.75} = \boxed{0.267}.$$

Bài tập luyện tập

Given $2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO_2(g)}$, $K_2 = 140$, find K for $4\,\mathrm{NO(g)} + 2\,\mathrm{O_2(g)} \rightleftharpoons 4\,\mathrm{NO_2(g)}$.

Lời giải chi tiết

The target reaction is the given reaction with every coefficient doubled, so

$$K = K_2^2 = (140)^2 = \boxed{19{,}600}.$$

Bài tập luyện tập

Using $\mathrm{SO_2(g)} + \mathrm{NO_2(g)} \rightleftharpoons \mathrm{SO_3(g)} + \mathrm{NO(g)}$, $K_1 = 3.75$, and $2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO_2(g)}$, $K_2 = 140$, find K for the target reaction $2\,\mathrm{SO_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{SO_3(g)}$.

Lời giải chi tiết

Double the first reaction (to supply $2\,\mathrm{SO_2}$ and $2\,\mathrm{SO_3}$), giving $K = K_1^2 = (3.75)^2 = 14.0625$:

$$2\,\mathrm{SO_2(g)} + 2\,\mathrm{NO_2(g)} \rightleftharpoons 2\,\mathrm{SO_3(g)} + 2\,\mathrm{NO(g)}.$$

Add the second reaction as written ($K_2 = 140$):

$$2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO_2(g)}.$$

Summing both equations, $2\,\mathrm{NO_2}$ and $2\,\mathrm{NO}$ each appear on both sides and cancel, leaving exactly the target: $2\,\mathrm{SO_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{SO_3(g)}$.

$$K = K_1^2 \times K_2 = (14.0625)(140) = \boxed{1968.75}.$$

Bài tập luyện tập

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$, $K_c = 8.30 \times 10^{-4}$ at a fixed temperature. A flask is charged with $[COCl_2]_0 = 0.0250$ M and no products. First check whether the 5% approximation is valid; then find the correct equilibrium concentrations of all three species.

Lời giải chi tiết

Attempted approximation: $x \approx \sqrt{K_c \cdot [COCl_2]_0} = \sqrt{(8.30 \times 10^{-4})(0.0250)} = \sqrt{2.075 \times 10^{-5}} = 4.56 \times 10^{-3}$.

$$\frac{x}{[COCl_2]_0} \times 100\% = \frac{4.56 \times 10^{-3}}{0.0250} \times 100\% = 18.2\% > 5\%,$$

so the approximation is **not valid**, and the exact quadratic must be solved.

$$K_c = \frac{x^2}{0.0250 - x} = 8.30 \times 10^{-4} \;\Rightarrow\; x^2 + (8.30 \times 10^{-4})x - (2.075 \times 10^{-5}) = 0.$$

With $A = 1$, $B = 8.30 \times 10^{-4}$, $C = -2.075 \times 10^{-5}$:

$$x = \frac{-8.30 \times 10^{-4} + \sqrt{(8.30 \times 10^{-4})^2 - 4(1)(-2.075 \times 10^{-5})}}{2} = \frac{-8.30 \times 10^{-4} + \sqrt{8.369 \times 10^{-5}}}{2}.$$

$$x = \frac{-8.30 \times 10^{-4} + 9.148 \times 10^{-3}}{2} = \frac{8.318 \times 10^{-3}}{2} = \boxed{4.16 \times 10^{-3}\ \text{M}}.$$

(The negative root is rejected as physically impossible.) So $[CO] = [Cl_2] = 4.16 \times 10^{-3}$ M, and $[COCl_2] = 0.0250 - 0.00416 = \boxed{0.0208\ \text{M}}$. Note that the exact answer ($x = 4.16 \times 10^{-3}$) differs meaningfully from the invalid approximate answer ($x = 4.56 \times 10^{-3}$), a roughly 10% discrepancy — exactly why the validity check must never be skipped.

Bài tập luyện tập

$A(g) \rightleftharpoons B(g) + C(g)$, $K_c = 4.5 \times 10^{-6}$, with $[A]_0 = 0.800$ M and no products initially. Use the 5% approximation (after verifying it is valid) to find the equilibrium concentrations.

Lời giải chi tiết

$$x \approx \sqrt{K_c[A]_0} = \sqrt{(4.5 \times 10^{-6})(0.800)} = \sqrt{3.6 \times 10^{-6}} = 1.90 \times 10^{-3}.$$

Validity check: $\dfrac{1.90 \times 10^{-3}}{0.800} \times 100\% = 0.237\% \le 5\%$ ✓ — valid.

$$[A] \approx 0.800 - 0.0019 = \boxed{0.798\ \text{M}}, \qquad [B] = [C] = \boxed{1.90 \times 10^{-3}\ \text{M}}.$$

Bài tập luyện tập

Set up the ICE table entries (in terms of x) for the equilibrium row only, for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, given initial concentrations $[PCl_5]_0 = 0.400$ M, $[PCl_3]_0 = 0$, $[Cl_2]_0 = 0$.

Lời giải chi tiết

	PCl_5	PCl_3	Cl_2
Initial (M)	0.400	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.400 - x$	x	x

The equilibrium-row entries are $[PCl_5] = 0.400 - x$, $[PCl_3] = x$, $[Cl_2] = x$, which would then be substituted into $K_c = x^2/(0.400 - x)$ to solve for x once a numeric value of K_c is given.

Bài tập luyện tập

For $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$, $K_c = 0.0330$, a flask initially contains *only* NO_2 at $[NO_2]_0 = 0.0500$ M (no N_2O_4). Find the equilibrium concentrations of both species.

Lời giải chi tiết

Since only the product (as the equation is written) is present initially, the net reaction must run in **reverse**, forming N_2O_4.

	N_2O_4	NO_2
Initial (M)	0	0.0500
Change (M)	$+x$	$-2x$
Equilibrium (M)	x	$0.0500 - 2x$

$$K_c = \frac{(0.0500 - 2x)^2}{x} = 0.0330.$$

Expanding: $0.0025 - 0.200x + 4x^2 = 0.0330x$, so $4x^2 - 0.233x + 0.0025 = 0$. Applying the quadratic formula with $A = 4$, $B = -0.233$, $C = 0.0025$:

$$x = \frac{0.233 \pm \sqrt{(0.233)^2 - 4(4)(0.0025)}}{2(4)} = \frac{0.233 \pm \sqrt{0.05429 - 0.0400}}{8} = \frac{0.233 \pm 0.1195}{8}.$$

This gives $x = 0.0441$ or $x = 0.0142$. The root $x = 0.0441$ is rejected because it would make $[NO_2] = 0.0500 - 2(0.0441) < 0$. Using $x = 0.0142$:

$$[N_2O_4] = \boxed{0.0142\ \text{M}}, \qquad [NO_2] = 0.0500 - 2(0.0142) = \boxed{0.0216\ \text{M}}.$$

Check: $(0.0216)^2/0.0142 = 4.67 \times 10^{-4}/0.0142 \approx 0.0329$, matching $K_c = 0.0330$ within rounding.

Bài tập luyện tập

A sealed box (equal volume, both panels) representing $2\,A(g) \rightleftharpoons B(g)$ shows, at equilibrium, 4 particles of A and 3 particles of B. Treating particle count as directly proportional to concentration in a 1.0-L box, calculate K.

Lời giải chi tiết

Treat each particle as representing 1 M (since the box volume is 1.0 L): $[\mathrm{A}] = 4$ M, $[\mathrm{B}] = 3$ M.

$$K = \frac{[\mathrm{B}]}{[\mathrm{A}]^2} = \frac{3}{4^2} = \frac{3}{16} = \boxed{0.1875}.$$

Bài tập luyện tập

Two particulate diagrams (equal box volumes) are shown for $\mathrm{X(g)} \rightleftharpoons \mathrm{Y(g)} + \mathrm{Z(g)}$: diagram (i) has 6 particles of X and 2 each of Y and Z; diagram (ii) has 1 particle of X and 5 each of Y and Z. Both diagrams claim to represent the *same* equilibrium at the same temperature. Is this possible? Justify using calculated K values.

Lời giải chi tiết

No, this is **not** possible for a single, fixed K at one temperature. Computing K from each diagram (treating particle count as proportional to concentration):

$$K_{(i)} = \frac{[\mathrm{Y}][\mathrm{Z}]}{[\mathrm{X}]} = \frac{(2)(2)}{6} = 0.667, \qquad K_{(ii)} = \frac{(5)(5)}{1} = 25.$$

These two implied K values are wildly different (0.667 versus 25), so the two diagrams cannot both represent equilibrium states of the same reaction at the same fixed temperature — only one (at most) could be a valid equilibrium diagram for a system with a single, well-defined K.

Bài tập luyện tập

For $2\,\mathrm{H_2S(g)} \rightleftharpoons 2\,\mathrm{H_2(g)} + \mathrm{S_2(g)}$ at equilibrium, predict the direction of shift if additional $\mathrm{H_2(g)}$ is injected into the container at constant volume and temperature.

Lời giải chi tiết

Adding $\mathrm{H_2}$ (a product) increases $[\mathrm{H_2}]$, making Q momentarily larger than K (since $\mathrm{H_2}$ sits in the numerator of $Q = [\mathrm{H_2}]^2[\mathrm{S_2}]/[\mathrm{H_2S}]^2$). Because $Q > K$, the system shifts in **reverse**, consuming some of the added $\mathrm{H_2}$ (along with $\mathrm{S_2}$) to regenerate $\mathrm{H_2S}$, partially counteracting the stress — consistent with Le Chatelier's principle.

Bài tập luyện tập

For $\mathrm{PCl_5(g)} \rightleftharpoons \mathrm{PCl_3(g)} + \mathrm{Cl_2(g)}$ at equilibrium, the container volume is suddenly increased at constant temperature. Which describes what happens immediately after the expansion, before the system re-equilibrates?

(A) Shifts forward; $Q < K$ immediately after the expansion

(B) Shifts in reverse; $Q > K$ immediately after the expansion

(C) No shift; $Q = K$ immediately after the expansion

(D) Shifts forward; $Q > K$ immediately after the expansion

Lời giải chi tiết

The correct answer is **(A)**. If the volume increases by a factor $f > 1$, every concentration is divided by f. Since $Q = [\mathrm{PCl_3}][\mathrm{Cl_2}]/[\mathrm{PCl_5}]$ has two concentration terms in the numerator and only one in the denominator,

$$Q_{\text{new}} = \frac{([\mathrm{PCl_3}]/f)([\mathrm{Cl_2}]/f)}{[\mathrm{PCl_5}]/f} = \frac{1}{f} \cdot \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = \frac{Q_{\text{old}}}{f} = \frac{K}{f}.$$

Since $f > 1$, $Q_{\text{new}} = K/f < K$, so the system must shift **forward** to climb back to $Q = K$ — consistent with the mole-counting rule (expanding favors the side with more moles of gas, here the product side with 2 mol versus 1 mol of reactant gas).

Bài tập luyện tập

$\mathrm{A(g)} \rightleftharpoons 2\,\mathrm{B(g)}$, $K = 0.360$. An equilibrium mixture has $[\mathrm{A}] = 0.250$ M and $[\mathrm{B}] = 0.300$ M (verify this satisfies K). Half of the B present is suddenly removed from the container at constant volume and temperature. Calculate Q immediately afterward and predict the direction of the resulting shift.

Lời giải chi tiết

Verify: $K = (0.300)^2/(0.250) = 0.090/0.250 = 0.360$ ✓.
Removing half of B leaves $[\mathrm{B}] = 0.150$ M, with $[\mathrm{A}] = 0.250$ M unchanged at that instant:

$$Q = \frac{[\mathrm{B}]^2}{[\mathrm{A}]} = \frac{(0.150)^2}{0.250} = \frac{0.0225}{0.250} = \boxed{0.0900}.$$

Since $Q(0.0900) < K(0.360)$, the system shifts **forward** (converting more A into B), partially replacing the B that was removed — exactly the qualitative prediction Le Chatelier's principle gives for removing a product.

Bài tập luyện tập

For an endothermic reaction, increasing the temperature at constant volume will _____ the value of K.

(A) Increase
(B) Decrease
(C) Leave unchanged
(D) Effect depends on the total pressure

Lời giải chi tiết

The correct answer is **(A)**. For an endothermic reaction, heat can be treated as a reactant. Raising the temperature is equivalent to adding more of that "reactant," shifting the equilibrium forward and increasing the equilibrium concentration of products relative to reactants — which corresponds to a genuine increase in the numeric value of K itself, not merely a shift in position.

Bài tập luyện tập

The reaction $2\,\mathrm{SO_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{SO_3(g)}$ is exothermic. Starting from an equilibrium mixture, predict both the direction of shift and the effect on K (increase, decrease, or no change) for each of the following stresses, applied one at a time: (a) adding $\mathrm{O_2(g)}$; (b) decreasing the

container volume; (c) increasing the temperature.

Lời giải chi tiết

(a) Adding O_2: a reactant is added, so the equilibrium shifts **forward** (toward SO_3). Concentration stresses never change K, so K is **unchanged**.

(b) Decreasing volume: the reactant side has $2 + 1 = 3$ mol of gas, the product side has 2 mol of gas, so compression shifts the equilibrium toward the side with fewer gas moles: **forward** (toward SO_3). Volume/pressure stresses never change K, so K is **unchanged**.

(c) Increasing temperature: because the reaction is exothermic, heat behaves like a product; adding heat shifts the equilibrium **in reverse** (toward SO_2 and O_2). Unlike the other two stresses, a temperature change genuinely alters the equilibrium constant: K **decreases**.

Bài tập luyện tập

AgI has $K_{sp} = 8.3 \times 10^{-17}$. Calculate its molar solubility in pure water at 25°C.

Lời giải chi tiết

$$\mathrm{AgI(s)} \rightleftharpoons \mathrm{Ag^+(aq) + I^-(aq)}, \qquad K_{sp} = s^2.$$

$$s = \sqrt{K_{sp}} = \sqrt{8.3 \times 10^{-17}} = \boxed{9.11 \times 10^{-9}\ \mathrm{M}}.$$

AgI is even less soluble than AgCl ($s = 1.34 \times 10^{-5}$ M), consistent with its far smaller K_{sp} (both salts share the same $1{:}1$ stoichiometry, so a direct K_{sp} comparison is valid here).

Bài tập luyện tập

$PbCl_2$ has $K_{sp} = 1.7 \times 10^{-5}$. Calculate its molar solubility in pure water at 25°C.

Lời giải chi tiết

$$\mathrm{PbCl_2(s)} \rightleftharpoons \mathrm{Pb^{2+}(aq) + 2\,Cl^-(aq)}, \qquad K_{sp} = (s)(2s)^2 = 4s^3.$$

$$s = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{1.7 \times 10^{-5}}{4}\right)^{1/3} = (4.25 \times 10^{-6})^{1/3} = \boxed{1.62 \times 10^{-2}\ \mathrm{M}}.$$

Check: $4s^3 = 4(1.62 \times 10^{-2})^3 = 4(4.25 \times 10^{-6}) = 1.70 \times 10^{-5}$, matching K_{sp} ✓.

Bài tập luyện tập

AgCl has $K_{sp} = 1.8 \times 10^{-10}$ and $Mg(OH)_2$ has $K_{sp} = 5.6 \times 10^{-12}$. Even though $Mg(OH)_2$ has the smaller K_{sp}, which salt has the *greater* molar solubility in pure water?

(A) AgCl, because smaller K_{sp} always means smaller solubility

(B) $Mg(OH)_2$, because its $1{:}2$ stoichiometry gives a cube-root relationship that outweighs its smaller K_{sp}

(C) They are exactly equal, since both are "sparingly soluble" salts

(D) Cannot be determined without additional data

Lời giải chi tiết

The correct answer is **(B)**. For AgCl (1:1), $s = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5}$ M. For $Mg(OH)_2$ (1:2), $s = (K_{sp}/4)^{1/3} = (5.6 \times 10^{-12}/4)^{1/3} = 1.12 \times 10^{-4}$ M. Despite its smaller K_{sp}, $Mg(OH)_2$ is roughly 8 times *more* soluble than AgCl, because the cube-root relationship for a $1{:}2$ salt grows much less steeply as K_{sp} shrinks than the square-root relationship for a $1{:}1$ salt. K_{sp} values can only be compared directly across salts that share the same ion stoichiometry.

Bài tập luyện tập

Calculate the molar solubility of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) in a solution that is 0.050 M in NaCl, and compare with its solubility in pure water (1.34×10^{-5} M).

Lời giải chi tiết

With $[Cl^-] \approx 0.050$ M held nearly constant by the large common-ion source:

$$K_{sp} = [Ag^+][Cl^-] \approx s(0.050) = 1.8 \times 10^{-10}.$$

$$s = \frac{1.8 \times 10^{-10}}{0.050} = \boxed{3.6 \times 10^{-9}\ \text{M}}.$$

This is smaller than the pure-water solubility by a factor of $1.34\times10^{-5}/3.6\times10^{-9} \approx 3730$ — the common-ion effect suppresses solubility dramatically, exactly as predicted by Le Chatelier's principle.

Bài tập luyện tập

Which of the following actions would decrease the molar solubility of solid $BaSO_4$ already in equilibrium with its saturated solution?

(A) Adding solid Na_2SO_4, which dissolves completely

(B) Adding solid KNO_3, which dissolves completely

(C) Adding more solid $BaSO_4$ to the same saturated solution

(D) Stirring the solution more vigorously

Lời giải chi tiết

The correct answer is **(A)**. Dissolved Na_2SO_4 supplies additional SO_4^{2-}, a common ion with $BaSO_4$'s dissolution equilibrium; by Le Chatelier's principle this shifts the equilibrium toward the solid, decreasing molar solubility. (B) supplies no common ion (neither K^+ nor NO_3^- participates in the $BaSO_4$ equilibrium) and has no effect. (C) does not change the solubility at all, since the solution is already saturated — the extra solid simply sits undissolved. (D) affects only how quickly equilibrium is reached, not the equilibrium concentrations themselves.

Bài tập luyện tập

Explain, using Le Chatelier's principle and the relevant chemical equilibria, why $CaCO_3$ dissolves more extensively in an acidic solution than in pure water, while AgCl's solubility is essentially unaffected by pH.

Lời giải chi tiết

$CaCO_3$'s dissolution equilibrium is $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$, and the carbonate ion is a base: $CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$. In acidic solution, the added H^+ continuously consumes CO_3^{2-}, removing a product from the dissolution equilibrium; by Le Chatelier's principle, this pulls the dissolution equilibrium **forward**, dissolving more $CaCO_3$ than would dissolve in neutral water. By contrast, AgCl's anion, Cl^-, is the conjugate base of the *strong* acid HCl and has essentially no tendency to react with H^+; because Cl^- is not consumed by acid, the AgCl dissolution equilibrium is not pulled forward, and its solubility shows no meaningful pH dependence.

Bài tập luyện tập

Using $K_{sp} = 5.6 \times 10^{-12}$ for $Mg(OH)_2$, calculate its molar solubility in a solution buffered at pH $= 10.00$, and compare with its solubility in pure water (1.12×10^{-4} M).

Lời giải chi tiết

pOH $= 14.00 - 10.00 = 4.00$, so $[OH^-] = 10^{-4.00} = 1.0 \times 10^{-4}$ M. With $[OH^-]$ fixed by the buffer:

$$s = \frac{K_{sp}}{[OH^-]^2} = \frac{5.6 \times 10^{-12}}{(1.0 \times 10^{-4})^2} = \frac{5.6 \times 10^{-12}}{1.0 \times 10^{-8}} = \boxed{5.6 \times 10^{-4}\ \text{M}}.$$

This is about $5.6 \times 10^{-4} / 1.12 \times 10^{-4} \approx 5.0$ times greater than the pure-water solubility, because pH 10.00 is more acidic (lower $[OH^-]$) than the natural pH of a saturated $Mg(OH)_2$ solution — consistent with the general rule that lowering the pH increases the solubility of a metal hydroxide.

Bài tập luyện tập

If a dissolution reaction has $K_{sp} \gg 1$ at a given temperature, what does this imply about the sign and approximate magnitude of ΔG° for that dissolution?

(A) ΔG° is large and positive

(B) ΔG° is large and negative

(C) ΔG° is exactly zero

(D) No conclusion about ΔG° can be drawn from K_{sp} alone

Lời giải chi tiết

The correct answer is **(B)**. Since $\Delta G^\circ = -RT \ln K_{sp}$, a value of $K_{sp} \gg 1$ gives $\ln K_{sp} \gg 0$, and the leading negative sign makes ΔG° large and negative — describing a salt so soluble that dissolution to standard-state (1 M) ion concentrations is strongly spontaneous. This is the opposite regime from a typical "sparingly soluble" salt, where $K_{sp} \ll 1$ and ΔG° is large and *positive*.

Bài tập luyện tập

Calculate ΔG° for the dissolution of $BaSO_4$ at 25°C (298 K), given $K_{sp} = 1.1 \times 10^{-10}$.

Lời giải chi tiết

$$\Delta G^\circ = -RT\ln K_{sp} = -(8.314\ \text{J/(mol K)})(298\ \text{K})\ln(1.1\times10^{-10}).$$

$$\ln(1.1\times10^{-10}) = -22.93.$$

$$\Delta G^\circ = -(8.314)(298)(-22.93) = \boxed{+56{,}800\ \text{J/mol}} = +56.8\ \text{kJ/mol}.$$

As with AgCl (Section 7.14), the large positive ΔG° reflects $BaSO_4$'s very small K_{sp} and confirms that its dissolution to standard-state concentrations is strongly non-spontaneous — consistent with $BaSO_4$'s use as an insoluble barium source safe enough for medical imaging (its extremely limited dissolution prevents toxic free Ba^{2+} from entering the bloodstream).

Acids and Bases

Mục tiêu Unit: Phân biệt và áp dụng ba định nghĩa acid–base (Arrhenius, Brønsted–Lowry, Lewis); xác định cặp acid–base liên hợp và nhận diện chất lưỡng tính (amphoteric); tính pH/pOH của acid mạnh và base mạnh (kể cả base mạnh phân li hai OH^-); thiết lập và giải bảng ICE để tính pH và phần trăm ion hóa của acid yếu và base yếu, đồng thời giải thích vì sao phần trăm ion hóa tăng khi nồng độ giảm; giải thích phản ứng trung hòa và cách hình thành dung dịch đệm (buffer) từ acid yếu hoặc base yếu bị trung hòa một phần; đọc và giải thích đường cong chuẩn độ acid mạnh–base mạnh và acid yếu–base mạnh, xác định điểm tương đương và điểm nửa tương đương; liên hệ cấu trúc phân tử (độ phân cực và độ bền liên kết H–X, độ âm điện nguyên tử trung tâm, số nguyên tử O trong oxoacid) với độ mạnh acid; sử dụng phương trình Henderson–Hasselbalch để tính pH đệm hoặc tỉ lệ thành phần cần thiết cho một pH mục tiêu; đánh giá khả năng đệm (buffer capacity) dựa trên nồng độ tuyệt đối và tỉ lệ $[A^-]/[HA]$.

8.1 Introduction to Acids and Bases

Chemists use three progressively broader definitions of acids and bases. Each definition is consistent with the ones before it but extends the concept to a wider range of chemical systems.

8.1.1 The Arrhenius definition

The earliest modern definition, due to Svante Arrhenius, is restricted to aqueous solutions: an **Arrhenius acid** is a substance that increases the concentration of hydrogen ion (H^+, more accurately hydronium, H_3O^+) when dissolved in water, and an **Arrhenius base** is a substance that increases the concentration of hydroxide ion (OH^-) when dissolved in water. For example, HCl dissolves in water to give H_3O^+ and Cl^-, and NaOH dissolves to give Na^+ and OH^-. The Arrhenius picture works well for the substances it was designed for, but it cannot explain why a substance with no OH^- in its formula, such as NH_3, produces a basic solution, and it has no meaning outside of water.

8.1.2 The Brønsted–Lowry definition

The **Brønsted–Lowry definition** defines acids and bases in terms of proton transfer, independent of solvent: a **Brønsted–Lowry acid** is a proton (H^+) donor, and a **Brønsted–Lowry base** is a proton acceptor. Every proton-transfer reaction can be written as an acid donating H^+ directly to a base:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq).$$

Here water acts as the Brønsted–Lowry acid (it donates a proton to NH_3) and ammonia acts as the Brønsted–Lowry base (it accepts the proton). Because the definition depends only on proton transfer and not on the presence of water, it also describes gas-phase and nonaqueous reactions, such as

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s),$$

in which gaseous HCl (the acid) transfers a proton directly to gaseous NH_3 (the base) with no solvent present at all. The Brønsted–Lowry definition is the one used throughout the rest of this unit.

Conjugate acid–base pairs

Every Brønsted–Lowry acid–base reaction produces two **conjugate acid–base pairs**, each pair differing by exactly one proton (H^+). When an acid HA donates a proton, it becomes its **con-**

jugate base A^-; when a base B accepts a proton, it becomes its **conjugate acid** BH^+:

$$HA + B \rightleftharpoons A^- + BH^+.$$

In the ammonia example above, H_2O/OH^- is one conjugate pair (acid/base) and NH_4^+/NH_3 is the other (conjugate acid/base). A general rule follows directly from this pairing: **the stronger an acid, the weaker its conjugate base**, and vice versa, because a species that holds on to a proton very weakly (strong acid) leaves behind a conjugate base with very little tendency to reclaim that proton.

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Theo Brønsted–Lowry, acid là chất **cho proton** (H^+), base là chất **nhận proton** – định nghĩa này áp dụng được cả trong môi trường không phải nước (ví dụ phản ứng pha khí giữa HCl và NH_3). Mỗi phản ứng acid–base Brønsted–Lowry tạo ra hai cặp acid–base liên hợp (conjugate pairs), mỗi cặp chỉ khác nhau đúng một proton. Quy tắc quan trọng: acid càng mạnh thì base liên hợp của nó càng yếu, và ngược lại.

8.1.3 The Lewis definition

The broadest definition, due to G. N. Lewis, is based on electron pairs rather than protons: a **Lewis acid** is an electron-pair acceptor, and a **Lewis base** is an electron-pair donor. Every Brønsted–Lowry acid–base reaction is also a Lewis acid–base reaction (a proton is an excellent electron-pair acceptor), but the Lewis definition additionally covers reactions with no protons involved at all. A classic example is the reaction between boron trifluoride and ammonia:

$$BF_3 + :NH_3 \rightarrow F_3B{-}NH_3.$$

Boron in BF_3 has only six electrons around it and an empty orbital, so BF_3 acts as the Lewis acid, accepting the lone pair donated by nitrogen in NH_3, which acts as the Lewis base. Metal cations such as Ag^+, Fe^{3+}, and Al^{3+} are Lewis acids whenever they accept electron pairs from surrounding ligands (for example, in $Ag(NH_3)_2^+$), even though they contain no protons to accept. The Lewis definition is used mainly to describe complex-ion formation and organic reaction mechanisms; the pH and equilibrium calculations in the rest of this unit are handled with the Brønsted–Lowry framework.

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Định nghĩa Lewis mở rộng khái niệm acid–base sang cặp electron thay vì proton: acid Lewis là chất **nhận cặp electron**, base Lewis là chất **cho cặp electron**. Mọi phản ứng Brønsted–Lowry đều là phản ứng Lewis, nhưng định nghĩa Lewis còn bao trùm cả những phản ứng không hề có proton, ví dụ BF_3 (acid Lewis, thiếu electron ở boron) phản ứng với NH_3 (base Lewis, có cặp electron chưa liên kết trên N).

8.1.4 Amphoteric species

A species that can act as either a Brønsted–Lowry acid or a Brønsted–Lowry base, depending on the partner it reacts with, is called **amphoteric**. Water is the most important example: it acts as a base (proton acceptor) toward a stronger acid such as HCl,

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-,$$

but as an acid (proton donor) toward a stronger base such as NH_3, as shown above. Water even reacts with itself in this way, in the **autoionization of water**,

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq),$$

which is the source of the equilibrium constant K_w used throughout this unit (Section 8.2). The hydrogen carbonate ion, HCO_3^-, is another common amphoteric species: it can donate a proton to become carbonate, or accept a proton to become carbonic acid,

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \qquad \text{(acting as acid)},$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \qquad \text{(acting as base)}.$$

Any species that lies in the "middle" of a polyprotic acid's proton-loss sequence (retaining at least one ionizable proton while also carrying a negative charge capable of accepting one) is generally amphoteric.

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Chất lưỡng tính (amphoteric) là chất có thể đóng vai trò acid hoặc base tùy vào chất phản ứng cùng nó. Nước là ví dụ điển hình nhất – vừa có thể cho proton (khi gặp base mạnh hơn) vừa có thể nhận proton (khi gặp acid mạnh hơn); chính phản ứng nước tự ion hóa với nhau là nguồn gốc của hằng số K_w. Ion HCO_3^- cũng lưỡng tính: có thể cho proton để tạo CO_3^{2-}, hoặc nhận proton để tạo H_2CO_3.

Identifying conjugate pairs and acid–base type

For the reaction $HSO_4^- + CO_3^{2-} \rightleftharpoons SO_4^{2-} + HCO_3^-$, identify the two conjugate acid–base pairs and label each species as a Brønsted–Lowry acid or base. Then identify the Lewis acid in the reaction $Al^{3+} + 6\,H_2O \rightarrow Al(H_2O)_6^{3+}$.

Conjugate pairs: HSO_4^- donates a proton to become SO_4^{2-}, so HSO_4^-/SO_4^{2-} is one conjugate acid/base pair, with HSO_4^- acting as the Brønsted–Lowry acid. CO_3^{2-} accepts that proton to become HCO_3^-, so HCO_3^-/CO_3^{2-} is the other conjugate acid/base pair, with CO_3^{2-} acting as the Brønsted–Lowry base.

Lewis acid: In $Al^{3+} + 6\,H_2O \rightarrow Al(H_2O)_6^{3+}$, no proton is transferred at all – six water molecules donate lone pairs to the aluminum ion. Al^{3+} is the **Lewis acid** (electron-pair acceptor, since it is a small, highly charged cation with empty orbitals), and H_2O is the **Lewis base** (electron-pair donor) in each Al–O bond formed.

(!) Lỗi thường gặp: Do not assume that "strong" and "concentrated" (or "weak" and "dilute") mean the same thing. **Strong/weak** describes the *extent of ionization* of an acid or base in water (a fixed chemical property of the substance), while **concentrated/dilute** describes the *amount of solute per unit volume* (a property of a particular solution that you can change by adding water). A dilute solution of a strong acid, such as 1×10^{-4} M HCl, is still 100% ionized – it is simply a small amount of a strong acid, not a "weak" one.

8.2 pH and pOH of Strong Acids and Bases

Strong acids and **strong bases** are those that ionize (or dissociate) essentially completely (100%) in aqueous solution. Because the reaction goes to completion rather than reaching a partial equilibrium, no equilibrium calculation (ICE table) is needed: the concentration of H_3O^+ or OH^- is determined directly from the stoichiometry of the ionization reaction and the labeled (analytical) concentration of the acid or base.

Strong acids (memorize this list – essentially the only common strong acids): HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4 (for its first ionizable proton). **Strong bases**: the Group 1 (alkali metal) hydroxides (LiOH, NaOH, KOH, RbOH, CsOH) and the heavier Group 2 hydroxides $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$, each of which releases *two* OH^- ions per formula unit. ($Mg(OH)_2$ and $Be(OH)_2$ are not treated as strong bases in this context because of their very low solubility.) Every acid or base not on these lists should be treated as weak unless stated otherwise.

For a monoprotic strong acid HA at labeled concentration C, ionization is complete, so $[H_3O^+] = C$ and

$$\text{pH} = -\log[H_3O^+] = -\log C.$$

For a strong base MOH at labeled concentration C, $[OH^-] = C$, while for a strong base of the form $M(OH)_2$ (e.g., $Ca(OH)_2$), each formula unit releases two hydroxide ions, so $[OH^-] = 2C$. In every case,

$$\text{pOH} = -\log[OH^-], \qquad \text{pH} + \text{pOH} = 14.00 \ \ (\text{at } 25^\circ\text{C}),$$

because $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C, and taking $-\log$ of both sides of that expression gives $\text{pH} + \text{pOH} = -\log K_w = 14.00$.

pH of a strong acid

Find the pH of a 0.045 M solution of HCl.

HCl is a strong acid, so ionization is complete: $[H_3O^+] = 0.045$ M. Then

$$\text{pH} = -\log(0.045) = 1.35.$$

pH of a strong base

Find the pH of a 0.0072 M solution of NaOH.

NaOH is a strong base with one OH^- per formula unit, so $[OH^-] = 0.0072$ M.

$$\text{pOH} = -\log(0.0072) = 2.14, \qquad \text{pH} = 14.00 - 2.14 = 11.86.$$

pH of a diprotic strong base

Find the pH of a 0.015 M solution of $Ca(OH)_2$.

$Ca(OH)_2$ is a strong base that releases *two* OH^- ions per formula unit:

$$Ca(OH)_2(s) \rightarrow Ca^{2+}(aq) + 2\,OH^-(aq).$$

So $[OH^-] = 2 \times 0.015 = 0.030$ M (*not* 0.015 M – this factor of two is the single most common source of error with these bases).

$$\text{pOH} = -\log(0.030) = 1.52, \qquad \text{pH} = 14.00 - 1.52 = 12.48.$$

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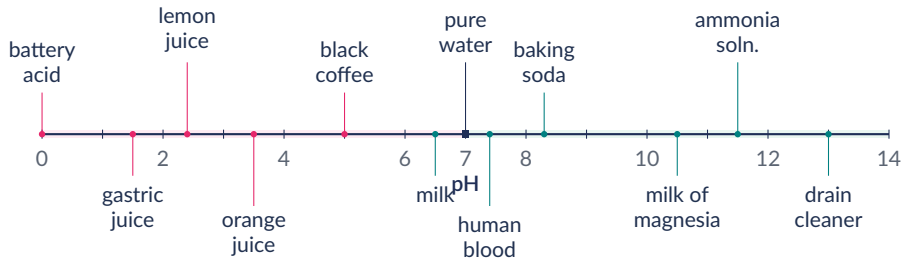
Với acid mạnh/base mạnh, phản ứng ion hóa xảy ra hoàn toàn (100%) nên không cần bảng ICE: $[H_3O^+]$ hoặc $[OH^-]$ bằng đúng nồng độ chất tan ban đầu (nhân với hệ số hợp thức nếu cần). Điểm cần đặc biệt lưu ý: với các base mạnh dạng $M(OH)_2$ như $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, mỗi công thức phân tử giải phóng **hai** ion OH^-, nên $[OH^-] = 2C$ chứ không phải C.



Approximate pH values of common substances at room temperature. Acidic solutions (pH < 7) have $[H_3O^+] > [OH^-]$; basic solutions (pH > 7) have $[OH^-] > [H_3O^+]$; at pH $= 7$ the two are equal.

8.3 Weak Acid and Base Equilibria

Unlike strong acids and bases, **weak acids** and **weak bases** ionize only *partially* in water, establishing a true equilibrium between the un-ionized and ionized forms. Most acids and bases encountered in chemistry are weak.

8.3.1 K_a and K_b expressions

For a generic weak acid HA in water,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq), \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}.$$

K_a is the **acid ionization (dissociation) constant**; the larger K_a is, the more the equilibrium favors products, and the stronger the acid. Water is the solvent and is omitted from the equilibrium expression by convention (its concentration is effectively constant). Analogously, for a generic weak base B,

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq), \qquad K_b = \frac{[BH^+][OH^-]}{[B]},$$

where K_b is the **base ionization constant**. Reference values used throughout this unit: $K_a(CH_3COOH) = 1.8 \times 10^{-5}$, $K_a(HF) = 6.8 \times 10^{-4}$, $K_a(HCN) = 6.2 \times 10^{-10}$, $K_a(NH_4^+) = 5.6 \times 10^{-10}$, $K_a(HNO_2) = 4.5 \times 10^{-4}$, and $K_b(NH_3) = 1.8 \times 10^{-5}$.

8.3.2 ICE tables and pH of weak acids and bases

Because ionization of a weak acid or base is an equilibrium, its pH is found by setting up an **ICE table** (Initial, Change, Equilibrium) and solving for the equilibrium concentration of H_3O^+ or OH^- using K_a or K_b.

Weak acid ICE table: pH and percent ionization

Find the pH of 0.20 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$), and the percent ionization of the acid at this concentration.

	CH_3COOH	H_3O^+	CH_3COO^-
I	0.20	0	0
C	$-x$	$+x$	$+x$
E	$0.20 - x$	x	x

$$K_a = \frac{x^2}{0.20 - x} = 1.8 \times 10^{-5}.$$

Since K_a is small relative to 0.20, try the approximation $0.20 - x \approx 0.20$: $x^2 = (1.8 \times 10^{-5})(0.20) = 3.6 \times 10^{-6}$, so $x \approx 1.90 \times 10^{-3}$. Checking the approximation, $x/0.20 = 0.95\% < 5\%$, so it is valid; solving the quadratic exactly gives $x = 1.888 \times 10^{-3}$ M, confirming the ap-

proximation.

$$[\mathrm{H_3O^+}] = 1.89 \times 10^{-3}\ \mathrm{M} \implies \mathrm{pH} = -\log(1.89 \times 10^{-3}) = 2.72.$$

$$\%\ \text{ionization} = \frac{[\mathrm{H_3O^+}]_{\text{ionized}}}{[\mathrm{HA}]_{\text{initial}}} \times 100\% = \frac{1.89 \times 10^{-3}}{0.20} \times 100\% = 0.94\%.$$

When the small-x approximation fails, and the dilution effect

(a) Find the pH and percent ionization of 0.10 M HF ($K_a = 6.8 \times 10^{-4}$). (b) Find the percent ionization of CH_3COOH at 0.020 M and compare it with the 0.94% value found above at 0.20 M.

(a) Setting up the same ICE table with $K_a = x^2/(0.10 - x) = 6.8 \times 10^{-4}$, the approximate solution would give $x \approx \sqrt{(6.8 \times 10^{-4})(0.10)} = 8.25 \times 10^{-3}$ M, but $8.25 \times 10^{-3}/0.10 = 8.3\% > 5\%$, so the approximation is *not* valid here and the quadratic must be solved exactly:

$$x^2 + (6.8 \times 10^{-4})x - (6.8 \times 10^{-4})(0.10) = 0 \implies x = 7.91 \times 10^{-3}\ \mathrm{M}.$$

$$\mathrm{pH} = -\log(7.91 \times 10^{-3}) = 2.10, \qquad \%\ \text{ionization} = \frac{7.91 \times 10^{-3}}{0.10} \times 100\% = 7.9\%.$$

(b) For CH_3COOH diluted to 0.020 M, $x^2/(0.020 - x) = 1.8 \times 10^{-5}$ gives $x = 5.91 \times 10^{-4}$ M, so

$$\%\ \text{ionization} = \frac{5.91 \times 10^{-4}}{0.020} \times 100\% = 2.96\%,$$

compared with 0.94% at 0.20 M. **Diluting a weak acid tenfold increases its percent ionization** (here, roughly by a factor of $\sqrt{10} \approx 3.2$, consistent with $x \approx \sqrt{K_a C}$ so $x/C \approx \sqrt{K_a/C}$), even though the *absolute* concentration of H_3O^+ decreases.

Percent ionization $= \dfrac{[\mathrm{H^+}]_{\text{ionized at equilibrium}}}{[\mathrm{HA}]_{\text{initial}}} \times 100\%$ **increases as the initial concentration of a weak acid decreases**, for a fixed K_a. Intuitively, Le Chatelier's principle explains this: diluting the solution shifts the ionization equilibrium $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ toward the side with more dissolved particles (the ionized products) to partially counteract the dilution, so a larger *fraction* of the original HA ionizes even though the absolute concentration of ions present is lower.

Weak base ICE table: pH

Find the pH of 0.15 M NH_3 ($K_b = 1.8 \times 10^{-5}$).

	NH_3	NH_4^+	OH^-
I	0.15	0	0
C	$-x$	$+x$	$+x$
E	$0.15 - x$	x	x

$$K_b = \frac{x^2}{0.15 - x} = 1.8 \times 10^{-5}.$$

Approximating $0.15 - x \approx 0.15$: $x = \sqrt{(1.8\times10^{-5})(0.15)} = 1.64\times10^{-3}$ M; check: $1.64\times10^{-3}/0.15 = 1.1\% < 5\%$, valid.

$[\text{OH}^-] = 1.63\times10^{-3}$ M $\Longrightarrow$ pOH $= -\log(1.63\times10^{-3}) = 2.79$, pH $= 14.00 - 2.79 = 11.21$.

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Với acid yếu/base yếu, phải lập bảng ICE và giải phương trình cân bằng (thường là phương trình bậc hai) để tìm $x = [\text{H}_3\text{O}^+]$ hoặc $[\text{OH}^-]$ – **không được** coi nồng độ ion hóa bằng nồng độ ban đầu như acid/base mạnh. Có thể xấp xỉ $C - x \approx C$ nếu x nhỏ hơn 5% của C; nếu không, phải giải chính xác phương trình bậc hai. Phần trăm ion hóa $= \dfrac{[\text{H}^+]_{\text{đã ion hóa}}}{[\text{HA}]_{\text{ban đầu}}} \times 100\%$ **tăng** khi nồng độ ban đầu giảm (ở cùng một K_a), theo nguyên lý Le Chatelier.

(!) Lỗi thường gặp: The most common error in this unit is applying the strong-acid shortcut ($[\text{H}_3\text{O}^+] = C$) to a *weak* acid, or vice versa. Before starting any pH calculation, always check first whether the species is on the strong-acid/strong-base list (Section 8.2, complete ionization, no ICE table needed) or not (weak, requires an ICE table and a K_a or K_b value).

8.4 Acid--Base Reactions and Buffers

8.4.1 Neutralization

A **neutralization reaction** is the reaction of an acid with a base, in which the acid's H^+ (or H_3O^+) combines with the base's OH^- (or the base directly accepts a proton) to form water (plus a salt, when a strong acid reacts with a strong base):

$$\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \rightarrow 2\,\text{H}_2\text{O}(l).$$

When a strong acid neutralizes a strong base in exactly stoichiometric amounts, the resulting solution is simply a salt solution with pH $= 7.00$ (assuming the salt's ions do not hydrolyze). When a *weak* acid or base is involved, however, neutralization does not necessarily give a neutral solution, because the conjugate species left behind can itself react with water (Section 8.5).

8.4.2 Buffer formation by partial neutralization

A **buffer solution** contains substantial, comparable amounts of a weak acid *and* its conjugate base simultaneously (or a weak base and its conjugate acid). The most common way to prepare a buffer in the laboratory (besides simply dissolving a weak acid together with a salt of its conjugate base) is to **partially neutralize** a weak acid with a strong base, or partially neutralize a weak base with a strong acid, stopping before the equivalence point so that some of the original weak acid (or base) remains unreacted alongside the newly formed conjugate species.

Buffer formation by partial neutralization

50.0 mL of 0.200 M CH_3COOH is mixed with 20.0 mL of 0.150 M NaOH. Find the pH of the resulting solution ($K_a = 1.8\times10^{-5}$).

Moles CH_3COOH initial $= 0.0500$ L $\times 0.200$ M $= 0.01000$ mol. Moles NaOH added $= 0.0200$ L $\times$ 0.150 M $= 0.00300$ mol. NaOH is the limiting reagent and reacts $1{:}1$ with CH_3COOH:

$$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}.$$

This consumes 0.00300 mol CH_3COOH and produces 0.00300 mol CH_3COO^-, leaving $0.01000 - 0.00300 = 0.00700$ mol CH_3COOH unreacted. Because both the weak acid and its conjugate base are now present in comparable amounts, **this is a buffer solution**. Since both species share the same total volume, the ratio of moles equals the ratio of concentrations, so (using the Henderson–Hasselbalch relationship developed fully in Section 8.9):

$$\text{pH} = pK_a + \log\frac{n(\text{A}^-)}{n(\text{HA})} = 4.74 + \log\left(\frac{0.00300}{0.00700}\right) = 4.74 - 0.37 = 4.38.$$

Why buffers resist pH change

A buffer resists changes in pH when small amounts of strong acid or strong base are added because it contains *two* reservoirs of chemical "protection": the weak acid component HA can neutralize any added OH^-, and the conjugate base component A^- can neutralize any added H_3O^+. In each case the strong, highly reactive species (H_3O^+ or OH^-) is converted into a comparatively small perturbation of the HA/A^- ratio rather than being left free in solution, so the pH – which depends only on the *logarithm* of that ratio – shifts only slightly. This mechanism is developed quantitatively in Sections 8.8–8.10.

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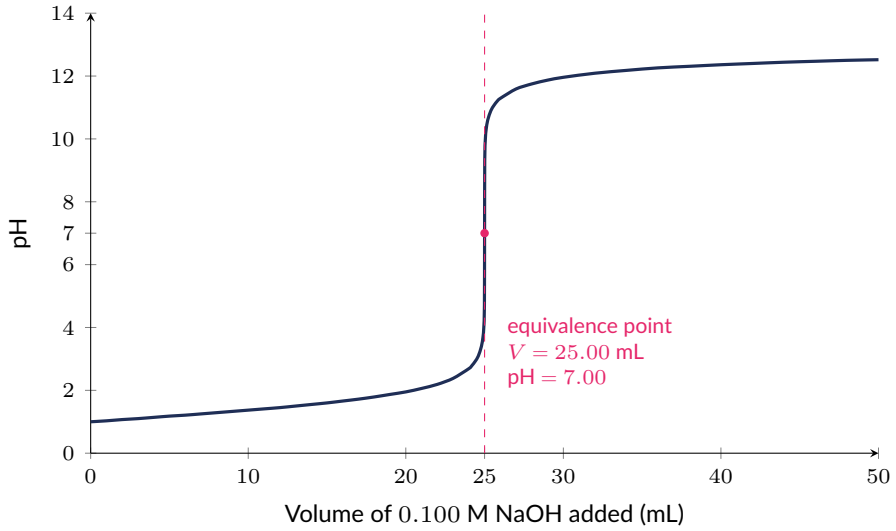
Trung hòa acid mạnh–base mạnh theo đúng tỉ lệ hợp thức cho dung dịch muối trung tính (pH $= 7.00$). Dung dịch đệm (buffer) được tạo ra khi trung hòa **một phần** acid yếu bằng base mạnh (hoặc base yếu bằng acid mạnh), khiến trong dung dịch còn lại đồng thời cả acid yếu ban đầu *và* base liên hợp mới tạo thành với lượng đáng kể. Buffer chống lại sự thay đổi pH vì thành phần acid yếu trung hòa OH^- thêm vào, còn thành phần base liên hợp trung hòa H_3O^+ thêm vào – pH chỉ phụ thuộc logarit của tỉ lệ hai thành phần nên thay đổi rất chậm.

8.5 Acid--Base Titrations

A **titration** is a controlled, stepwise addition of a solution of known concentration (the **titrant**) to a solution of unknown or analyzed concentration (the **analyte**), while monitoring pH, until the reaction between them is complete. Plotting pH (vertical axis) against volume of titrant added (horizontal axis) produces a **titration curve** whose shape depends on whether the acid and base involved are strong or weak.

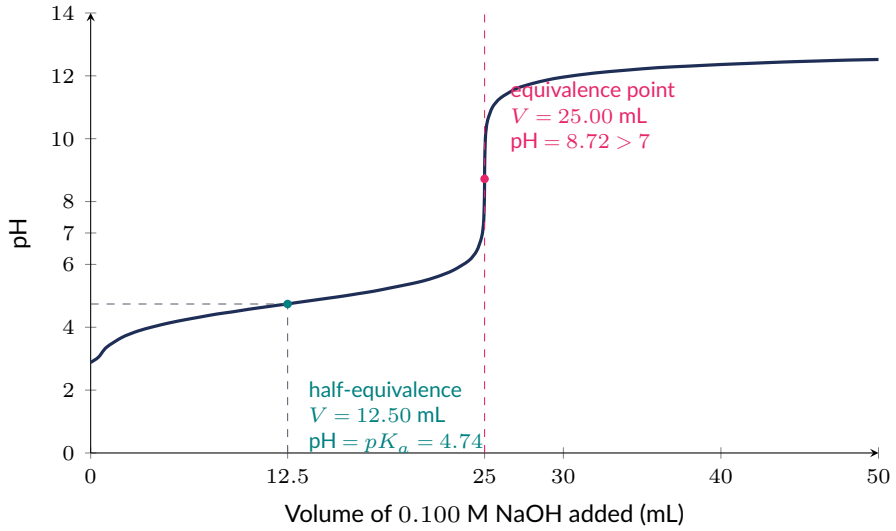
8.5.1 Strong acid–strong base titrations



Titration curve for 25.00 mL of 0.100 M HCl titrated with 0.100 M NaOH. The curve is symmetric about the equivalence point and the pH rises almost vertically there because both species are fully ionized; the equivalence-point pH is exactly 7.00 because neither Na^+ nor Cl^- undergoes hydrolysis.

For a titration of a strong acid with a strong base (or the reverse), the curve begins at a low pH set by the initial strong-acid concentration, rises slowly at first, then shoots up almost vertically through pH $= 7$ at the **equivalence point** – the point at which moles of titrant added exactly equal the moles of analyte originally present (by stoichiometry) – before leveling off at a high pH set by the excess strong base. Because the product salt (here NaCl) is formed from the conjugate base of a strong acid and the conjugate acid of a strong base, neither ion reacts with water, so **the equivalence-point pH is exactly 7.00 for a strong acid–strong base titration, and only for this case**.

8.5.2 Weak acid–strong base titrations



Titration curve for 25.00 mL of 0.100 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) titrated with 0.100 M NaOH. The initial rise is gradual and the curve flattens through the buffer region, where the Henderson–Hasselbalch equation (Section 8.9) applies; pH $= pK_a$ exactly at the half-equivalence point. The equivalence point lies above pH 7 because the conjugate base CH_3COO^- hydrolyzes water.

The weak acid–strong base curve differs from the strong–strong curve in three important ways. First, the **initial pH is higher** than for a strong acid of the same concentration, because the weak

acid is only partially ionized. Second, soon after titrant addition begins, the curve enters a long, gently sloped **buffer region**, where comparable amounts of HA and A^- are simultaneously present and the solution strongly resists pH change (Sections 8.8–8.10); the midpoint of this region is the **half-equivalence point**. Third, the **equivalence-point pH is greater than** 7, because at that point the solution contains only the conjugate base A^- (plus spectator cations and water), and A^- is a weak base that hydrolyzes water to produce a basic solution:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq).$$

(By the same logic, titrating a *weak base* with a strong acid gives an equivalence-point pH *less* than 7, because the conjugate acid BH^+ left behind hydrolyzes water to produce an acidic solution.)

Equivalence point: the volume of titrant at which moles of titrant added exactly equal the moles of analyte originally present, in the stoichiometric ratio of the balanced neutralization equation. **Half-equivalence point**: the volume at which exactly *half* the volume needed to reach equivalence has been added; at this point $[HA] = [A^-]$ (or $[B] = [BH^+]$ for a weak base), so from the Henderson–Hasselbalch equation, pH $= pK_a$ (Sections 8.7 and 8.9). Reading the pH at the half-equivalence point directly off a titration curve is the standard experimental method for measuring an unknown acid's pK_a.

Reading a titration curve

Using the weak acid–strong base curve above, identify (a) the equivalence-point volume and pH, (b) the half-equivalence-point volume and pH, and (c) the approximate K_a of the acid being titrated.

(a) The curve rises steeply and inflects at $V = 25.00$ mL, where pH $= 8.72$; this is the equivalence point.

(b) Half of 25.00 mL is 12.50 mL; reading the curve at that volume gives pH $= 4.74$; this is the half-equivalence point.

(c) Since pH $= pK_a$ at the half-equivalence point, $pK_a = 4.74$, so $K_a = 10^{-4.74} = 1.8 \times 10^{-5}$ – consistent with CH_3COOH.

Titration calculation: equivalence volume and pH

35.00 mL of 0.100 M HF ($K_a = 6.8 \times 10^{-4}$) is titrated with 0.150 M NaOH. Find (a) the volume of NaOH needed to reach the equivalence point, and (b) the pH at the equivalence point.

(a) Moles HF $= 0.03500$ L $\times\ 0.100$ M $= 3.500 \times 10^{-3}$ mol. At equivalence, moles NaOH added must equal moles HF (1:1 stoichiometry):

$$V_{\text{NaOH}} = \frac{3.500 \times 10^{-3}\ \text{mol}}{0.150\ \text{M}} = 0.02333\ \text{L} = 23.33\ \text{mL}.$$

(b) At equivalence, total volume $= 35.00 + 23.33 = 58.33$ mL, and all the HF has been converted to F^-:

$$[F^-] = \frac{3.500 \times 10^{-3}\ \text{mol}}{0.05833\ \text{L}} = 0.0600\ \text{M}.$$

F^- hydrolyzes water with $K_b = K_w/K_a = (1.0 \times 10^{-14})/(6.8 \times 10^{-4}) = 1.47 \times 10^{-11}$. Setting up an ICE table for $F^- + H_2O \rightleftharpoons HF + OH^-$:

$$x = \sqrt{K_b \times 0.0600} = \sqrt{(1.47 \times 10^{-11})(0.0600)} = 9.39 \times 10^{-7}\ \text{M} = [OH^-].$$

$$\text{pOH} = -\log(9.39 \times 10^{-7}) = 6.03, \qquad \text{pH} = 14.00 - 6.03 = 7.97.$$

(Only mildly basic, consistent with F^- being a very weak base – HF is a relatively strong weak acid.)

(!) Lỗi thường gặp: An equivalence-point pH of exactly 7.00 applies **only** to a strong acid–strong base titration. Do not assume equivalence always occurs at neutral pH: a weak acid titrated with a strong base gives an equivalence point *above* 7 (conjugate-base hydrolysis), and a weak base titrated with a strong acid gives an equivalence point *below* 7 (conjugate-acid hydrolysis).

8.6 Molecular Structure of Acids and Bases

The strength of an acid – how completely it ionizes and how large its K_a is – can often be predicted directly from its molecular structure, without needing a memorized or measured K_a value.

8.6.1 Binary acids: bond polarity and bond strength

For binary acids H—X (where X is a nonmetal), two competing structural factors control acid strength: the **polarity** of the H—X bond (how easily the bond can heterolyze to release H^+) and the **strength** of the H—X bond (how much energy is required to break it). Their relative importance depends on whether the comparison is made across a period or down a group.

Across a period, bond length changes only modestly, so **electronegativity of** X dominates: a more electronegative X polarizes the H—X bond more strongly (pulling electron density away from H) and better stabilizes the resulting negative charge on X^- in the conjugate base, so acid strength *increases* left to right across a period, e.g.

$$CH_4 \ll NH_3 < H_2O < HF \qquad (\text{increasing acid strength}).$$

Down a group, however, bond *strength* dominates over the (decreasing) electronegativity trend: as X gets larger down a group, the H—X bond gets longer and weaker (poorer orbital overlap), and this effect outweighs X's lower electronegativity. So among the hydrohalic acids,

$$HF < HCl < HBr < HI \qquad (\text{increasing acid strength}),$$

even though fluorine is the most electronegative halogen – HF is in fact a *weak* acid ($K_a \approx 6.8 \times 10^{-4}$) precisely because the short, strong H—F bond (≈ 570 kJ/mol) is so difficult to break, while HI (weakest bond, ≈ 298 kJ/mol) is one of the strongest common acids.

8.6.2 Oxoacids

An **oxoacid** has the general structure H—O—Y, where the ionizable proton is attached to an oxygen that is itself bonded to a central atom Y (which may carry additional oxygen atoms, as $=$O). Two structural trends govern oxoacid strength.

For a series of oxoacids of the same central atom, acid strength increases as the number of oxygen atoms bonded to the central atom increases, for two related reasons: (1) each additional highly electronegative oxygen inductively withdraws electron density through the Y—O bonds, further polarizing and weakening the O—H bond; and (2) the negative charge on the conjugate base is delocalized (by resonance) over a greater number of oxygen atoms as more oxygens are present, which stabilizes the conjugate base and shifts the ionization equilibrium further toward products.

Oxoacid	Total O atoms	Approx. pK_a	Relative strength
HClO	1	≈ 7.5	weakest
$HClO_2$	2	≈ 1.9	
$HClO_3$	3	< 0 (essentially strong)	
$HClO_4$	4	≈ -8	strongest

Acid strength increases steadily with the number of oxygen atoms bonded to chlorine, $HClO < HClO_2 < HClO_3 < HClO_4$; $HClO_4$ is one of the strongest common acids known.

A second, related structural effect is the **electronegativity of the central atom** itself when comparing oxoacids with the same number of oxygens: for example, HClO (Cl, more electronegative) is a stronger acid than HBrO (Br, less electronegative), because the more electronegative central atom pulls more electron density away from the O—H bond by the same inductive mechanism.

8.6.3 Inductive and resonance stabilization of the conjugate base

The same two effects – inductive electron withdrawal and resonance delocalization – also explain why substituting more electronegative groups near the acidic proton increases acid strength even for organic acids. **Trichloroacetic acid**, CCl_3COOH, is dramatically more acidic ($K_a \approx 3 \times 10^{-1}$) than acetic acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$), because the three highly electronegative chlorine atoms inductively withdraw electron density through the carbon skeleton, both weakening the O—H bond and strongly stabilizing the resulting carboxylate anion's negative charge; the effect diminishes rapidly with distance from the acidic proton (fewer or more distant electronegative substituents give a smaller boost to acid strength).

Ranking acid strength from molecular structure

Rank the following acids from weakest to strongest, giving the structural reasoning in each case: (a) H_2Se, H_2S, H_2O (same group, Group 16 hydrides); (b) $HClO_2$ and $HClO_4$.

(a) These are binary acids of elements in the same group, so bond strength dominates: bond strength decreases (bonds get longer/weaker) going down the group from O to S to Se, so acid strength *increases* down the group:

$$H_2O < H_2S < H_2Se \qquad \text{(weakest to strongest)}.$$

(b) These are oxoacids of the same central atom (Cl) with different numbers of oxygen atoms. $HClO_4$ has more oxygens (4 vs. 2), giving greater inductive withdrawal and greater resonance delocalization of charge in the conjugate base, so

$$HClO_2 < HClO_4 \qquad \text{(weaker to stronger)}.$$

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Với acid nhị nguyên H—X: theo **chu kỳ** (cùng hàng), độ âm điện của X quyết định – X càng âm điện thì acid càng mạnh (CH_4<NH_3<H_2O<HF). Theo **nhóm** (cùng cột), độ bền liên kết H–X chiếm ưu thế – liên kết càng dài/yếu (xuống dưới nhóm) thì acid càng mạnh, dù độ âm điện giảm (HF<HCl<HBr<HI). Với oxoacid, càng nhiều nguyên tử O gắn vào nguyên tử trung tâm thì acid càng mạnh, do hiệu ứng cảm ứng (inductive) rút electron và hiệu ứng cộng hưởng (resonance) giải tỏa điện tích âm trên base liên hợp.

8.7 pH and pK_a

It is often more convenient to compare acid strengths using $pK_a = -\log K_a$ rather than K_a itself, exactly as pH is a more convenient scale than $[H_3O^+]$. Because pK_a is a negative logarithm of K_a, **the relationship between pK_a and acid strength is inverted relative to K_a**: a *larger* K_a (stronger acid) corresponds to a *smaller* (or more negative) pK_a.

The lower the pK_a, the stronger the acid. Equivalently, for a base, the lower the pK_b, the stronger the base. For any conjugate acid–base pair at 25°C,

$$K_a \times K_b = K_w = 1.0 \times 10^{-14}, \qquad \text{equivalently} \qquad pK_a + pK_b = 14.00.$$

This identity follows directly from taking $-\log$ of both sides of $K_aK_b = K_w$, and it lets you compute the K_b (or pK_b) of any conjugate base directly from the K_a (or pK_a) of its parent acid, without needing a separate table of base constants.

The relationship between pH, pK_a, and the composition of a HA/A^- mixture is central to buffers and titrations: **pH $= pK_a$ precisely when** $[A^-] = [HA]$ (equal concentrations of the weak acid and its conjugate base), which is exactly the condition that holds at the half-equivalence point of a titration (Section 8.5) or in any $1{:}1$ buffer mixture (Sections 8.8–8.9). This falls directly out of the Henderson–Hasselbalch equation, developed in Section 8.9: when $[A^-]/[HA] = 1$, $\log(1) = 0$, so pH $= pK_a + 0 = pK_a$.

Using $K_aK_b = K_w$ to find a conjugate base's K_b

Given $K_a(CH_3COOH) = 1.8 \times 10^{-5}$, find K_b and pK_b of the acetate ion, CH_3COO^-. Then find the pOH of a 0.10 M solution of CH_3COO^-.

CH_3COO^- is the conjugate base of CH_3COOH, so

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}, \qquad pK_b = -\log(5.6 \times 10^{-10}) = 9.25.$$

Check: $pK_a(CH_3COOH) + pK_b(CH_3COO^-) = 4.74 + 9.25 = 13.99 \approx 14.00$ ✓ (rounding).

For a 0.10 M CH_3COO^- solution, ICE table with $K_b = 5.6 \times 10^{-10}$:

$$x = \sqrt{K_b \times 0.10} = \sqrt{(5.6 \times 10^{-10})(0.10)} = 7.5 \times 10^{-6}\ \text{M} = [OH^-],$$

$$\text{pOH} = -\log(7.5 \times 10^{-6}) = 5.12.$$

(!) Lỗi thường gặp: Never confuse K_a with pK_a: they move in **opposite** directions. A stronger acid has a *larger* K_a but a *smaller* (more negative or closer to zero, and possibly negative) pK_a. Students frequently rank acids backward by comparing pK_a values the same way they would compare K_a values – always double-check which quantity ("K" or "pK") a problem is asking you to rank.

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$pK_a = -\log K_a$: pK_a càng **nhỏ** thì acid càng **mạnh** (ngược chiều với K_a). Với một cặp acid–base liên hợp, luôn có $K_a \times K_b = K_w$ và $pK_a + pK_b = 14.00$ ở 25°C – dùng công thức này để suy ra K_b của base liên hợp từ K_a của acid ban đầu (hoặc ngược lại) mà không cần tra bảng riêng. pH $= pK_a$ đúng khi $[A^-] = [HA]$, tức tại điểm nửa tương đương của chuẩn độ hoặc trong buffer có tỉ lệ $1{:}1$.

8.8 Properties of Buffers

Sections 8.4 and 8.7 introduced how buffers form and why pH $= pK_a$ at a $1{:}1$ mixture; this section examines the buffering *mechanism* in more quantitative detail.

A buffer solution contains a weak acid HA and its conjugate base A^- (or a weak base B and its conjugate acid BH^+) in comparable, appreciable amounts. When a small amount of strong base

(OH^-) is added to a HA/A^- buffer, it is consumed almost entirely by the weak acid component,

$$HA + OH^- \rightarrow A^- + H_2O,$$

converting a small amount of HA into A^-. When a small amount of strong acid (H_3O^+) is added, it is consumed almost entirely by the conjugate base component,

$$A^- + H_3O^+ \rightarrow HA + H_2O,$$

converting a small amount of A^- back into HA. In both cases, the strong acid or base that was added is converted into a small change in the *ratio* $[A^-]/[HA]$, rather than remaining as free H_3O^+ or OH^- in solution. Because pH depends only on the *logarithm* of that ratio (Section 8.9), even a substantial percentage change in the ratio produces only a small change in pH – this is the essence of buffering.

Buffer resistance versus an unbuffered solution

A buffer contains 0.40 M CH_3COOH and 0.10 M CH_3COO^- ($K_a = 1.8 \times 10^{-5}$, $pK_a = 4.74$). Find the pH of the buffer, then find the pH after 0.020 mol/L of NaOH is added to it, and compare the resulting change with the pH change that the same addition would cause in 1 L of pure water.

Initial pH:

$$\text{pH} = pK_a + \log\frac{[A^-]}{[HA]} = 4.74 + \log\left(\frac{0.10}{0.40}\right) = 4.74 - 0.60 = 4.14.$$

After adding 0.020 mol/L NaOH: HA decreases by 0.020 M and A^- increases by 0.020 M:

$$[HA] = 0.40 - 0.02 = 0.38 \text{ M}, \qquad [A^-] = 0.10 + 0.02 = 0.12 \text{ M},$$

$$\text{pH} = 4.74 + \log\left(\frac{0.12}{0.38}\right) = 4.74 - 0.50 = 4.24.$$

The pH shifted by only $\Delta\text{pH} = 0.10$ units. **Compare with pure water:** adding 0.020 mol NaOH to 1 L of pure water gives $[OH^-] = 0.020$ M directly, so $\text{pOH} = -\log(0.020) = 1.70$ and $\text{pH} = 14.00 - 1.70 = 12.30$ – a swing of over 5 pH units from neutral. The buffered solution changed by only about $\frac{1}{50}$ as much.

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Cơ chế đệm: khi thêm một lượng nhỏ base mạnh, thành phần acid yếu HA trong buffer sẽ trung hòa nó (tạo thêm A^-); khi thêm một lượng nhỏ acid mạnh, thành phần base liên hợp A^- sẽ trung hòa nó (tạo thêm HA). Nhờ vậy, acid/base mạnh thêm vào chỉ làm thay đổi nhẹ **tỉ lệ** $[A^-]/[HA]$ thay vì tồn tại tự do trong dung dịch, và vì pH chỉ phụ thuộc logarit của tỉ lệ này nên pH thay đổi rất ít so với dung dịch không có buffer.

8.9 The Henderson--Hasselbalch Equation

The **Henderson–Hasselbalch equation** is the standard tool for calculating buffer pH directly from the concentrations of the weak acid and conjugate base, without setting up a full ICE table each time.

8.9.1 Derivation

Starting from the K_a expression for a weak acid HA,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \implies [H_3O^+] = K_a \times \frac{[HA]}{[A^-]}.$$

Taking $-\log$ of both sides,

$$-\log[\mathrm{H_3O^+}] = -\log K_a - \log\frac{[\mathrm{HA}]}{[\mathrm{A^-}]} = -\log K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]},$$

which gives the **Henderson–Hasselbalch equation**:

$$\boxed{\mathrm{pH} = pK_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}}.$$

The concentrations used are normally the *initial (analytical)* concentrations of the acid and conjugate base as mixed, rather than true equilibrium concentrations – this approximation is valid whenever the buffer components are present in large enough amounts that the small extent of further ionization or hydrolysis does not meaningfully change either concentration (true for essentially all buffers prepared by mixing appreciable, comparable amounts of HA and $\mathrm{A^-}$, as opposed to a dilute solution of the acid or salt alone).

Henderson–Hasselbalch: buffer pH from component concentrations

Find the pH of a buffer containing 0.30 M $\mathrm{CH_3COOH}$ and 0.20 M $\mathrm{CH_3COONa}$ ($K_a = 1.8\times10^{-5}$).

$pK_a = -\log(1.8\times10^{-5}) = 4.74$.

$$\mathrm{pH} = pK_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = 4.74 + \log\left(\frac{0.20}{0.30}\right) = 4.74 + (-0.18) = 4.57.$$

Because $[\mathrm{A^-}] < [\mathrm{HA}]$, the ratio is less than 1, its logarithm is negative, and the buffer's pH is slightly below its pK_a – reasonable, since acid is in excess.

Buffer preparation: solving for the required ratio and mass

What mass of $\mathrm{CH_3COONa}$ ($M = 82.03$ g/mol) must be dissolved in 500.0 mL of 0.40 M $\mathrm{CH_3COOH}$ to produce a buffer of pH $= 4.50$ ($K_a = 1.8\times10^{-5}$, $pK_a = 4.74$)? Assume the volume stays at 500.0 mL.

Solve the Henderson–Hasselbalch equation for the required ratio:

$$4.50 = 4.74 + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} \implies \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = 4.50 - 4.74 = -0.24 \implies \frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = 10^{-0.24} = 0.569.$$

Moles $\mathrm{CH_3COOH}$ present $= 0.5000$ L $\times\ 0.40$ M $= 0.200$ mol. Since $[\mathrm{A^-}]/[\mathrm{HA}]$ equals the mole ratio (same volume for both),

$$n(\mathrm{CH_3COO^-}) = 0.569 \times 0.200 \text{ mol} = 0.1138 \text{ mol}.$$

$$\text{mass of } \mathrm{CH_3COONa} = 0.1138 \text{ mol} \times 82.03 \text{ g/mol} = 9.34 \text{ g}.$$

Because the Henderson–Hasselbalch equation depends only on the *ratio* $[\mathrm{A^-}]/[\mathrm{HA}]$, diluting a buffer (adding water to both components equally) does not change its pH, to a good approximation – the ratio is unaffected by dilution even though both concentrations decrease. (Extreme dilution eventually breaks this approximation, but it holds well over the normal working range of a buffer.)

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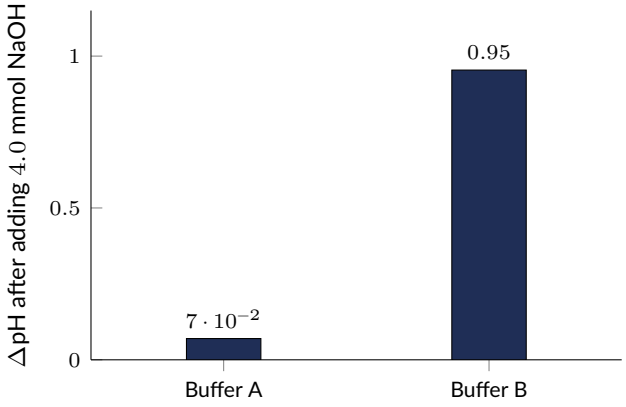
Phương trình Henderson–Hasselbalch: pH $= pK_a + \log \dfrac{[\text{A}^-]}{[\text{HA}]}$, được suy ra trực tiếp từ biểu thức K_a. Công thức này cho phép tính nhanh pH của buffer từ nồng độ (hoặc số mol, nếu cùng thể tích) hai thành phần, hoặc ngược lại tính tỉ lệ $[\text{A}^-]/[\text{HA}]$ cần thiết để đạt một pH mục tiêu – rất hữu ích khi pha chế buffer trong phòng thí nghiệm.

8.10 Buffer Capacity

Buffer capacity is a measure of how much strong acid or strong base a buffer solution can absorb before its pH changes significantly. It depends on two separate structural features of the buffer: the *absolute* concentrations of HA and A^-, and the *ratio* between them.

Buffer capacity increases with the absolute (analytical) concentrations of HA and A^-. A buffer made from 0.50 M HA/0.50 M A^- contains far more moles of each species per liter than a buffer made from 0.050 M HA/0.050 M A^- (even though both have identical pH, since the *ratio* is the same $1{:}1$ in both), so the more concentrated buffer can absorb a much larger *amount* (in moles) of added strong acid or base before either component is nearly used up.
For a fixed total buffer concentration, buffer capacity is greatest when $[\text{A}^-] = [\text{HA}]$ (ratio $= 1$, so pH $= pK_a$), because that is the composition that maximizes *both* reservoirs simultaneously – enough HA to neutralize added base and enough A^- to neutralize added acid. A buffer with a very lopsided ratio (e.g., $[\text{A}^-] \gg [\text{HA}]$) can absorb a large amount of added acid but only a small amount of added base before HA runs out.



Change in pH after adding the same absolute amount of strong base (4.0 mmol NaOH) to 100 mL of two CH_3COOH/CH_3COO^- buffers with identical $1{:}1$ ratio (both start at pH $= pK_a = 4.74$) but different total concentration: Buffer A is 0.50 M/0.50 M ($50.0/50.0$ mmol); Buffer B is 0.050 M/0.050 M ($5.0/5.0$ mmol). The more concentrated buffer resists the same absolute addition far more effectively.

Buffer capacity: concentrated versus dilute buffers

Buffer A contains 50.0 mmol CH_3COOH and 50.0 mmol CH_3COO^- in 100 mL; Buffer B contains 5.0 mmol of each in 100 mL ($K_a = 1.8 \times 10^{-5}$, $pK_a = 4.74$). Both buffers start at pH $= pK_a = 4.74$ (equal ratio). Find the pH of each after 4.0 mmol NaOH is added.

Buffer A: HA decreases by 4.0 mmol, A^- increases by 4.0 mmol:

$$\text{HA} = 50.0 - 4.0 = 46.0 \text{ mmol}, \quad \text{A}^- = 50.0 + 4.0 = 54.0 \text{ mmol},$$

$$\text{pH} = 4.74 + \log\left(\frac{54.0}{46.0}\right) = 4.74 + 0.07 = 4.81, \qquad \Delta\text{pH} = 0.07.$$

Buffer B:

$$\text{HA} = 5.0 - 4.0 = 1.0 \text{ mmol}, \quad \text{A}^- = 5.0 + 4.0 = 9.0 \text{ mmol},$$

$$\text{pH} = 4.74 + \log\left(\frac{9.0}{1.0}\right) = 4.74 + 0.95 = 5.70, \qquad \Delta\text{pH} = 0.95.$$

Buffer A's pH shifted by only 0.07 units, while Buffer B's shifted by 0.95 units – more than 13 times as much – because Buffer B had far less HA in reserve relative to the amount of base added. Had 6.0 mmol NaOH been added to Buffer B instead, it would exceed the 5.0 mmol of HA available entirely, exhausting the buffer's capacity to neutralize added base.

A buffer is generally considered **effective** only within about **one pH unit of its** pK_a, i.e., $\text{pH} = pK_a \pm 1$. This range corresponds to a ratio $[\text{A}^-]/[\text{HA}]$ between $1{:}10$ and $10{:}1$ (since $\log(10) = 1$ and $\log(0.1) = -1$). Outside this range, one of the two buffering components is present in such a small amount relative to the other that it is quickly exhausted by even a modest addition of strong acid or base, and the solution's pH begins to change rapidly, behaving more like an unbuffered solution.

VN **GIẢI THÍCH TIẾNG VIỆT**

Khả năng đệm (buffer capacity) phụ thuộc vào (1) nồng độ tuyệt đối của HA và A^- – nồng độ càng cao thì khả năng đệm càng lớn (có nhiều "dự trữ" hơn để trung hòa acid/base thêm vào); và (2) tỉ lệ $[\text{A}^-]/[\text{HA}]$ – khả năng đệm lớn nhất khi tỉ lệ gần 1 (tức pH gần pK_a), vì khi đó cả hai thành phần đều dồi dào. Một buffer chỉ thực sự hiệu quả trong khoảng $\text{pH} = pK_a \pm 1$ (tương ứng tỉ lệ từ $1{:}10$ đến $10{:}1$); ngoài khoảng này, một thành phần gần cạn kiệt và dung dịch mất khả năng chống lại sự thay đổi pH.

8.11 Practice Problems

Problem 1

Which of the following species is amphoteric in aqueous solution?

(A) NH_4^+ **(C)** Cl^-

(B) HCO_3^- **(D)** CH_3COO^-

Lời giải chi tiết

NH_4^+ can only act as a Brønsted–Lowry acid (it has a proton to donate but no lone pair suited to accepting one favorably); Cl^- and CH_3COO^- can only act as bases (conjugate bases of strong/weak acids). HCO_3^- can both donate a proton (to become CO_3^{2-}) and accept a proton (to become H_2CO_3), so it is amphoteric. **Answer: (B).**

Problem 2

For the reaction $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$, identify both conjugate acid–base pairs and state which species is the Brønsted–Lowry acid and which is the base in the forward reaction.

Lời giải chi tiết

Forward reaction: H_2O donates a proton to NH_3, so H_2O is the Brønsted–Lowry **acid** and NH_3 is the Brønsted–Lowry **base**. The two conjugate pairs (each differing by one proton) are H_2O/OH^- (acid/conjugate base) and NH_4^+/NH_3 (conjugate acid/base).

Problem 3

In the reaction $BF_3 + :NH_3 \rightarrow F_3B{-}NH_3$, which species is the Lewis acid?

(A) BF_3

(B) NH_3

(C) F^-

(D) Neither – no electron pair is transferred

Lời giải chi tiết

Boron in BF_3 has only six valence electrons and an empty p orbital, making it an electron-pair acceptor (Lewis acid); nitrogen in NH_3 donates its lone pair (Lewis base) to form the new B–N bond. **Answer: (A).**

Problem 4

Find the pH of a 0.062 M solution of HNO_3.

Lời giải chi tiết

HNO_3 is a strong acid (complete ionization), so $[H_3O^+] = 0.062$ M.

$$\text{pH} = -\log(0.062) = 1.21.$$

Problem 5

Find the pH of a 0.0038 M solution of $Sr(OH)_2$.

Lời giải chi tiết

$Sr(OH)_2$ is a strong base releasing two OH^- per formula unit: $[OH^-] = 2 \times 0.0038 = 0.0076$ M.

$$\text{pOH} = -\log(0.0076) = 2.12, \qquad \text{pH} = 14.00 - 2.12 = 11.88.$$

Problem 6

What is $[H_3O^+]$ in 0.10 M HCl?

(A) 0.10 M

(B) 1.0×10^{-13} M

(C) 0.050 M

(D) 1.0×10^{-1} M, but only after equilibrium is reached over time

Lời giải chi tiết

HCl is a strong acid and ionizes completely and essentially instantaneously, so $[H_3O^+]$ equals the full labeled concentration, 0.10 M. **Answer: (A).**

Problem 7

30.0 mL of 0.050 M HCl is mixed with 20.0 mL of 0.060 M NaOH. Find the pH of the resulting solution.

Lời giải chi tiết

Moles HCl $= 0.0300$ L $\times\ 0.050$ M $= 1.50 \times 10^{-3}$ mol. Moles NaOH$= 0.0200$ L $\times\ 0.060$ M $= 1.20 \times 10^{-3}$ mol. HCl is in excess:

$$n(\mathrm{H_3O^+})_{\text{excess}} = 1.50 \times 10^{-3} - 1.20 \times 10^{-3} = 3.0 \times 10^{-4}\ \text{mol}.$$

Total volume $= 30.0 + 20.0 = 50.0$ mL $= 0.0500$ L.

$$[\mathrm{H_3O^+}] = \frac{3.0 \times 10^{-4}}{0.0500} = 6.0 \times 10^{-3}\ \text{M}, \qquad \text{pH} = -\log(6.0 \times 10^{-3}) = 2.22.$$

Problem 8

Write the K_a expression for HNO_2 and find the pH of a 0.050 M solution ($K_a = 4.5 \times 10^{-4}$). Also find its percent ionization.

Lời giải chi tiết

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{NO_2^-}]}{[\mathrm{HNO_2}]}.$$

ICE table: $x^2/(0.050 - x) = 4.5 \times 10^{-4}$. Approximate $x \approx \sqrt{(4.5 \times 10^{-4})(0.050)} = 4.74 \times 10^{-3}$; check $4.74 \times 10^{-3}/0.050 = 9.5\% > 5\%$, so solve the quadratic exactly: $x^2 + (4.5 \times 10^{-4})x - (4.5 \times 10^{-4})(0.050) = 0$ gives $x = 4.52 \times 10^{-3}$ M.

$$\text{pH} = -\log(4.52 \times 10^{-3}) = 2.34, \qquad \%\ \text{ionization} = \frac{4.52 \times 10^{-3}}{0.050} \times 100\% = 9.0\%.$$

Problem 9

Find the percent ionization of CH_3COOH ($K_a = 1.8 \times 10^{-5}$) at (a) 0.50 M and (b) 0.0050 M, and explain the trend.

Lời giải chi tiết

(a) $x^2/(0.50 - x) = 1.8 \times 10^{-5} \implies x = 2.99 \times 10^{-3}$ M; $\%$ ion $= \dfrac{2.99 \times 10^{-3}}{0.50} \times 100\% = 0.60\%$.

(b) $x^2/(0.0050 - x) = 1.8 \times 10^{-5} \implies x = 2.91 \times 10^{-4}$ M; $\%$ ion $= \dfrac{2.91 \times 10^{-4}}{0.0050} \times 100\% = 5.82\%$.

Diluting the acid 100-fold increased percent ionization from 0.60% to 5.82% (roughly a factor of $\sqrt{100} = 10$), consistent with $x \approx \sqrt{K_a C}$ so $x/C \approx \sqrt{K_a/C}$: as C decreases, the fraction ionized increases even though the absolute $[\mathrm{H_3O^+}]$ decreases.

Problem 10

Rank 1.0 M, 0.10 M, 0.010 M, and 0.0010 M solutions of the same weak acid by percent ionization, from lowest to highest.

(A) $1.0\ \text{M} < 0.10\ \text{M} < 0.010\ \text{M} < 0.0010\ \text{M}$

(B) $0.0010\ \text{M} < 0.010\ \text{M} < 0.10\ \text{M} < 1.0\ \text{M}$

(C) All four have equal percent ionization since K_a is fixed

(D) Percent ionization cannot be ranked without knowing K_a

Lời giải chi tiết

Percent ionization increases as concentration decreases for a fixed K_a (Problem 9), so the most concentrated solution has the lowest percent ionization and the most dilute has the highest. **Answer: (A).**

Problem 11

Find the pH of a 0.075 M solution of NH_3 ($K_b = 1.8 \times 10^{-5}$).

Lời giải chi tiết

$x^2/(0.075 - x) = 1.8 \times 10^{-5}$; approximate $x = \sqrt{(1.8 \times 10^{-5})(0.075)} = 1.16 \times 10^{-3}$ M (check: $1.5\% < 5\%$, valid).

$$[\text{OH}^-] = 1.15 \times 10^{-3}\ \text{M}, \qquad \text{pOH} = -\log(1.15 \times 10^{-3}) = 2.94, \qquad \text{pH} = 14.00 - 2.94 = 11.06.$$

Problem 12

What volume of 0.200 M KOH is required to completely neutralize 25.0 mL of 0.150 M H_2SO_4?

Lời giải chi tiết

$H_2SO_4 + 2\,KOH \rightarrow K_2SO_4 + 2\,H_2O$: each mole of H_2SO_4 requires *two* moles of KOH.

$$n(H_2SO_4) = 0.0250\ \text{L} \times 0.150\ \text{M} = 3.75 \times 10^{-3}\ \text{mol}, \qquad n(\text{KOH})_{\text{needed}} = 2 \times 3.75 \times 10^{-3} = 7.50 \times 10^{-3}\ \text{mol}.$$

$$V(\text{KOH}) = \frac{7.50 \times 10^{-3}\ \text{mol}}{0.200\ \text{M}} = 0.0375\ \text{L} = 37.5\ \text{mL}.$$

Problem 13

Which of the following mixtures forms a buffer solution?

(A) 0.10 mol HCl + 0.10 mol NaCl

(B) 0.20 mol CH_3COOH + 0.10 mol NaOH

(C) 0.10 mol NaOH + 0.10 mol HCl

(D) 0.10 mol NaOH + 0.10 mol HNO_3

Lời giải chi tiết

(A) is a strong acid with its salt – no conjugate weak-acid/weak-base pair, not a buffer. (C) and (D) are complete strong acid–strong base neutralizations, leaving only a neutral salt solution. In (B), NaOH partially neutralizes the weak acid CH_3COOH: it consumes 0.10 mol CH_3COOH and produces 0.10 mol CH_3COO^-, leaving 0.10 mol CH_3COOH unreacted alongside 0.10 mol CH_3COO^- – a true HA/A^- buffer. **Answer: (B).**

Problem 14

40.0 mL of 0.250 M NH_3 is mixed with 15.0 mL of 0.400 M HCl. Find the pH of the resulting solution ($K_a(NH_4^+) = 5.6 \times 10^{-10}$).

Lời giải chi tiết

$n(NH_3) = 0.0400 \times 0.250 = 0.0100$ mol; $n(HCl) = 0.0150 \times 0.400 = 0.00600$ mol. HCl converts 0.00600 mol NH_3 to NH_4^+, leaving $0.0100 - 0.00600 = 0.00400$ mol NH_3 and 0.00600 mol NH_4^+ – a buffer.

$$pK_a(NH_4^+) = -\log(5.6 \times 10^{-10}) = 9.25.$$

$$\text{pH} = 9.25 + \log\left(\frac{0.00400}{0.00600}\right) = 9.25 - 0.18 = 9.08.$$

Problem 15

What volume of 0.125 M NaOH is required to reach the equivalence point when titrating 20.0 mL of 0.150 M HBr?

Lời giải chi tiết

HBr is a strong acid; the neutralization is 1:1 with NaOH. $n(HBr) = 0.0200 \times 0.150 = 3.00 \times 10^{-3}$ mol.

$$V(\text{NaOH}) = \frac{3.00 \times 10^{-3}\ \text{mol}}{0.125\ \text{M}} = 0.0240\ \text{L} = 24.0\ \text{mL}.$$

Problem 16

30.0 mL of 0.100 M HNO_2 ($K_a = 4.5 \times 10^{-4}$) is titrated with 0.100 M NaOH. Find (a) the volume of NaOH needed to reach the equivalence point, (b) the volume and pH at the half-equivalence point, and (c) the pH at the equivalence point.

Lời giải chi tiết

(a) $n(HNO_2) = 0.0300 \times 0.100 = 3.00 \times 10^{-3}$ mol; since the NaOH concentration equals the acid's, $V_{eq} = 30.0$ mL.

(b) $V_{half} = 15.0$ mL; at half-equivalence $[HNO_2] = [NO_2^-]$, so pH $= pK_a = -\log(4.5 \times 10^{-4}) = 3.35$.

(c) At equivalence, total volume $= 30.0 + 30.0 = 60.0$ mL, and all the acid is converted to NO_2^-:

$$[NO_2^-] = \frac{3.00 \times 10^{-3}}{0.0600} = 0.0500\ \text{M}, \qquad K_b = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.22 \times 10^{-11}.$$

$$x = \sqrt{(2.22 \times 10^{-11})(0.0500)} = 1.05 \times 10^{-6}\ \text{M} = [OH^-], \qquad \text{pOH} = 5.98, \qquad \text{pH} = 14.00 - 5.98 = 8.02.$$

Problem 17

On a titration curve for an unknown monoprotic weak acid titrated with NaOH, the half-equivalence point occurs at pH $= 5.20$. Find pK_a and K_a of the acid.

Lời giải chi tiết

At the half-equivalence point, pH $= pK_a$, so $pK_a = 5.20$.

$$K_a = 10^{-5.20} = 6.3 \times 10^{-6}.$$

Problem 18

On a titration curve for a weak acid titrated with a strong base, the pH at the equivalence point is found to be 8.9. What does this indicate about the species present at that point?

(A) The titrant was a weak base

(B) The conjugate base of the acid is hydrolyzing water, producing a basic solution

(C) An arithmetic error must have occurred, since equivalence points are always at pH 7

(D) The acid used must have been diprotic

Lời giải chi tiết

At the equivalence point of a weak acid–strong base titration, the solution contains only the conjugate base A^- (plus spectator ions and water). A^- is a weak base and hydrolyzes water, $A^- + H_2O \rightleftharpoons HA + OH^-$, producing a solution with pH above 7 – exactly as observed. **Answer: (B).**

Problem 19

Rank HF, HCl, HBr, and HI from weakest to strongest acid, and explain the structural basis for the trend.

Lời giải chi tiết

These are binary acids of elements in the same group (halogens), so H–X bond strength – not electronegativity – controls the trend. Bond length increases and bond strength decreases going down the group, so acid strength increases down the group:

$$HF < HCl < HBr < HI.$$

HF is a weak acid despite fluorine's high electronegativity because its very short, strong H–F bond is difficult to break; HI, with the weakest H–X bond, ionizes essentially completely.

Problem 20

Explain, using molecular structure, why $HClO_4$ is a much stronger acid than $HClO_2$.

Lời giải chi tiết

$HClO_4$ has four oxygen atoms bonded to chlorine, versus two for $HClO_2$. The additional, highly electronegative oxygen atoms in $HClO_4$ withdraw electron density inductively from the O–H bond through the Cl–O framework, weakening it and making the proton easier to remove; in addition, the negative charge on the conjugate base ClO_4^- is delocalized by resonance over four oxygen atoms (versus two for ClO_2^-), which stabilizes ClO_4^- far more effectively. Both effects favor greater ionization for $HClO_4$, consistent with $pK_a(HClO_4) \approx -8$ versus $pK_a(HClO_2) \approx 1.9$.

Problem 21

Trichloroacetic acid, CCl_3COOH, has $K_a \approx 3 \times 10^{-1}$, dramatically larger than acetic acid's $K_a = 1.8 \times 10^{-5}$. Explain this difference using the inductive effect.

Lời giải chi tiết

The three chlorine atoms in CCl_3COOH are highly electronegative and pull electron density toward themselves through the carbon framework (the inductive effect), which both weakens the O–H bond (making the proton easier to remove) and stabilizes the negative charge that develops on the carboxylate oxygen atoms of the conjugate base CCl_3COO^- after ionization. Acetic acid's methyl group has no such electron-withdrawing substituents, so its conjugate base is far less stabilized and its K_a is nearly four orders of magnitude smaller.

Problem 22

Acid X has $pK_a = 3.2$; acid Y has $pK_a = 7.4$. Which is the stronger acid?

(A) Acid X
(B) Acid Y
(C) They are equally strong
(D) Cannot be determined from pK_a alone

Lời giải chi tiết

Lower pK_a corresponds to larger K_a and therefore a stronger acid. **Answer: (A), Acid X.**

Problem 23

A weak base has $K_b = 4.0 \times 10^{-4}$. Find the K_a and pK_a of its conjugate acid.

Lời giải chi tiết

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}, \qquad pK_a = -\log(2.5 \times 10^{-11}) = 10.60.$$

Problem 24

A weak acid HA has $pK_a = 5.10$. (a) At what pH does a solution contain $[HA] = [A^-]$? (b) What is the ratio $[A^-]/[HA]$ at pH $= 6.10$?

Lời giải chi tiết

(a) By definition, pH $= pK_a$ when $[HA] = [A^-]$, so pH $= 5.10$.

(b) From Henderson–Hasselbalch, $6.10 = 5.10 + \log\left(\dfrac{[A^-]}{[HA]}\right) \implies \log\left(\dfrac{[A^-]}{[HA]}\right) = 1.00 \implies \dfrac{[A^-]}{[HA]} = 10^{1.00} = 10.0.$

Problem 25

Describe, at the level of chemical species reacting, what happens when a small amount of HCl is added to a CH_3COOH/CH_3COONa buffer.

Lời giải chi tiết

The added HCl fully ionizes, releasing H_3O^+. This H_3O^+ reacts with the conjugate base component of the buffer, CH_3COO^-: $CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$. Nearly all of the added H_3O^+ is consumed this way, converting a small amount of CH_3COO^- into CH_3COOH rather than remaining free in solution. The ratio $[CH_3COO^-]/[CH_3COOH]$ decreases slightly, so by Henderson–Hasselbalch the pH decreases slightly – but far less than if the same HCl had been added to an unbuffered solution.

Problem 26

Which of the following combinations will *not* function as an effective buffer?

(A) HF/NaF
(B) $HCl/NaCl$
(C) CH_3COOH/CH_3COONa
(D) NH_3/NH_4Cl

Lời giải chi tiết

A buffer requires a weak acid (or weak base) together with its conjugate partner. HCl is a strong acid, and its conjugate base Cl^- is negligibly basic (essentially a spectator ion) – adding strong acid or base to this mixture is not resisted the way a true weak-conjugate-pair buffer resists it. **Answer: (B).**

Problem 27

A buffer contains 0.25 M HF and 0.40 M NaF ($K_a(\text{HF}) = 6.8 \times 10^{-4}$). Find its pH.

Lời giải chi tiết

$pK_a = -\log(6.8 \times 10^{-4}) = 3.17.$

$$\text{pH} = 3.17 + \log\left(\frac{0.40}{0.25}\right) = 3.17 + 0.20 = 3.37.$$

Problem 28

What ratio $[NH_3]/[NH_4^+]$ is needed to prepare a buffer with pH $= 9.00$ ($K_a(NH_4^+) = 5.6 \times 10^{-10}$)?

Lời giải chi tiết

$pK_a(NH_4^+) = -\log(5.6 \times 10^{-10}) = 9.25.$

$$9.00 = 9.25 + \log\left(\frac{[NH_3]}{[NH_4^+]}\right) \implies \log\left(\frac{[NH_3]}{[NH_4^+]}\right) = -0.25 \implies \frac{[NH_3]}{[NH_4^+]} = 10^{-0.25} = 0.56.$$

Problem 29

What mass of NaF ($M = 41.99$ g/mol) must be added to 250.0 mL of 0.30 M HF to produce a buffer with pH $= 3.50$ ($K_a(\text{HF}) = 6.8 \times 10^{-4}$)?

Lời giải chi tiết

$pK_a = 3.17$.

$$3.50 = 3.17 + \log\left(\frac{[\mathrm{F}^-]}{[\mathrm{HF}]}\right) \implies \log\left(\frac{[\mathrm{F}^-]}{[\mathrm{HF}]}\right) = 0.33 \implies \frac{[\mathrm{F}^-]}{[\mathrm{HF}]} = 10^{0.33} = 2.15.$$

$n(\mathrm{HF}) = 0.2500 \times 0.30 = 0.0750$ mol, so $n(\mathrm{F}^-)_{\text{needed}} = 2.15 \times 0.0750 = 0.161$ mol.

$$\text{mass NaF} = 0.161 \text{ mol} \times 41.99 \text{ g/mol} = 6.77 \text{ g}.$$

Problem 30

The Henderson–Hasselbalch equation gives an accurate buffer pH under which condition?

(A) Only when $[\mathrm{HA}]$ and $[\mathrm{A}^-]$ are both exactly 1 M

(B) When the initial (analytical) concentrations of HA and A^- are large enough that ionization/hydrolysis does not significantly change them

(C) Only when pH $= 7$

(D) Only for strong acids

Lời giải chi tiết

The Henderson–Hasselbalch equation substitutes initial (analytical) concentrations for true equilibrium concentrations. This is an accurate approximation whenever those initial concentrations are large enough, relative to K_a, that the small amount of further ionization or hydrolysis does not meaningfully change either concentration – true for essentially any buffer prepared with appreciable, comparable amounts of HA and A^-. **Answer: (B).**

Problem 31

Buffer 1 contains 10.0 mmol $\mathrm{CH_3COOH}$/10.0 mmol $\mathrm{CH_3COO^-}$; Buffer 2 contains 1.0 mmol $\mathrm{CH_3COOH}$/1.0 mmol $\mathrm{CH_3COO^-}$ ($K_a = 1.8 \times 10^{-5}$). Both start at pH $= pK_a = 4.74$. Find the pH of each after 0.50 mmol $\mathrm{H_3O^+}$ is added, and compare the pH changes.

Lời giải chi tiết

Added strong acid converts A^- into HA, mole for mole.

Buffer 1: HA $= 10.0 + 0.50 = 10.5$ mmol; $\mathrm{A}^- = 10.0 - 0.50 = 9.5$ mmol.

$$\text{pH} = 4.74 + \log\left(\frac{9.5}{10.5}\right) = 4.74 - 0.04 = 4.70, \qquad \Delta\text{pH} = 0.04.$$

Buffer 2: HA $= 1.0 + 0.50 = 1.5$ mmol; $\mathrm{A}^- = 1.0 - 0.50 = 0.5$ mmol.

$$\text{pH} = 4.74 + \log\left(\frac{0.5}{1.5}\right) = 4.74 - 0.48 = 4.27, \qquad \Delta\text{pH} = 0.48.$$

Buffer 1, with ten times the absolute concentration, changes barely a tenth as much as Buffer 2 for the same addition, demonstrating that buffer capacity increases with the absolute concentrations of the buffer components even when the ratio (and hence starting pH) is identical.

Problem 32

For a fixed total buffer concentration, at what ratio of $[A^-]$ to [HA] is buffer capacity greatest?

(A) 10:1

(B) 1:10

(C) 1:1

(D) Buffer capacity does not depend on this ratio

Lời giải chi tiết

Buffer capacity is greatest when $[A^-] = [HA]$ (ratio 1:1, so pH $= pK_a$), since this composition provides the largest simultaneous reserve of both the weak acid (to neutralize added base) and the conjugate base (to neutralize added acid). **Answer: (C).**

Problem 33

A buffer is prepared from a weak acid with $pK_a = 4.74$, but a measurement shows the solution's actual pH is 6.90. Is this buffer still within its effective buffering range? Justify your answer.

Lời giải chi tiết

The effective range of a buffer is approximately $pK_a \pm 1$, i.e., 3.74 to 5.74 here.

$$|\text{pH} - pK_a| = |6.90 - 4.74| = 2.16,$$

which is well outside the ± 1 range. **This buffer is not within its effective range** – at pH $= 6.90$, the ratio $[A^-]/[HA] = 10^{6.90-4.74} = 10^{2.16} \approx 145$, meaning HA is almost entirely depleted relative to A^-; the solution has essentially no reserve left to neutralize additional added base and will resist further pH increases very poorly.

Problem 34

A student titrates 20.00 mL of an unknown monoprotic weak acid with 0.100 M NaOH and finds the equivalence point at $V = 32.00$ mL and the half-equivalence point at pH $= 4.60$. Find (a) the original concentration of the weak acid, and (b) its K_a.

Lời giải chi tiết

(a) At equivalence, moles NaOH added equal moles of acid originally present:

$$n(\text{acid}) = 0.03200\ \text{L} \times 0.100\ \text{M} = 3.20 \times 10^{-3}\ \text{mol}, \qquad [\text{acid}]_0 = \frac{3.20 \times 10^{-3}}{0.02000\ \text{L}} = 0.160\ \text{M}.$$

(b) At the half-equivalence point, pH $= pK_a = 4.60$, so

$$K_a = 10^{-4.60} = 2.5 \times 10^{-5}.$$

Applications of Thermodynamics

Mục tiêu Unit: Giải thích entropy như thước đo mức độ phân tán năng lượng/số trạng thái vi mô có thể tiếp cận; dự đoán định tính dấu của ΔS cho các quá trình vật lý và hoá học; tính ΔS° phản ứng từ bảng entropy tuyệt đối chuẩn; tính ΔG theo $\Delta G = \Delta H - T\Delta S$ và xác định chiều thuận lợi nhiệt động ở một nhiệt độ cho trước, kể cả nhiệt độ chuyển tiếp khi $\Delta G = 0$; phân biệt phản ứng thuận lợi về nhiệt động (kiểm soát nhiệt động) với phản ứng xảy ra nhanh (kiểm soát động học); liên hệ ΔG° với hằng số cân bằng K qua $\Delta G^\circ = -RT \ln K$; áp dụng khái niệm phản ứng ghép cặp (coupled reactions) để làm thuận lợi một quá trình vốn bất lợi; phân biệt pin điện hoá (galvanic/voltaic) tự phát với bình điện phân (electrolytic) cần nguồn điện ngoài, xác định đúng anode/cathode và chiều dòng electron; tính E°_{pin} từ hai thế khử chuẩn và liên hệ với $\Delta G^\circ = -nFE^\circ$; áp dụng phương trình Nernst cho điều kiện không chuẩn; áp dụng định luật Faraday để tính khối lượng/thể tích sản phẩm điện phân từ cường độ dòng điện và thời gian.

9.1 Introduction to entropy

Entropy, symbol S, is a thermodynamic state function that measures the number of ways a system's energy and particles can be arranged among the **microstates** accessible to it — informally, how "spread out," or dispersed, the energy and matter of a system are. A system with many equally probable microstates (many ways to arrange its particles' positions and energies while still looking the same at the macroscopic level) has high entropy; a highly ordered system with few accessible microstates has low entropy. Unlike enthalpy, for which only *changes* ΔH can be measured directly, entropy has an absolute, always-positive value for any pure substance at a given temperature (Section 9.2).

Entropy is a **state function**: ΔS for a process depends only on the initial and final states, never on the path taken. The second law of thermodynamics requires that the entropy of the *universe* (system plus surroundings) increase for any spontaneous process — but the entropy change of the *system* alone (for example, a reacting mixture) can be positive or negative; the surroundings' entropy change compensates. This unit focuses on predicting and calculating ΔS for the chemical system itself.

Qualitative rules for predicting the sign of ΔS

- **Phase.** For a given substance, $S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$ per mole. Gas particles have vastly more accessible positions and translational energy states than a liquid, which in turn has more than a rigid solid lattice. Melting, vaporizing, or subliming increases S; freezing, condensing, or depositing decreases S.
- **Moles of gas.** A reaction that increases the total moles of gas (comparing gas-phase species only) has $\Delta S > 0$; one that decreases moles of gas has $\Delta S < 0$. This is usually the dominant factor in predicting ΔS_{rxn}, since gas-phase molar entropy is so much larger than condensed-phase entropy that solids and liquids barely move the total.
- **Dissolution.** Dissolving a molecular or ionic solid in a solvent generally increases S: a rigid lattice breaks apart into freely moving, solvated particles that can occupy far more positions than in the solid. (Exception: dissolving a *gas* in a liquid *decreases* S, since the dissolved gas

particles lose the enormous positional and translational freedom they had in the gas phase.)

- **Temperature.** Raising the temperature of any single phase increases S: more thermal energy is available to populate a larger number of accessible vibrational, rotational, and translational energy levels.
- **Mixing.** Mixing pure substances (two gases, or a solute dispersing through a solvent) increases S relative to the separated pure components — there are more ways to arrange a mixture than to arrange components kept apart.

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Entropy (S) đo mức độ "phân tán" của năng lượng và vật chất — số cách sắp xếp vi mô (microstates) mà hệ có thể có. Quy tắc dự đoán dấu ΔS: khí có entropy lớn hơn nhiều so với lỏng, lỏng lớn hơn rắn; phản ứng làm tăng số mol khí thì $\Delta S > 0$; hoà tan chất rắn vào dung môi thường làm tăng S (trừ hoà tan khí vào lỏng thì S giảm); tăng nhiệt độ luôn làm tăng S; trộn lẫn các chất tinh khiết làm tăng S so với để riêng từng chất.

Predicting the sign of ΔS

Predict the sign of ΔS for each process, with reasoning.

(a) $\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$

(b) $\mathrm{2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)}$

(c) $\mathrm{NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)}$

(d) $\mathrm{I_2(g) \rightarrow I_2(s)}$ (deposition)

(e) Heating a fixed sample of $\mathrm{Ar(g)}$ from 250 K to 400 K at constant volume.

(a) Positive. One mole of gas (CO_2) appears where the reactant side had none — moles of gas increase from 0 to 1.
(b) Negative. Moles of gas decrease from 3 ($2 + 1$) to 2.
(c) Positive. A rigid ionic lattice dissociates into freely moving, hydrated ions in solution — a large increase in accessible positions.
(d) Negative. Gas condenses directly into an ordered solid; particles lose the enormous freedom of the gas phase.
(e) Positive. Raising temperature at constant volume increases the number of thermally accessible translational energy levels.

(!) Lỗi thường gặp: "More moles of gas" compares the *gas-phase* mole count on each side only, not the total number of chemical species written (including solids and liquids). The reaction $\mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}$ has ΔS° governed almost entirely by the fact that gas moles stay the same ($1 \rightarrow 1$), so ΔS° for this reaction turns out to be small in magnitude (Section 9.2, Practice Problem) — the solid reactant's disappearance barely affects the total, even though the number of terms in the equation changes.

9.2 Absolute entropy and entropy change

The **third law of thermodynamics** states that a perfect crystal at exactly 0 K has zero entropy, $S = 0$: at absolute zero, a perfectly ordered crystalline solid has only one possible microstate (every particle locked into its single lowest-energy configuration), so there is no positional or energetic disorder left to count. Because entropy has this unambiguous zero point, every pure substance has a well-defined,

measurable **absolute (standard molar) entropy**, S°, at any other temperature (conventionally 298 K, 1 atm) — unlike enthalpy, which has no natural zero and is reported only as differences or relative to a defined reference state.

> [Absolute entropy versus enthalpy of formation] Because every substance's entropy is measured from the same absolute zero point, **standard molar entropies S° are always positive numbers** — including for elements in their standard states. This is fundamentally different from standard enthalpies of formation ΔH_f°, which are defined to be exactly zero for elements in their standard states purely as a bookkeeping convention with no absolute physical zero point. **Never set $S^\circ = 0$ for an element** in an entropy calculation — only $\Delta H_f^\circ = 0$ for elements, never S°.

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Định luật III nhiệt động lực học: một tinh thể hoàn hảo ở 0 K có entropy bằng 0 (chỉ có duy nhất một cách sắp xếp vi mô). Nhờ điểm gốc tuyệt đối này, mọi chất đều có entropy tuyệt đối S° xác định — khác với ΔH_f° vốn chỉ là quy ước tương đối, quy định bằng 0 cho đơn chất. **Lưu ý quan trọng:** S° của đơn chất KHÔNG bằng 0 — chỉ có ΔH_f° của đơn chất mới bằng 0; S° luôn là một số dương.

The entropy change of a reaction, $\Delta S^\circ_{\text{rxn}}$, is calculated from tabulated absolute entropies using the same Hess's-law-style pattern used for $\Delta H^\circ_{\text{rxn}}$ from formation enthalpies:

$$\boxed{\Delta S^\circ_{\text{rxn}} = \sum n_p\, S^\circ(\text{products}) - \sum n_r\, S^\circ(\text{reactants})}$$

where n_p and n_r are the coefficients from the balanced equation.

Species	S° (J/(mol·K))	Species	S° (J/(mol·K))
$O_2(g)$	205.0	$CO_2(g)$	213.7
$H_2(g)$	130.6	$NH_3(g)$	192.3
$N_2(g)$	191.6	C(graphite, s)	5.7
$H_2O(l)$	69.9	C(diamond, s)	2.4
$H_2O(g)$	188.8		

Standard molar entropies S° at 298 K, 1 atm. Every value is positive, including for the elements H_2, N_2, O_2, and both carbon allotropes.

Calculating $\Delta S^\circ_{\text{rxn}}$ from tabulated entropies

Calculate ΔS° for the Haber synthesis of ammonia, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.

$$\Delta S^\circ = [2\, S^\circ(NH_3)] - [S^\circ(N_2) + 3\, S^\circ(H_2)]$$

$$\Delta S^\circ = [2(192.3)] - [191.6 + 3(130.6)] = 384.6 - (191.6 + 391.8) = 384.6 - 583.4$$

$$\boxed{\Delta S^\circ = -198.8 \text{ J/(mol·K)}}$$

The large negative value makes physical sense: 4 mol of gas (reactants) become 2 mol of gas (product) — the reaction sharply reduces the number of independently moving gas particles, so the system becomes markedly less disordered.

9.3 Gibbs free energy, ΔG, and thermodynamic favorability

Whether a process occurs spontaneously — proceeding on its own in the direction written, without continuous outside intervention — depends on both its enthalpy change and its entropy change, together with the temperature. Combining these gives the **Gibbs free energy** change for a process at constant temperature and pressure:

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

with T in kelvin. ΔG packages the full spontaneity criterion (an increase in the entropy of the universe) into a single quantity evaluated using only properties of the reacting *system* — ΔH and ΔS of the reaction itself — because the $-T\Delta S$ term stands in for the entropy change of the surroundings.

[The spontaneity criterion]

- $\Delta G < 0$: the process is **thermodynamically favorable (spontaneous) as written**, at the specified temperature.
- $\Delta G > 0$: the process as written is **not** favorable at that temperature — the *reverse* process is favorable instead.
- $\Delta G = 0$: the system is at **equilibrium**, with no net driving force in either direction (Section 9.5).

Because $\Delta G = \Delta H - T\Delta S$ contains a temperature-dependent term, favorability can depend on temperature. There are four possible sign combinations of ΔH and ΔS:

ΔH	ΔS	Sign of ΔG	Favorable at…
$-$ (exothermic)	$+$ (increases)	always negative	**all temperatures**
$+$ (endothermic)	$-$ (decreases)	always positive	**no temperature**
$-$ (exothermic)	$-$ (decreases)	negative only if $T < \Delta H/\Delta S$	**low temperatures only**
$+$ (endothermic)	$+$ (increases)	negative only if $T > \Delta H/\Delta S$	**high temperatures only**

Sign of $\Delta G = \Delta H - T\Delta S$ for each combination of ΔH and ΔS signs. The two mixed cases have a crossover temperature $T = \Delta H/\Delta S$ where ΔG changes sign.

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$\Delta G = \Delta H - T\Delta S$ kết hợp cả enthalpy và entropy để dự đoán chiều thuận lợi nhiệt động của phản ứng. $\Delta G < 0$: phản ứng thuận lợi (tự diễn biến) theo chiều đã viết; $\Delta G > 0$: chiều ngược lại mới thuận lợi; $\Delta G = 0$: cân bằng. Có 4 trường hợp dấu: (1) $\Delta H < 0, \Delta S > 0$ — luôn thuận lợi mọi nhiệt độ; (2) $\Delta H > 0, \Delta S < 0$ — không bao giờ thuận lợi; (3) $\Delta H < 0, \Delta S < 0$ — chỉ thuận lợi ở nhiệt độ thấp; (4) $\Delta H > 0, \Delta S > 0$ — chỉ thuận lợi ở nhiệt độ cao. Nhiệt độ chuyển tiếp (nơi $\Delta G = 0$) là $T = \Delta H/\Delta S$.

Calculating ΔG at a given temperature and classifying favorability

For the Haber synthesis, $\Delta H^\circ = -92.0$ kJ/mol and (Section 9.2) $\Delta S^\circ = -198.8$ J/(mol K). Calculate ΔG° at 298 K, classify the sign combination, and state whether the forward reaction is favorable.

Convert to consistent units: $\Delta H^\circ = -92{,}000$ J/mol.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92{,}000 - (298)(-198.8) = -92{,}000 + 59{,}242$$

$$\boxed{\Delta G^\circ = -32{,}758 \text{ J/mol} = -32.76 \text{ kJ/mol}}$$

Since $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, this is the "favorable at low temperature only" case. At 298 K, $\Delta G^\circ < 0$, so ammonia formation **is** thermodynamically favorable at room temperature.

Finding the crossover temperature where $\Delta G = 0$

Using the same Haber data, find the temperature above which the forward reaction stops being favorable.

At the crossover temperature, $\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$, so

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-92{,}000 \text{ J/mol}}{-198.8 \text{ J/(mol K)}}$$

$$\boxed{T = 462.8 \text{ K } (189.6^\circ\text{C})}$$

Below 462.8 K, $\Delta G^\circ < 0$ and ammonia formation is favorable; above it, $\Delta G^\circ > 0$ and decomposition back to N_2 and H_2 becomes the favorable direction instead. Industrially, the Haber process nonetheless runs at 450–500°C — well above this crossover — for reasons explored in Section 9.4.

9.4 Thermodynamic versus kinetic control

A negative ΔG guarantees only that a reaction is thermodynamically **favorable**: that products are more stable than reactants under the stated conditions, so the system will move toward products given enough time. It says nothing about *how fast* that motion happens. Reaction rate is governed by kinetics — specifically by the activation energy E_a, the height of the barrier the system must climb on its way from reactants to products, regardless of how far downhill the products ultimately sit. A reaction with a very negative ΔG can still be immeasurably slow at a given temperature if E_a is large, because ΔG (a difference between two energy *states*) carries no information about the *path* connecting them.

Kinetic vs. thermodynamic control: diamond and graphite

Converting diamond to graphite, $\text{C(diamond, s)} \rightarrow \text{C(graphite, s)}$, is thermodynamically favorable at every ordinary temperature. Using $\Delta H^\circ = -1.90$ kJ/mol (graphite is very slightly lower in enthalpy) and, from the Section 9.2 table, $\Delta S^\circ = S^\circ(\text{graphite}) - S^\circ(\text{diamond}) = 5.7 - 2.4 = +3.3$ J/(mol K) $= 0.0033$ kJ/(mol K):

$$\Delta G^\circ_{298} = -1.90 - (298)(0.0033) = -1.90 - 0.98 = -2.88 \text{ kJ/mol}.$$

Since $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$, this reaction is favorable at **all** temperatures (Section 9.3, case 1) — graphite is the thermodynamically more stable form of carbon. Yet diamonds do not visibly turn into graphite on a jeweler's shelf, or even over a human lifetime: converting the rigid three-dimensional network of strong covalent C — C bonds in diamond into graphite's stacked planar sheets requires breaking a very large number of strong bonds nearly simultaneously, giving this transformation an enormous activation energy. At room temperature essentially no atoms have enough thermal energy to surmount that barrier, so the reaction proceeds at a rate indistinguishable from zero — **thermodynamically favorable but kinetically forbidden** under ordinary conditions.

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$\Delta G < 0$ chỉ cho biết phản ứng **thuận lợi về mặt nhiệt động** (sản phẩm bền hơn chất đầu), KHÔNG cho biết phản ứng nhanh hay chậm — tốc độ phụ thuộc hoàn toàn vào năng lượng hoạt hoá E_a (yếu tố động học). Ví dụ kinh điển: kim cương chuyển thành than chì có $\Delta G^\circ < 0$ ở mọi nhiệt độ (thuận lợi), nhưng E_a cực lớn (phải phá vỡ rất nhiều liên kết cộng hoá trị bền cùng lúc) khiến phản ứng không quan sát được ở nhiệt độ phòng — thuận lợi về nhiệt động nhưng bị "khoá" về động học.

This tension between favorability and rate also explains a puzzle from Section 9.3: the Haber process is favorable only below 462.8 K (189.6°C), yet industrial plants run it at 450–500°C — above the crossover temperature, where $\Delta G^\circ > 0$. The higher temperature is chosen for **kinetic**, not thermodynamic, reasons: at lower temperature the reaction is more favorable but proceeds far too slowly (even with an iron catalyst) to be industrially useful, since breaking the very strong N $\equiv$ N triple bond requires substantial activation energy. Engineers accept a smaller equilibrium yield per pass — a consequence of operating above the crossover temperature — in exchange for a commercially viable rate, then improve overall output by continuously removing NH_3 and recycling unreacted gases. This is a practical illustration that industrial conditions are chosen by balancing thermodynamic favorability against kinetic feasibility, not by thermodynamics alone.

(!) Lỗi thường gặp: Do not equate "$\Delta G < 0$" with "fast," or "$\Delta G > 0$" with "slow." Favorability (thermodynamics) and rate (kinetics) are governed by entirely different quantities: ΔG depends only on the energies of the initial and final states, while rate depends on E_a, the height of the barrier between them. A reaction can be slow and favorable (diamond $\rightarrow$ graphite), fast and favorable (most exothermic reactions with low barriers, once ignited), or slow and unfavorable (most "shelf-stable" substances) — thermodynamic favorability and kinetic speed must always be evaluated independently.

9.5 Free energy and equilibrium

ΔG° — the free energy change under standard conditions (all species at 1 M or 1 atm, 298 K) — is directly related to the equilibrium constant K of a reaction:

$$\boxed{\Delta G^\circ = -RT \ln K}$$

with $R = 8.314$ J/(mol K), T in kelvin, and K dimensionless. This equation bridges the thermodynamic quantity ΔG° and the equilibrium quantity K: each can be calculated directly from the other.

[Reading the ΔG°–K relationship]

- Very negative $\Delta G^\circ \Rightarrow$ large positive $\ln K \Rightarrow K \gg 1$: at equilibrium, products are strongly favored.
- Very positive $\Delta G^\circ \Rightarrow$ large negative $\ln K \Rightarrow K \ll 1$: at equilibrium, reactants are strongly favored.
- $\Delta G^\circ = 0 \Rightarrow \ln K = 0 \Rightarrow K = 1$: products and reactants are equally favored at equilibrium.

More generally, at any composition, $\Delta G = \Delta G^\circ + RT \ln Q$, where Q is the reaction quotient for the system's *current* composition. As a reaction proceeds, Q moves toward K; the reaction continues spontaneously in whichever direction drives Q toward K — which is exactly why $\Delta G \neq 0$ away from equilibrium. Precisely at equilibrium, $Q = K$, so $\Delta G = \Delta G^\circ + RT \ln K = \Delta G^\circ - \Delta G^\circ = 0$, recovering the equilibrium criterion of Section 9.3 and confirming that $\Delta G^\circ = -RT \ln K$ is the special case of $\Delta G = \Delta G^\circ + RT \ln Q$ evaluated at $Q = K$.

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$\Delta G^\circ = -RT \ln K$ liên hệ trực tiếp năng lượng tự do chuẩn với hằng số cân bằng: ΔG° càng âm thì K càng lớn (sản phẩm chiếm ưu thế lúc cân bằng); ΔG° càng dương thì K càng nhỏ; $\Delta G^\circ = 0$ thì $K = 1$. Ở điều kiện không chuẩn, $\Delta G = \Delta G^\circ + RT \ln Q$; phản ứng tiếp tục tự diễn biến theo chiều đưa Q tiến về K, và $\Delta G = 0$ chính xác khi $Q = K$ (tại cân bằng).

Finding K from ΔG°

Using $\Delta G^\circ = -32.76$ kJ/mol found in Section 9.3 for the Haber synthesis at 298 K, find K.

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{32{,}760 \text{ J/mol}}{(8.314 \text{ J/(mol K)})(298 \text{ K})} = \frac{32{,}760}{2477.6} = 13.22$$

$$K = e^{13.22}$$

$$\boxed{K \approx 5.5 \times 10^5}$$

The large K confirms strongly favored products at equilibrium, consistent with the negative ΔG° — even though (Section 9.4) the reaction is far too slow at 298 K to reach that equilibrium in any practical time without a catalyst and elevated temperature.

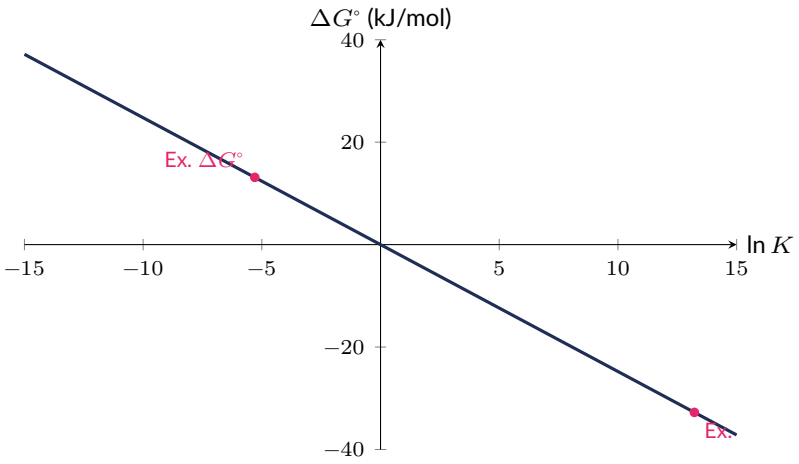
Finding ΔG° from K

A reaction has $K = 5.0 \times 10^{-3}$ at 298 K. Find ΔG°.

$$\Delta G^\circ = -RT \ln K = -(8.314)(298) \ln(5.0 \times 10^{-3}) = -(2477.6)(-5.298)$$

$$\boxed{\Delta G^\circ = +13{,}130 \text{ J/mol} = +13.1 \text{ kJ/mol}}$$

The positive ΔG° is consistent with $K < 1$: at equilibrium this mixture favors reactants.



ΔG° versus $\ln K$ at 298 K: a straight line through the origin with slope $-RT = -2.478$ kJ/mol per unit $\ln K$. Both worked examples above fall exactly on this single universal line, since $\Delta G^\circ = -RT \ln K$ holds at fixed T regardless of the reaction involved.

9.6 Coupled reactions

Because ΔG is a state function, free energy changes for two (or more) reactions occurring together can simply be **added**, exactly as enthalpies are added in Hess's law. This underlies **coupled reactions**: a thermodynamically unfavorable reaction (positive ΔG) can be driven forward by pairing it with

a strongly favorable one (sufficiently negative ΔG), provided the two reactions share a common intermediate species that cancels when the equations are summed — so the overall coupled process has a net negative ΔG, even though one component reaction is individually unfavorable.

Coupling in metal extraction

Many metals occur naturally as oxides, and extracting the free metal requires reducing the oxide, $\mathrm{MO(s)} \rightarrow \mathrm{M(s)} + \frac{1}{2}\mathrm{O_2(g)}$ — a process with a strongly positive ΔG on its own, since metal oxides are generally far more thermodynamically stable than the free metal plus oxygen gas. Smelting furnaces drive this unfavorable step forward by coupling it to the combustion of carbon (coke), $\mathrm{C(s)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO(g)}$, which has a strongly negative ΔG: the $\mathrm{O_2}$ released by the oxide's decomposition is immediately consumed by carbon's combustion, and summing the two free-energy changes can turn an otherwise unfavorable extraction into a net-favorable coupled process.

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Vì ΔG là hàm trạng thái, có thể **cộng** ΔG của nhiều phản ứng lại (giống định luật Hess với ΔH). Phản ứng ghép cặp (coupled reactions): một phản ứng bất lợi ($\Delta G > 0$) có thể được "kéo" theo chiều thuận lợi nếu ghép với một phản ứng khác đủ thuận lợi (ΔG rất âm), miễn là hai phản ứng có chung một tiểu phân trung gian triệt tiêu khi cộng phương trình. Ví dụ kinh điển: khử oxit kim loại (bất lợi) ghép với đốt cháy than cốc thành CO (rất thuận lợi) trong luyện kim.

Coupled-reaction ΔG addition

The reduction of a metal oxide, $\mathrm{MO(s)} \rightarrow \mathrm{M(s)} + \frac{1}{2}\mathrm{O_2(g)}$, has $\Delta G^\circ = +120.0$ kJ/mol at the furnace operating temperature. This is coupled with the combustion of carbon to carbon monoxide, $\mathrm{C(s)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO(g)}$, for which $\Delta G^\circ = -137.2$ kJ/mol (a well-established real value near 298 K, applied here at process temperature for illustration). Find ΔG° for the coupled overall reaction and state whether it is favorable.

Adding the two equations (the $\frac{1}{2}\mathrm{O_2(g)}$ released by the first is exactly consumed by the second, so it cancels):

$$\mathrm{MO(s)} \rightarrow \mathrm{M(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \qquad \Delta G_1^\circ = +120.0 \text{ kJ/mol}$$

$$\mathrm{C(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO(g)} \qquad \Delta G_2^\circ = -137.2 \text{ kJ/mol}$$

$$\mathrm{MO(s)} + \mathrm{C(s)} \rightarrow \mathrm{M(s)} + \mathrm{CO(g)} \qquad \Delta G^\circ_{\text{overall}} = \Delta G_1^\circ + \Delta G_2^\circ$$

$$\boxed{\Delta G^\circ_{\text{overall}} = 120.0 + (-137.2) = -17.2 \text{ kJ/mol}}$$

Although the direct reduction of MO is unfavorable on its own ($\Delta G_1^\circ > 0$), coupling it with carbon's combustion to CO makes the overall two-step process favorable — the thermodynamic principle underlying carbothermic metal extraction.

9.7 Galvanic (voltaic) and electrolytic cells

Electrochemistry connects redox chemistry (reactions in which electrons transfer from one species to another) to electrical work. Two complementary types of electrochemical cell physically separate the oxidation and reduction half-reactions into two distinct compartments (**half-cells**), forcing the transferred electrons to travel through an external wire rather than passing directly between species in solution.

- A **galvanic (voltaic) cell** houses a spontaneous redox reaction ($\Delta G < 0$) and harnesses the electron flow it produces to do useful electrical work — the operating principle of batteries.

- An **electrolytic cell** uses an external power source (electrical work supplied from outside) to force a nonspontaneous redox reaction ($\Delta G > 0$) to occur — the basis of electrolysis (Section 9.10) and electroplating.

In **both** cell types, the same vocabulary applies: the **anode** is the electrode where **oxidation** occurs (electrons are released into the external circuit), and the **cathode** is the electrode where **reduction** occurs (electrons are consumed from the external circuit). A useful mnemonic: *An Ox, Red Cat* — ANode = OXidation, REDuction = CAThode.

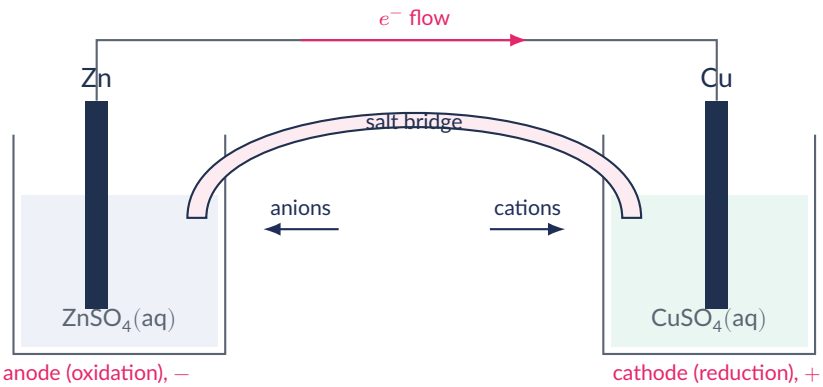
(!) Lỗi thường gặp: Electrode *polarity* (which terminal is "+" and which is "−") is **opposite** between the two cell types, even though the anode/cathode = oxidation/reduction assignment never changes. In a **galvanic** cell, the cathode is the positive terminal (electrons flow toward it through the external circuit) and the anode is negative. In an **electrolytic** cell, the external power source forces electrons *into* the cathode and withdraws them *from* the anode, so the cathode connects to the source's negative terminal and the anode to its positive terminal. Anode = oxidation and cathode = reduction remain true in every case; only the sign of the terminal switches.

VN **GIẢI THÍCH TIẾNG VIỆT**
Pin điện hoá (galvanic/voltaic cell) chứa phản ứng oxi hoá-khử tự phát ($\Delta G < 0$), dùng dòng electron sinh ra để sinh công điện. Bình điện phân (electrolytic cell) dùng nguồn điện ngoài để ép một phản ứng bất lợi ($\Delta G > 0$) xảy ra. Ở CẢ HAI loại: anode luôn là nơi oxi hoá, cathode luôn là nơi khử (ghi nhớ "An Ox, Red Cat"). Tuy nhiên cực dương/âm thì NGƯỢC nhau: ở pin galvanic, cathode là cực dương; ở bình điện phân, cathode nối cực âm của nguồn điện ngoài.

9.7.1 Cell construction, the salt bridge, and standard notation

A typical galvanic cell — the classic Zn/Cu **Daniell cell** — places a zinc electrode in $ZnSO_4(aq)$ and a copper electrode in $CuSO_4(aq)$, in two separate beakers connected by (1) an external wire joining the electrodes and (2) a **salt bridge**, a tube of inert electrolyte (e.g., KNO_3 in a gel) connecting the two solutions. At the zinc anode, $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; the released electrons travel through the wire to the copper cathode, where $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$.

Without the salt bridge, charge would rapidly build up in each compartment — the anode side accumulating excess positive charge as Zn^{2+} forms, the cathode side accumulating excess negative charge as Cu^{2+} is consumed — and current would stop almost immediately. The salt bridge maintains **electroneutrality** in both half-cells: anions migrate through it toward the anode compartment (balancing the growing Zn^{2+} concentration), and cations migrate toward the cathode compartment (replacing consumed Cu^{2+}), completing the circuit without letting the two solutions mix directly.



The Zn/Cu Daniell cell. Oxidation ($Zn \rightarrow Zn^{2+} + 2e^-$) at the anode releases electrons that travel through the external wire to the cathode, where reduction ($Cu^{2+} + 2e^- \rightarrow Cu$) occurs. The salt bridge carries anions toward the anode compartment and cations toward the cathode compartment, preserving electroneutrality as the cell operates.

Cells are described compactly with **standard cell notation**, read left to right: anode → anode solution → (salt bridge) → cathode solution → cathode. A single vertical line, |, marks a phase boundary; a double vertical line, ‖, marks the salt bridge. For the Daniell cell:

$$\mathrm{Zn(s)} \mid \mathrm{Zn^{2+}(aq)} \parallel \mathrm{Cu^{2+}(aq)} \mid \mathrm{Cu(s)}.$$

Identifying anode and cathode from standard cell notation

The cell $\mathrm{Pb(s)} \mid \mathrm{Pb^{2+}(aq)} \parallel \mathrm{Ag^{+}(aq)} \mid \mathrm{Ag(s)}$ is built from $E^\circ(\mathrm{Pb^{2+}/Pb} = -0.13$ V and $E^\circ(\mathrm{Ag^{+}/Ag}) = +0.80$ V. Identify the anode and cathode, write the half-reactions and overall balanced equation, and calculate E°_{cell}.

The species written on the **left** of the notation is the anode, on the **right** is the cathode — consistent here with the thermodynamics, since the more positive reduction potential ($\mathrm{Ag^{+}/Ag}$) identifies the spontaneous cathode:

$$\text{Anode (oxidation):} \quad \mathrm{Pb(s) \rightarrow Pb^{2+}(aq) + 2e^{-}}$$

$$\text{Cathode (reduction, } \times 2\text{):} \quad \mathrm{2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)}$$

$$\text{Overall:} \quad \mathrm{Pb(s) + 2Ag^{+}(aq) \rightarrow Pb^{2+}(aq) + 2Ag(s)}, \qquad n = 2$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 - (-0.13) = \boxed{+0.93\ \text{V}}$$

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Ký hiệu pin chuẩn viết từ trái sang phải: anode → dung dịch anode ‖ (cầu muối) ‖ dung dịch cathode → cathode. Dấu "|" là ranh giới pha, dấu "‖" là cầu muối. Chất bên trái luôn là anode (oxi hoá), chất bên phải luôn là cathode (khử).

9.8 Cell potential and free energy

Each half-reaction has an intrinsic tendency to occur as a **reduction**, quantified by its **standard reduction potential**, E°, in volts, measured against the standard hydrogen electrode ($E^\circ = 0.00$ V for $\mathrm{2H^{+} + 2e^{-} \rightarrow H_2}$, by definition). A more positive E° means a stronger pull toward reduction (that species is a better oxidizing agent); a more negative E° means it is harder to reduce (its reduced form is a better reducing agent).

Half-reaction (reduction)	E° (V)
$\mathrm{F_2 + 2e^{-} \rightarrow 2F^{-}}$	$+2.87$
$\mathrm{MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O}$	$+1.51$
$\mathrm{Cl_2 + 2e^{-} \rightarrow 2Cl^{-}}$	$+1.36$
$\mathrm{O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O}$	$+1.23$
$\mathrm{Ag^{+} + e^{-} \rightarrow Ag}$	$+0.80$
$\mathrm{Cu^{2+} + 2e^{-} \rightarrow Cu}$	$+0.34$
$\mathrm{2H^{+} + 2e^{-} \rightarrow H_2}$	0.00
$\mathrm{Pb^{2+} + 2e^{-} \rightarrow Pb}$	-0.13
$\mathrm{Ni^{2+} + 2e^{-} \rightarrow Ni}$	-0.26
$\mathrm{Fe^{2+} + 2e^{-} \rightarrow Fe}$	-0.44
$\mathrm{Zn^{2+} + 2e^{-} \rightarrow Zn}$	-0.76
$\mathrm{Al^{3+} + 3e^{-} \rightarrow Al}$	-1.66
$\mathrm{Mg^{2+} + 2e^{-} \rightarrow Mg}$	-2.37
$\mathrm{Na^{+} + e^{-} \rightarrow Na}$	-2.71
$\mathrm{Li^{+} + e^{-} \rightarrow Li}$	-3.04

Standard reduction potentials at 298 K, ordered from most easily reduced (strongest oxidizing agent, top) to least easily reduced (strongest reducing agent in its reduced form, bottom) — a standard electrochemical activity series.

The **standard cell potential** for any pairing of two half-reactions is

$$\boxed{E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}}$$

where *both* potentials are looked up as **reduction** potentials — never flip the sign of either table value, even though the anode reaction physically runs in reverse (as an oxidation); the reversal is already accounted for by the subtraction itself. To identify the cathode, choose the half-reaction with the **more positive** (or less negative) E°; it runs as written (reduction), while the other runs in reverse (oxidation) as the anode.

[Predicting galvanic versus electrolytic behavior] Pairing two half-reactions so the more positive potential becomes the cathode **always** gives $E^\circ_{\text{cell}} > 0$ — guaranteed by construction, since subtracting a smaller (more negative) value from a larger one is always positive. A **specific** reaction, written in a **specific** direction, is spontaneous (galvanic) only if $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ evaluated *for that direction* is positive; if the reaction as written corresponds to $E^\circ_{\text{cell}} < 0$, that specific process is nonspontaneous and requires electrolysis to proceed.

Determining E°_{cell} and classifying galvanic vs. electrolytic

Two half-cells are available: Al^{3+}/Al ($E^\circ = -1.66$ V) and Cu^{2+}/Cu ($E^\circ = +0.34$ V). Determine the spontaneous combination, calculate E°_{cell}, write the balanced overall equation with n, and classify the cell.

Cu^{2+}/Cu has the more positive potential, so it is the **cathode**; Al^{3+}/Al is the **anode** (oxidized):

$$E^\circ_{\text{cell}} = 0.34 - (-1.66) = \boxed{+2.00\ \text{V}}$$

Balancing electrons (Al loses $3e^-$; Cu^{2+} gains $2e^-$; LCM $= 6$):

$$2\text{Al(s)} \rightarrow 2\text{Al}^{3+}\text{(aq)} + 6\text{e}^-, \qquad 3\text{Cu}^{2+}\text{(aq)} + 6\text{e}^- \rightarrow 3\text{Cu(s)}$$

$$\text{Overall:}\quad 2\text{Al(s)} + 3\text{Cu}^{2+}\text{(aq)} \rightarrow 2\text{Al}^{3+}\text{(aq)} + 3\text{Cu(s)}, \qquad n = 6$$

Since $E^\circ_{\text{cell}} = +2.00\ \text{V} > 0$, this reaction is spontaneous as written: a **galvanic (voltaic) cell**. Forcing Cu to be oxidized by Al^{3+} (the reverse reaction) would give $E^\circ_{\text{cell}} = -2.00$ V and would require electrolysis.

The free energy change and cell potential are directly proportional:

$$\boxed{\Delta G^\circ = -nFE^\circ_{\text{cell}}}$$

where $F = 96{,}485$ C/mol (Faraday's constant, the charge on one mole of electrons) and n is the number of moles of electrons transferred, taken from the **fully balanced overall equation** — not from either half-reaction alone, since the two half-reactions may need different integer multiples to make their electron counts match (as above, where $n = 6$, not 2 or 3). A positive E°_{cell} always gives a negative ΔG° and a large $K > 1$: E°_{cell}, ΔG°, and K always agree on whether a reaction is favorable.

(!) Lỗi thường gặp: Two sign errors are especially common with $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. First, do not flip the sign of a negative anode potential before subtracting — the formula already handles this correctly, since subtracting a negative number correctly *adds* its magnitude, as in $0.34 - (-1.66) = +2.00$. Second, do not compute anode − cathode instead of cathode

– anode: this gives the right magnitude but the wrong sign, silently flipping a spontaneous cell into an apparently nonspontaneous one, or vice versa. Always identify the cathode (more positive E°) first, then subtract the anode's value — never the reverse order.

Calculating ΔG° from E°_{cell}

For the Daniell cell, $\text{Zn(s)} + \text{Cu}^{2+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{Cu(s)}$, $E^\circ_{\text{cell}} = 0.34 - (-0.76) = +1.10$ V, with $n = 2$. Find ΔG°.

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(2)(96{,}485\ \text{C/mol})(1.10\ \text{V})$$

$$\boxed{\Delta G^\circ = -212{,}267\ \text{J/mol} = -212.3\ \text{kJ/mol}}$$

The large negative ΔG° confirms a strongly favorable, essentially irreversible galvanic reaction, consistent with the large positive E°_{cell}.

VN **GIẢI THÍCH TIẾNG VIỆT**

$E^\circ_{\text{pin}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ (luôn lấy cả hai giá trị dưới dạng thế khử, không đảo dấu). Nếu $E^\circ_{\text{pin}} > 0$: phản ứng tự phát (pin galvanic); nếu < 0: cần điện phân. Liên hệ với năng lượng tự do: $\Delta G^\circ = -nFE^\circ$, với n là số mol electron trao đổi lấy từ PHƯƠNG TRÌNH TỔNG đã cân bằng, không phải từ một trong hai nửa phản ứng riêng lẻ. E°_{pin}, ΔG°, và K luôn thống nhất về chiều thuận lợi của phản ứng.

9.9 Cell potential under nonstandard conditions

Standard cell potentials apply only when every species is at standard conditions. Real cells almost always operate away from these conditions, and E_{cell} changes accordingly. The **Nernst equation** extends the relationship to any composition, described by the reaction quotient Q:

$$\boxed{E = E^\circ - \frac{RT}{nF}\ln Q}$$

At 298 K, converting ln to $\log_{10}$ and evaluating the constants gives the commonly used working form:

$$\boxed{E = E^\circ - \frac{0.0592}{n}\log Q \quad \text{(at 298 K)}}$$

Q is built from the balanced overall equation exactly as always — products over reactants, each raised to its coefficient, with pure solids and liquids omitted.

(!) Lỗi thường gặp: The constant 0.0592 is valid **only at 298 K** — it is a numerical shortcut for $2.303RT/F$ at that specific temperature, not a universal constant. At any other temperature, recompute $2.303RT/F$, or use the original natural-log form $E = E^\circ - (RT/nF)\ln Q$. Also, do not confuse the reaction quotient Q in the Nernst equation with the electric charge Q in Faraday's law (Section 9.10) — both are conventionally written Q, but they are entirely different quantities.

Applying the Nernst equation

A cell, $\text{Zn(s)} \mid \text{Zn}^{2+}\text{(aq, 0.0100 M)} \parallel \text{Cu}^{2+}\text{(aq, 1.50 M)} \mid \text{Cu(s)}$, has $E^\circ_{\text{cell}} = 1.10$ V, $n = 2$. Find E_{cell} at 298 K.

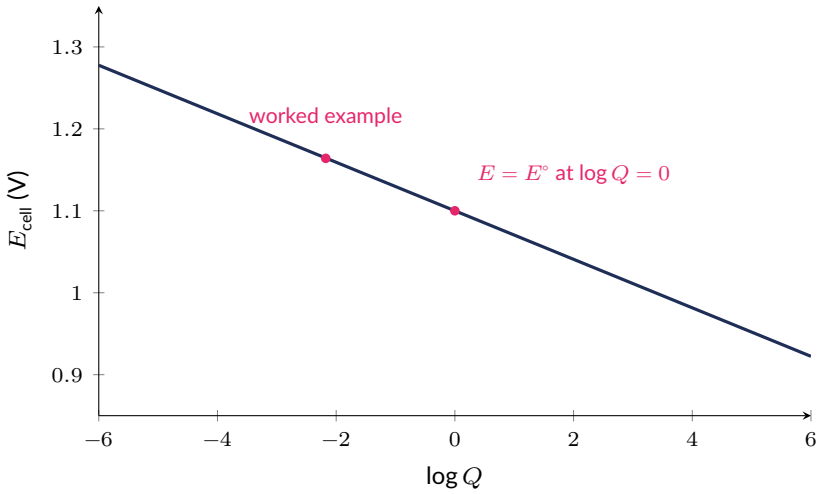
For $\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$ (solids omitted from Q):

$$Q = \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]} = \frac{0.0100}{1.50} = 6.67 \times 10^{-3}, \qquad \log Q = -2.176$$

$$E = 1.10 - \frac{0.0592}{2}(-2.176) = 1.10 + 0.0644$$

$$\boxed{E = 1.164\ \mathrm{V}}$$

E exceeds E° because $Q < 1$: the lower-than-standard $[\mathrm{Zn^{2+}}]$ and higher-than-standard $[\mathrm{Cu^{2+}}]$ both push the system further from equilibrium in the forward direction, increasing the driving force.



E_{cell} versus $\log Q$ for the Zn/Cu cell ($E^\circ = 1.10$ V, $n = 2$): a straight line of slope $-0.0592/n = -0.0296$ V per unit $\log Q$, passing through $E = E^\circ$ at $\log Q = 0$.

As a galvanic cell operates, reactants are consumed and products accumulate, so Q steadily increases; the Nernst equation shows E_{cell} correspondingly **decreases**. This continues until $Q = K$ (equilibrium), where $E_{\mathrm{cell}} = 0$ — the cell is "dead," with no further driving force, consistent with $\Delta G = 0$ at equilibrium (Section 9.5). This is exactly what happens as a battery discharges: its voltage gradually drops, reaching zero once the internal reaction reaches equilibrium.

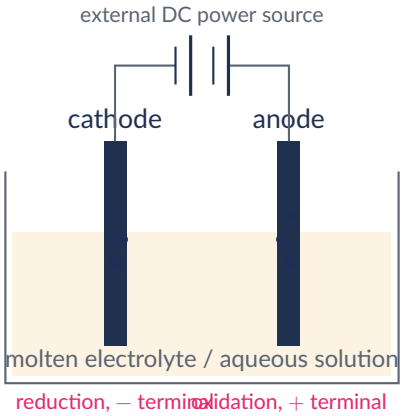
A special case is the **concentration cell**, built from the *same* electrode/ion couple in both half-cells at different concentrations, so $E^\circ_{\mathrm{cell}} = 0$ (the two standard reduction potentials are identical and cancel). Any voltage produced comes entirely from the concentration difference, driving the system toward equalizing the two concentrations — the more concentrated half-cell acts as the cathode, since depositing metal there lowers its ion concentration back toward the dilute side's value.

VN GIẢI THÍCH TIẾNG VIỆT

Phương trình Nernst mở rộng E° sang điều kiện không chuẩn: $E = E^\circ - \frac{RT}{nF}\ln Q$, hay ở 298 K: $E = E^\circ - \frac{0.0592}{n}\log Q$. Khi pin hoạt động, Q tăng dần tới K, làm E giảm dần về 0 (pin "hết điện", đúng lúc cân bằng, $\Delta G = 0$). Pin nồng độ (concentration cell) dùng cùng một cặp điện cực nhưng nồng độ khác nhau ở hai bên, có $E^\circ = 0$; điện thế sinh ra hoàn toàn do chênh lệch nồng độ, và nửa pin đặc hơn luôn đóng vai trò cathode.

9.10 Electrolysis and Faraday's law

An **electrolytic cell** uses an external DC power source to force electrons in the nonspontaneous direction, driving a reaction with $E^\circ_{\text{cell}} < 0$ (equivalently $\Delta G^\circ > 0$) forward. The source's negative terminal supplies electrons to the cathode (forcing reduction), while its positive terminal withdraws electrons from the anode (forcing oxidation) — the same anode-oxidation/cathode-reduction assignment as a galvanic cell, but with terminal polarities reversed (Section 9.7).



An electrolytic cell. The external power source forces electrons into the cathode (reduction) and withdraws them from the anode (oxidation) — note the terminal polarity is opposite that of a galvanic cell, even though anode = oxidation and cathode = reduction remain unchanged. Rising bubbles represent gaseous product forming at each electrode.

Electrolysis of a molten pure salt (e.g., molten NaCl, no water present) has only one species available to reduce and one to oxidize: at the cathode, $\text{Na}^+ + \text{e}^- \rightarrow \text{Na(l)}$; at the anode, $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$. **Electrolysis of an aqueous solution** is more subtle, because water itself can be oxidized or reduced, and may be preferentially involved instead of a dissolved ion. In aqueous NaCl electrolysis (the industrial chloralkali process), the cathode reaction is reduction of water, $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$, rather than reduction of Na^+ — consistent with the large gap between the reduction potentials of Na^+/Na (-2.71 V) and water (roughly -0.83 V under basic conditions), since water is far easier to reduce. At the anode, $\text{Cl}_2(\text{g})$ commonly forms from oxidation of Cl^- rather than O_2 from water, an outcome shaped both by the relatively high Cl^- concentration typically used and by kinetic (overpotential) effects that make water's oxidation slower in practice than a simple standard-potential comparison alone would predict.

VN **GIẢI THÍCH TIẾNG VIỆT**

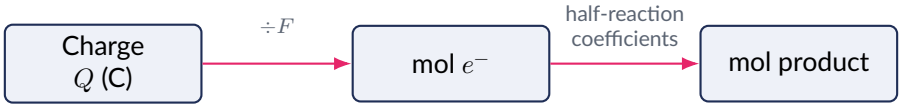
Bình điện phân dùng nguồn điện ngoài để ép phản ứng bất lợi xảy ra: cathode nối cực âm nguồn điện (khử), anode nối cực dương (oxi hoá) — ngược cực so với pin galvanic dù vai trò oxi hoá/khử không đổi. Điện phân muối nóng chảy (không có nước) chỉ có một khả năng khử/oxi hoá duy nhất. Điện phân dung dịch nước phức tạp hơn vì nước cũng có thể bị oxi hoá/khử — ví dụ điện phân dung dịch NaCl tạo H_2 ở cathode (khử nước, dễ hơn khử Na^+ rất nhiều) thay vì kim loại Na.

9.10.1 Faraday's law of electrolysis

The amount of chemical change produced by electrolysis is directly proportional to the total electric charge passed through the cell. **Faraday's law** links the measurable quantities current I (amps) and time t (seconds) to moles of electrons transferred, and from there — via half-reaction stoichiometry — to moles or mass of product:

$$\boxed{Q = It} \qquad \boxed{\text{mol } e^- = \frac{Q}{F}} \qquad F = 96{,}485 \text{ C/mol}$$

The half-reaction's coefficient on e^- then converts moles of electrons to moles of electrode product, which converts to mass using molar mass as usual.



Faraday's-law electrolysis calculation

A steady current of 2.50 A is passed through $CuSO_4(aq)$ for 1.00 hour, depositing copper via $Cu^{2+} + 2e^- \to Cu$. Find the mass of copper deposited (molar mass Cu $= 63.55$ g/mol).

$$Q = It = (2.50\ \text{A})(3600\ \text{s}) = 9000\ \text{C}$$

$$\text{mol } e^- = \frac{9000}{96{,}485} = 0.0933\ \text{mol}$$

$$\text{mol Cu} = 0.0933\ \text{mol } e^- \times \frac{1\ \text{mol Cu}}{2\ \text{mol } e^-} = 0.0466\ \text{mol}$$

$$\boxed{\text{mass Cu} = (0.0466\ \text{mol})(63.55\ \text{g/mol}) = 2.96\ \text{g}}$$

VN **GIẢI THÍCH TIẾNG VIỆT**

Định luật Faraday: điện lượng $Q = I \times t$ (C); số mol electron $= Q/F$; dùng hệ số của bán phản ứng để chuyển sang số mol chất sinh ra ở điện cực, rồi nhân khối lượng mol để ra khối lượng. Đây là bài toán tỉ lượng điện hoá cơ bản nhất trong điện phân.

[Electrochemistry summary]

- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ (both as reduction potentials); $E^\circ_{\text{cell}} > 0 \Leftrightarrow$ galvanic/spontaneous $\Leftrightarrow \Delta G^\circ < 0 \Leftrightarrow K > 1$.
- $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT \ln K$: three equivalent ways to describe how favorable a redox reaction is.
- $E = E^\circ - \dfrac{0.0592}{n} \log Q$ (at 298 K): cell potential at any composition; $E \to 0$ as $Q \to K$.
- $Q = It$, mol $e^- = Q/F$: bridges measurable current and time to moles of electrode product via half-reaction stoichiometry.

9.11 Practice Problems

Bài tập luyện tập

Which process below is accompanied by the largest positive ΔS?

(A) Freezing of liquid water

(B) $2NO_2(g) \to N_2O_4(g)$

(C) Dissolving solid NaCl in water

(D) $N_2(g) + 3H_2(g) \to 2NH_3(g)$

Lời giải chi tiết

(A) freezing: liquid → solid, $\Delta S < 0$. (B) 2 mol gas → 1 mol gas, $\Delta S < 0$. (D) 4 mol gas → 2 mol gas, $\Delta S < 0$. (C) an ionic lattice breaks into freely moving hydrated ions — a large positive

ΔS, and the only positive option here. **(C)**.

Bài tập luyện tập

Predict the sign of ΔS for each: (a) sublimation of dry ice, $CO_2(s) \rightarrow CO_2(g)$; (b) $3O_2(g) \rightarrow 2O_3(g)$; (c) mixing two ideal gases initially kept in separate connected chambers when the partition between them is removed; (d) condensation of steam to liquid water.

Lời giải chi tiết

(a) Positive — solid to gas is a large increase in accessible microstates.
(b) Negative — 3 mol gas become 2 mol gas.
(c) Positive — mixing increases the number of ways the particles of both gases can be arranged compared with keeping them separated.
(d) Negative — gas to liquid is a large decrease in accessible microstates.

Bài tập luyện tập

A sample of gas is compressed at constant temperature into a smaller volume. What happens to its entropy?

(A) Increases, because temperature is constant

(B) Decreases, because the gas molecules have fewer accessible positions

(C) Stays exactly the same

(D) Cannot be determined without knowing the gas's identity

Lời giải chi tiết

Compressing a gas confines its particles to a smaller volume, reducing the number of accessible positional microstates even though T (and hence average kinetic energy) is unchanged. **(B)**.

Bài tập luyện tập

Calculate ΔS° for $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ using the entropy table of Section 9.2.

Lời giải chi tiết

$$\Delta S^\circ = 2S^\circ(H_2O, g) - [2S^\circ(H_2) + S^\circ(O_2)] = 2(188.8) - [2(130.6) + 205.0]$$

$$\Delta S^\circ = 377.6 - (261.2 + 205.0) = 377.6 - 466.2 = \boxed{-88.6\ \text{J/(mol K)}}$$

Negative, as expected: 3 mol gas ($2\,H_2 + 1\,O_2$) form 2 mol gas ($2\,H_2O$).

Bài tập luyện tập

Calculate ΔS° for $C(\text{graphite, s}) + O_2(g) \rightarrow CO_2(g)$ using the entropy table of Section 9.2.

Lời giải chi tiết

$$\Delta S^\circ = S^\circ(CO_2) - [S^\circ(\text{C, graphite}) + S^\circ(O_2)] = 213.7 - (5.7 + 205.0) = 213.7 - 210.7$$

$$\boxed{\Delta S^\circ = +3.0 \text{ J/(mol K)}}$$

Small and positive, consistent with moles of gas staying the same ($1 \to 1$) — the small increase reflects CO_2's slightly higher molar entropy than O_2's, not a change in gas-mole count.

Bài tập luyện tập

Calculate ΔS° for $4NH_3(g) + 3O_2(g) \to 2N_2(g) + 6H_2O(g)$ using the entropy table of Section 9.2, and rationalize the sign using the moles-of-gas rule.

Lời giải chi tiết

$$\Delta S^\circ = [2S^\circ(N_2) + 6S^\circ(H_2O, g)] - [4S^\circ(NH_3) + 3S^\circ(O_2)]$$

$$= [2(191.6)+6(188.8)]-[4(192.3)+3(205.0)] = [383.2+1132.8]-[769.2+615.0] = 1516.0-1384.2$$

$$\boxed{\Delta S^\circ = +131.8 \text{ J/(mol K)}}$$

Positive, consistent with the moles-of-gas rule: reactant side has $4 + 3 = 7$ mol gas, product side has $2 + 6 = 8$ mol gas — a net increase of 1 mol gas.

Bài tập luyện tập

A reaction has $\Delta H^\circ = +128$ kJ/mol and $\Delta S^\circ = +35$ J/(mol K). (a) Calculate ΔG° at 298 K and state whether it is favorable. (b) Find the temperature above which it becomes favorable.

Lời giải chi tiết

(a) $\Delta G^\circ = 128{,}000 - (298)(35) = 128{,}000 - 10{,}430 = +117{,}570$ J/mol $= +117.6$ kJ/mol. Positive, so **not** favorable at 298 K (this is the $\Delta H > 0, \Delta S > 0$ case, favorable only at high T).

(b) $T = \dfrac{\Delta H^\circ}{\Delta S^\circ} = \dfrac{128{,}000}{35} = 3657$ K. This crossover temperature is extremely high — well beyond what is practically attainable for most chemical systems — so this reaction is essentially never favorable under realistic conditions despite technically having a high-temperature crossover.

Bài tập luyện tập

A reaction has $\Delta H^\circ = -55$ kJ/mol, $\Delta S^\circ = +12$ J/(mol K). Show that it is favorable at both 100 K and 500 K, and explain why no crossover temperature exists.

Lời giải chi tiết

$$\Delta G^\circ(100 \text{ K}) = -55{,}000 - (100)(12) = -56{,}200 \text{ J/mol} = -56.2 \text{ kJ/mol}$$

$$\Delta G^\circ(500 \text{ K}) = -55{,}000 - (500)(12) = -61{,}000 \text{ J/mol} = -61.0 \text{ kJ/mol}$$

Both negative. Since $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ is the sum of two negative contributions at *every* positive T — there is no positive-T solution to $\Delta G^\circ = 0$, so this reaction is favorable at all temperatures, and becomes *more* favorable (more negative ΔG°) as T increases.

Bài tập luyện tập

Thermal decomposition of limestone, $\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$, has $\Delta H^\circ = +178$ kJ/mol, $\Delta S^\circ = +160$ J/(mol K). (a) Is it favorable at 298 K? (b) At what temperature does it become favorable?

Lời giải chi tiết

(a) $\Delta G^\circ(298) = 178{,}000 - (298)(160) = 178{,}000 - 47{,}680 = +130{,}320$ J/mol $= +130.3$ kJ/mol. Positive — **not** favorable at 298 K.

(b) $T = \dfrac{178{,}000}{160} = 1112.5$ K $= 839.4^\circ$C. Above this temperature, decomposition becomes favorable — consistent with the strong heating (well above 800°C) required industrially to decompose limestone in a lime kiln.

Bài tập luyện tập

A reaction has $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$. It is thermodynamically favorable:

(A) at all temperatures

(B) at low temperatures only

(C) at high temperatures only

(D) at no temperature

Lời giải chi tiết

With $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, $-T\Delta S^\circ$ becomes an increasingly large *positive* term as T rises, eventually overwhelming the negative ΔH°; the reaction is favorable only while T is small enough that $T\Delta S^\circ$ (in magnitude) stays smaller than $|\Delta H^\circ|$. **(B).**

Bài tập luyện tập

Explain, in terms of ΔG and E_a, why a match must be struck to ignite the combustion of wood, even though wood combustion is enormously thermodynamically favorable (very negative ΔG).

Lời giải chi tiết

Wood combustion has a very negative ΔG (strongly favorable), but the reaction has a substantial activation energy E_a: at room temperature essentially no wood/$\mathrm{O_2}$ collisions carry enough energy to surmount this barrier, so the reaction proceeds at a negligible rate despite being thermodynamically favorable — it is kinetically inert under ordinary conditions. Striking a match supplies a localized burst of energy (friction/heat) that raises a small region of material over E_a, initiating combustion; the heat released by that initial reaction then supplies E_a to neighboring material, sustaining a sped-up, self-propagating reaction. This shows $\Delta G < 0$ is necessary but not sufficient for a reaction to be observed proceeding on a human timescale — kinetics (E_a) governs whether it actually happens.

Bài tập luyện tập

Which statement correctly relates the sign of ΔG to reaction rate?

(A) A more negative ΔG always corresponds to a faster reaction

(B) ΔG determines whether a reaction is favorable, not how fast it proceeds

(C) A reaction with $\Delta G > 0$ cannot occur at any measurable rate

(D) Reaction rate can be calculated directly from ΔG

Lời giải chi tiết

ΔG is a thermodynamic quantity depending only on initial and final states; reaction rate is a kinetic quantity depending on E_a (via the Arrhenius equation), which is unrelated to ΔG in general. **(B)**.

Bài tập luyện tập

A reaction has $\Delta G^\circ = +45.0$ kJ/mol at 298 K. Find K.

Lời giải chi tiết

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-45{,}000}{(8.314)(298)} = \frac{-45{,}000}{2477.6} = -18.16$$

$$\boxed{K = e^{-18.16} \approx 1.3 \times 10^{-8}}$$

An extremely small K: at equilibrium, essentially only reactants are present, consistent with the large positive ΔG°.

Bài tập luyện tập

A reaction has $K = 250$ at 298 K. Find ΔG°.

Lời giải chi tiết

$$\Delta G^\circ = -RT \ln K = -(8.314)(298)\ln(250) = -(2477.6)(5.521)$$

$$\boxed{\Delta G^\circ = -13{,}680 \text{ J/mol} = -13.7 \text{ kJ/mol}}$$

Negative, consistent with $K > 1$.

Bài tập luyện tập

As ΔG° becomes more negative (at fixed T), K:

(A) becomes smaller

(B) becomes larger

(C) is unaffected

(D) becomes exactly zero

Lời giải chi tiết

$\Delta G^\circ = -RT \ln K$: a more negative ΔG° requires a larger, more positive $\ln K$, hence a larger K. **(B)**.

Bài tập luyện tập

Reaction 1: $\mathrm{X(s)} \rightarrow \mathrm{Y(s)}$, $\Delta G_1^\circ = +65$ kJ/mol. Reaction 2: $\mathrm{Y(s)} \rightarrow \mathrm{Z(g)}$, $\Delta G_2^\circ = -90$ kJ/mol. Find ΔG° for the coupled overall reaction $\mathrm{X(s)} \rightarrow \mathrm{Z(g)}$, and state whether it is favorable.

Lời giải chi tiết

Adding the two equations, the intermediate $\mathrm{Y(s)}$ cancels (produced in Reaction 1, consumed in Reaction 2):

$$\Delta G^\circ_{\text{overall}} = \Delta G_1^\circ + \Delta G_2^\circ = 65 + (-90) = \boxed{-25 \text{ kJ/mol}}$$

Negative — the overall coupled process $\mathrm{X(s)} \rightarrow \mathrm{Z(g)}$ is favorable, even though Reaction 1 alone is not.

Bài tập luyện tập

$\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}$ has $\Delta G_f^\circ(\mathrm{CO_2}, g) = -394.4$ kJ/mol (a real, well-established value). The reduction of a certain metal oxide, $\mathrm{MO_2(s)} \rightarrow \mathrm{M(s)} + \mathrm{O_2(g)}$, requires $\Delta G^\circ = +205$ kJ/mol. Find ΔG° for the coupled overall reaction $\mathrm{MO_2(s)} + \mathrm{C(s)} \rightarrow \mathrm{M(s)} + \mathrm{CO_2(g)}$, and state whether coupling makes extraction favorable.

Lời giải chi tiết

The $\mathrm{O_2(g)}$ released by the oxide reduction is exactly consumed by carbon's combustion, so it cancels on addition:

$$\Delta G^\circ_{\text{overall}} = 205 + (-394.4) = \boxed{-189.4 \text{ kJ/mol}}$$

Strongly favorable overall — carbon's combustion to $\mathrm{CO_2}$ is favorable enough to drive even a substantially unfavorable oxide-reduction step forward.

Bài tập luyện tập

In a galvanic cell, oxidation occurs at the:

(A) cathode
(B) anode
(C) salt bridge
(D) external wire

Lời giải chi tiết

By definition, oxidation occurs at the anode in every electrochemical cell (galvanic or electrolytic). **(B)**.

Bài tập luyện tập

Two half-reactions are available: $\mathrm{Ni^{2+}} + 2\mathrm{e^-} \rightarrow \mathrm{Ni}$ ($E^\circ = -0.26$ V) and $\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5\mathrm{e^-} \rightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O}$ ($E^\circ = +1.51$ V). Identify the cathode and anode when combined spontaneously, write the balanced overall equation with n, and calculate E°_{cell}.

Lời giải chi tiết

MnO_4^-/Mn^{2+} has the more positive E°, so it is the **cathode**; Ni/Ni^{2+} is oxidized, the **anode**. The Mn half-reaction needs $5e^-$ and the Ni half-reaction supplies $2e^-$ per Ni; LCM $= 10$ (multiply the Mn half by 2, the Ni half by 5):

$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

$$5Ni(s) \rightarrow 5Ni^{2+}(aq) + 10e^-$$

Overall: $2MnO_4^-(aq) + 16H^+(aq) + 5Ni(s) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Ni^{2+}(aq), \quad n = 10$

$$E^\circ_{cell} = 1.51 - (-0.26) = \boxed{+1.77\ \text{V}}$$

Bài tập luyện tập

In the external circuit of an operating galvanic cell, electrons flow:

(A) from cathode to anode

(B) from anode to cathode

(C) from the salt bridge to both electrodes

(D) they do not flow through the external circuit

Lời giải chi tiết

Electrons are released by oxidation at the anode and travel through the external wire to the cathode, where they are consumed by reduction. **(B)**.

Bài tập luyện tập

Explain the role of the salt bridge in a galvanic cell, and predict the direction of ion migration through it for a cell with a Zn anode and Ag cathode.

Lời giải chi tiết

The salt bridge maintains electroneutrality in both half-cells as the reaction proceeds: without it, the anode compartment would accumulate excess positive charge (from newly formed cations) and the cathode compartment would accumulate excess negative charge (as cations are consumed by reduction), and current would stop almost immediately once charge buildup opposed further electron flow. For a Zn/Ag cell, Zn is oxidized at the anode ($Zn \rightarrow Zn^{2+} + 2e^-$), so anions from the salt bridge migrate toward the Zn compartment to balance the growing Zn^{2+} concentration; Ag^+ is reduced at the cathode, so cations from the salt bridge migrate toward the Ag compartment to replace the consumed Ag^+.

Bài tập luyện tập

A cell has $E^\circ_{cell} = +0.46$ V and $n = 2$. What is ΔG°?

(A) -88.8 kJ/mol

(B) $+88.8$ kJ/mol

(C) -44.4 kJ/mol

(D) $-186{,}000$ kJ/mol

Lời giải chi tiết

$$\Delta G^\circ = -nFE^\circ = -(2)(96{,}485)(0.46) = -88{,}766 \text{ J/mol} = -88.8 \text{ kJ/mol}$$

(A). (B) is the right magnitude with the sign flipped; (C) mistakenly divides by n instead of multiplying; (D) mistakenly leaves the answer in joules while relabeling it kJ.

Bài tập luyện tập

Half-reactions MnO_4^-/Mn^{2+} ($E^\circ = +1.51$ V) and Fe^{2+}/Fe ($E^\circ = -0.44$ V). Determine E°_{cell}, the balanced overall equation with n, and ΔG°.

Lời giải chi tiết

Cathode = MnO_4^-/Mn^{2+} ($+1.51$ V); anode = Fe^{2+}/Fe (oxidized: $Fe \to Fe^{2+} + 2e^-$).

$$E^\circ_{\text{cell}} = 1.51 - (-0.44) = +1.95 \text{ V}$$

Balancing electrons (Mn half needs $5e^-$, Fe half gives $2e^-$; LCM $= 10$):

$$2MnO_4^-(aq) + 16H^+(aq) + 5Fe(s) \to 2Mn^{2+}(aq) + 8H_2O(l) + 5Fe^{2+}(aq), \quad n = 10$$

$$\Delta G^\circ = -nFE^\circ = -(10)(96{,}485)(1.95) = \boxed{-1{,}881{,}458 \text{ J/mol} = -1881.5 \text{ kJ/mol}}$$

The unusually large magnitude simply reflects that ΔG° here is reported per mole of reaction *as balanced* — i.e., per 10 mol of electrons (5 mol Fe) transferred, not per single electron.

Bài tập luyện tập

Which of the following, as written, requires an external power source (electrolysis) rather than occurring spontaneously?

(A) $Zn(s) + Cu^{2+}(aq) \to Zn^{2+}(aq) + Cu(s)$

(B) $Cu(s) + 2Ag^+(aq) \to Cu^{2+}(aq) + 2Ag(s)$

(C) $Mg(s) + 2H^+(aq) \to Mg^{2+}(aq) + H_2(g)$

(D) $Cu(s) + Zn^{2+}(aq) \to Cu^{2+}(aq) + Zn(s)$

Lời giải chi tiết

Evaluate E°_{cell} for each as written: (A) cathode Cu, anode Zn: $0.34 - (-0.76) = +1.10$ V, spontaneous. (B) cathode Ag, anode Cu: $0.80 - 0.34 = +0.46$ V, spontaneous. (C) cathode H_2/H^+, anode Mg: $0.00 - (-2.37) = +2.37$ V, spontaneous. (D) here Cu is oxidized and Zn^{2+} is reduced — the reverse of (A): $E^\circ_{\text{cell}} = (-0.76) - (0.34) = -1.10 \text{ V} < 0$, nonspontaneous as written. **(D)**.

Bài tập luyện tập

Find ΔG° for reaction (D) of the previous problem ($Cu(s) + Zn^{2+}(aq) \to Cu^{2+}(aq) + Zn(s)$), $n = 2$, $E^\circ_{\text{cell}} = -1.10$ V, and confirm consistency with the previous answer.

Lời giải chi tiết

$$\Delta G^\circ = -nFE^\circ = -(2)(96{,}485)(-1.10) = \boxed{+212{,}267 \text{ J/mol} = +212.3 \text{ kJ/mol}}$$

Positive ΔG° confirms this reaction is nonspontaneous as written, requiring electrolysis — con-

sistent with the negative E°_{cell} found above. Note this is equal in magnitude but opposite in sign to the Daniell cell's $\Delta G^\circ = -212.3$ kJ/mol (Section 9.8 worked example), since reaction (D) is simply the reverse of the Daniell cell reaction.

Bài tập luyện tập

As a galvanic cell discharges and Q approaches K, E_{cell}:

(A) increases toward E°

(B) decreases toward zero

(C) stays constant at E°

(D) becomes negative

Lời giải chi tiết

As $Q \to K$, $\log Q \to \log K$ and the Nernst equation drives E toward 0 (the cell approaches equilibrium, where $\Delta G = 0$). **(B)**.

Bài tập luyện tập

A concentration cell is built from two Cu electrodes: $[\text{Cu}^{2+}] = 1.00$ M in the cathode compartment, $[\text{Cu}^{2+}] = 0.0100$ M in the anode compartment, $n = 2$. Find E_{cell} at 298 K.

Lời giải chi tiết

Same electrode/ion couple on both sides, so $E^\circ = 0$. The net process transfers Cu^{2+} from the concentrated (cathode) side to the dilute (anode) side, so

$$Q = \frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}} = \frac{0.0100}{1.00} = 0.0100$$

$$E = 0 - \frac{0.0592}{2}\log(0.0100) = 0 - (0.0296)(-2)$$

$$\boxed{E = +0.0592\ \text{V}}$$

Bài tập luyện tập

A Zn/Cu cell ($E^\circ = 1.10$ V, $n = 2$) has $[\text{Zn}^{2+}] = 1.00$ M fixed by large excess. The measured cell potential is 0.950 V. Find Q and the corresponding $[\text{Cu}^{2+}]$.

Lời giải chi tiết

$$0.950 = 1.10 - \frac{0.0592}{2}\log Q \;\Rightarrow\; \log Q = \frac{1.10 - 0.950}{0.0296} = 5.07 \;\Rightarrow\; Q = 10^{5.07} = 1.17 \times 10^5$$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1.00}{[\text{Cu}^{2+}]} \;\Rightarrow\; [\text{Cu}^{2+}] = \frac{1.00}{1.17 \times 10^5}$$

$$\boxed{[\text{Cu}^{2+}] \approx 8.6 \times 10^{-6}\ \text{M}}$$

The very low remaining $[\text{Cu}^{2+}]$ shows the cell has run nearly to completion (close to equilibrium), consistent with E_{cell} having dropped substantially below E°.

Bài tập luyện tập

The slope of a plot of E versus $\log Q$ at 298 K, for a process with $n = 1$, is:

(A) $+0.0592$
(B) -0.0592
(C) -0.0296
(D) $+2.303$

Lời giải chi tiết

$E = E^\circ - \dfrac{0.0592}{n} \log Q$ has slope $-0.0592/n$; with $n = 1$, slope $= -0.0592$. **(B).**

Bài tập luyện tập

In the electrolysis of molten (pure, water-free) NaCl, which half-reaction occurs at the cathode?

(A) $2Cl^- \rightarrow Cl_2 + 2e^-$
(B) $Na^+ + e^- \rightarrow Na$
(C) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
(D) $Na \rightarrow Na^+ + e^-$

Lời giải chi tiết

The cathode is always the site of reduction; with no water present, Na^+ is the only species available to be reduced. **(B).**

Bài tập luyện tập

Electrolysis of molten $MgCl_2$ uses a current of 5.00 A for 2.00 hours. Find the mass of Mg deposited at the cathode (molar mass Mg $= 24.31$ g/mol).

Lời giải chi tiết

$$Q = It = (5.00)(2.00 \times 3600) = 36{,}000 \text{ C}$$

$$\text{mol } e^- = \frac{36{,}000}{96{,}485} = 0.3731 \text{ mol}$$

$$\text{mol Mg} = 0.3731 \times \frac{1 \text{ mol Mg}}{2 \text{ mol } e^-} = 0.1866 \text{ mol} \qquad (Mg^{2+} + 2e^- \rightarrow Mg)$$

$$\boxed{\text{mass Mg} = (0.1866)(24.31) = 4.54 \text{ g}}$$

Bài tập luyện tập

Find the time required to produce 10.0 L of $H_2(g)$ at STP (22.4 L/mol) at the cathode of an aqueous electrolysis cell using a current of 3.00 A, via $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$.

Lời giải chi tiết

$$\text{mol } H_2 = \frac{10.0}{22.4} = 0.4464 \text{ mol}$$

$$\text{mol } e^- = 2 \times 0.4464 = 0.8929 \text{ mol} \qquad (2 \text{ mol } e^- \text{ per mol } H_2)$$

$$Q = (0.8929)(96{,}485) = 86{,}147 \text{ C}$$

$$t = \frac{Q}{I} = \frac{86{,}147}{3.00} = 28{,}716 \text{ s}$$

$$\boxed{t = 28{,}716 \text{ s} \approx 7.98 \text{ hours}}$$

Bài tập luyện tập

Two electrolytic cells are connected in series (identical current and time in both) — one deposits Ag via $Ag^+ + e^- \rightarrow Ag$, the other deposits Cu via $Cu^{2+} + 2e^- \rightarrow Cu$. If 0.100 mol of electrons pass through the circuit, how do the moles of metal deposited compare?

(A) Equal moles of Ag and Cu are deposited

(B) Moles of Ag deposited is twice moles of Cu deposited

(C) Moles of Cu deposited is twice moles of Ag deposited

(D) No metal is deposited without a salt bridge

Lời giải chi tiết

$$\text{mol Ag} = 0.100 \text{ mol } e^- \times \frac{1 \text{ mol Ag}}{1 \text{ mol } e^-} = 0.100 \text{ mol}$$

$$\text{mol Cu} = 0.100 \text{ mol } e^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} = 0.0500 \text{ mol}$$

The same charge deposits twice as many moles of Ag (which needs only 1 electron per ion) as Cu (which needs 2). **(B)**.

[Ôn tập nhanh]

- Mol và khối lượng mol: $n = m/M$; số hạt $= n \times N_A$ ($N_A = 6.022 \times 10^{23}$).
- Phổ quang electron (PES): mỗi đỉnh ứng với một phân lớp electron; đỉnh có năng lượng liên kết càng lớn thì càng gần hạt nhân; diện tích đỉnh tỉ lệ với số electron trong phân lớp đó.
- VSEPR và lai hoá: số vùng electron (liên kết + cặp electron riêng) quanh nguyên tử trung tâm quyết định hình học phân tử và trạng thái lai hoá.
- Phương trình khí lý tưởng: $PV = nRT$ ($R = 0.0821$ atm·L/(mol·K) hoặc 8.314 J/(mol·K)).
- Định luật tốc độ: rate $= k[A]^m[B]^n$, bậc phản ứng xác định bằng thực nghiệm, không suy ra từ hệ số cân bằng; phương trình Arrhenius: $k = Ae^{-E_a/RT}$.
- Nhiệt lượng: $q = mc\Delta T$; $\Delta H^\circ_{\text{pư}} = \sum \Delta H^\circ_f(\text{sản phẩm}) - \sum \Delta H^\circ_f(\text{chất đầu})$; định luật Hess: cộng các phương trình trung gian để được ΔH tổng.
- Hằng số cân bằng K: $K > 1$ thiên về sản phẩm, $K < 1$ thiên về chất đầu; nguyên lý Le Chatelier: hệ dịch chuyển để chống lại sự thay đổi nồng độ/áp suất/nhiệt độ.
- K_{sp} và độ tan: so sánh Q với K_{sp} để dự đoán kết tủa ($Q > K_{sp}$: kết tủa; $Q < K_{sp}$: tan hết).
- pH/pOH: pH $= -\log[\text{H}^+]$, pOH $= -\log[\text{OH}^-]$, pH + pOH $= 14$ ở 25°C; phương trình Henderson–Hasselbalch cho đệm: pH $= \text{p}K_a + \log([\text{base}]/[\text{acid}])$.
- Entropy: S càng lớn khi chất càng "phân tán" (khí $>$ lỏng $>$ rắn); $\Delta S^\circ_{\text{pư}} = \sum S^\circ(\text{sản phẩm}) - \sum S^\circ(\text{chất đầu})$ (S° của đơn chất KHÔNG bằng 0).
- Năng lượng tự do Gibbs: $\Delta G = \Delta H - T\Delta S$; phản ứng thuận lợi về nhiệt động (tự diễn biến) khi $\Delta G < 0$.
- Liên hệ ΔG° với hằng số cân bằng và điện thế: $\Delta G^\circ = -RT \ln K = -nFE^\circ$.
- Thế điện cực chuẩn của pin: $E^\circ_{\text{pin}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$; pin galvanic tự phát khi $E^\circ_{\text{pin}} > 0$.
- Phương trình Nernst: $E = E^\circ - (0.0592/n)\log Q$ ở 25°C — tính thế pin khi nồng độ khác điều kiện chuẩn.
- Định luật Faraday: điện lượng $Q = I \times t$; số mol electron $= Q/F$ ($F = 96{,}485$ C/mol), kết hợp với phương trình bán phản ứng để tính khối lượng chất sinh ra ở điện cực.

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- Lộ trình cá nhân hoá, theo sát tiến độ từng học viên; lớp OFFLINE tại TP.HCM & ONLINE toàn quốc.

Bảng vàng học viên

AP 5/5 — Calculus AB/BC	**AP** 4–5 — Biology, Chemistry	**IB** 90/100 — Economics
SAT 1590 / 1570 / 1550	**IELTS** 8.0–9.0	**Duolingo** 110 · **PTE** 90

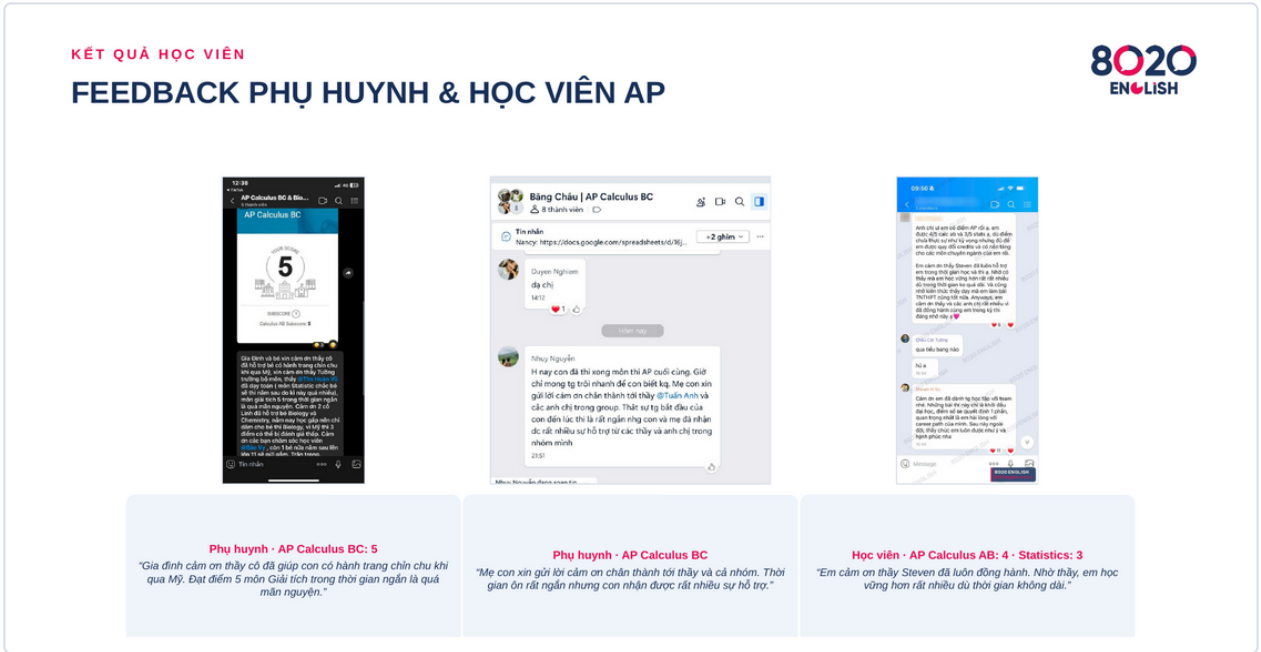
Cảm nhận học viên & phụ huynh

> *"Bạn đã cải thiện được tư duy Writing — kỹ năng từng là nỗi sợ lớn nhất — và cuối cùng đã đậu vào trường top như mong muốn. Thái độ học tập cực kỳ nghiêm túc; ngay cả khi nằm viện vẫn cố gắng học đều đặn."*
>
> — Phan Thị Thanh Hằng · IELTS Overall 8.5

> *"Cần tất cả kỹ năng trên 7.5 để xét vào trường top 1 Anh Quốc về Y học (chương trình UKFPO của NHS) — và đã đạt mục tiêu sau khi học Writing 1–1."*
>
> — Trần Hoàng Bảo Ngọc · IELTS Overall 8.0 (Writing 6.0 → 7.5)

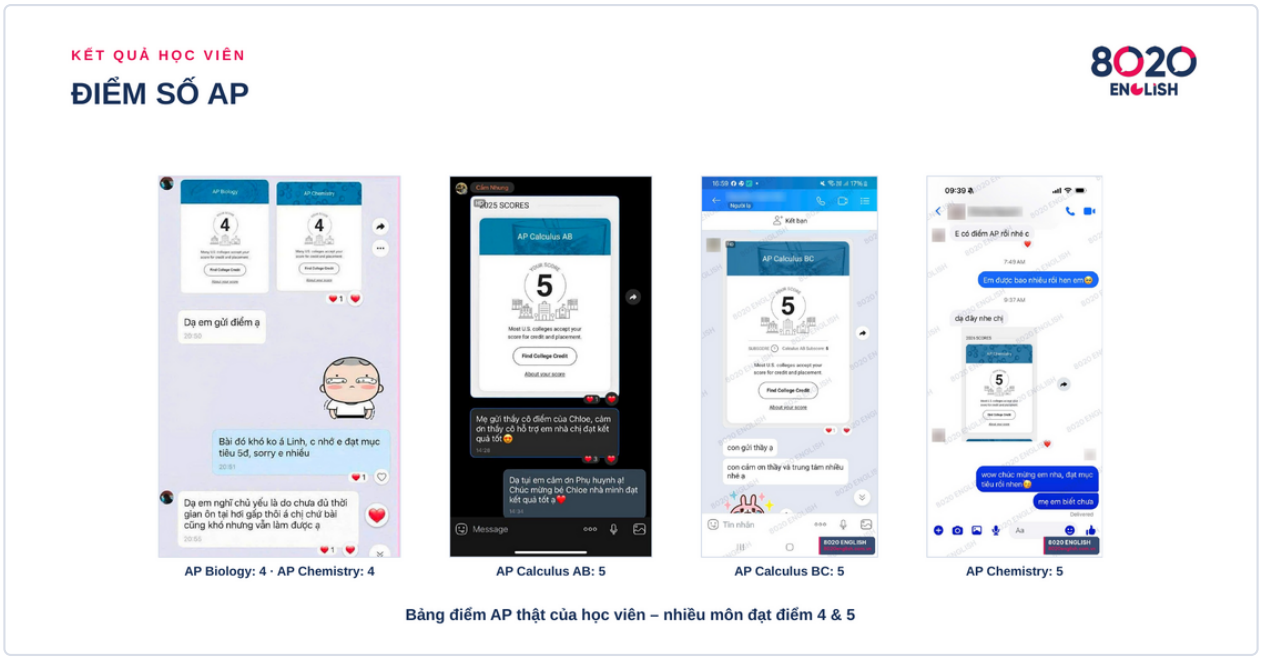
> *"Gia đình và bé xin cảm ơn thầy cô đã giúp con có hành trang chỉn chu khi qua Mỹ. Đạt điểm 5 môn Giải tích trong thời gian ngắn là quá mãn nguyện."*
>
> — Phụ huynh · AP Calculus BC 5/5

> *"Em cảm ơn thầy đã luôn đồng hành. Nhờ thầy, em học vững hơn rất nhiều dù thời gian ôn không dài."*
>
> — Học viên · AP Calculus AB 4

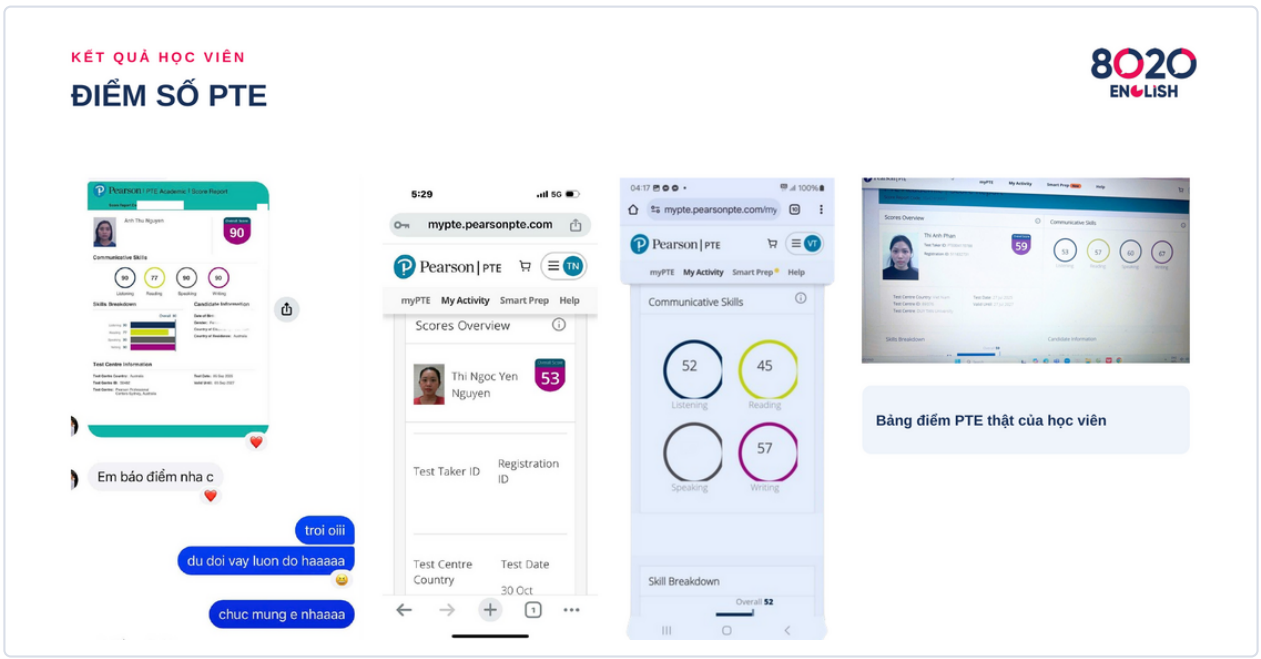


Feedback phụ huynh & học viên AP — nhiều môn đạt điểm 4 & 5

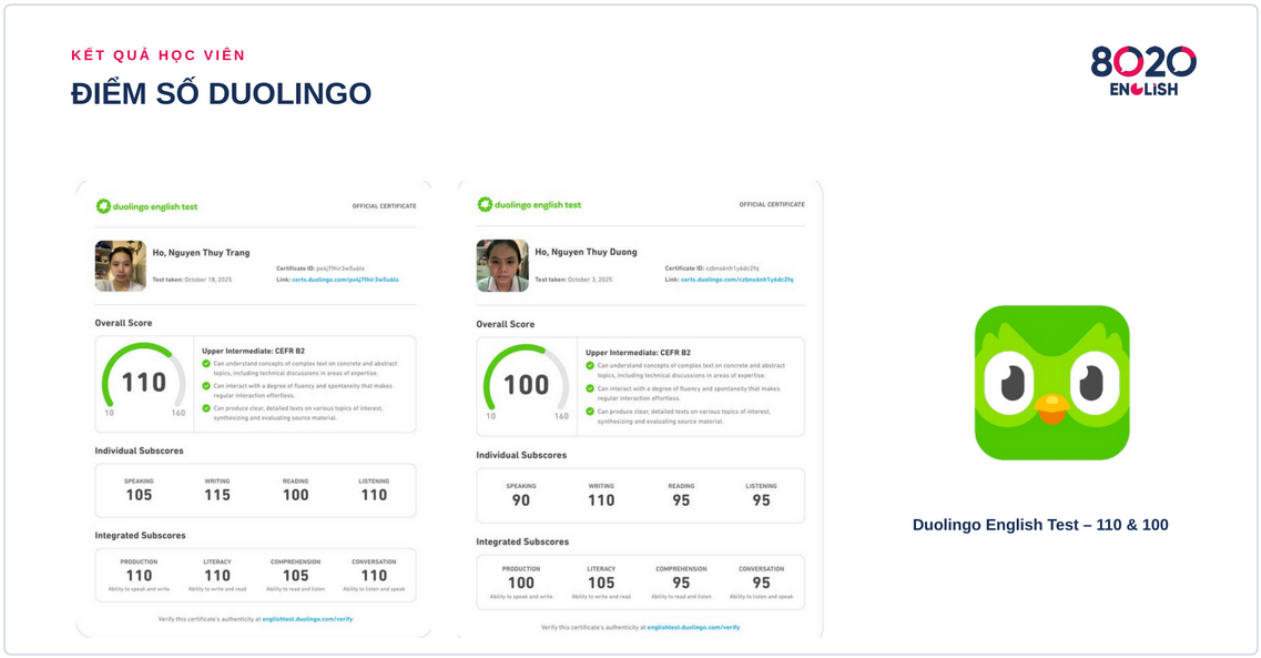
Điểm thi thật của học viên



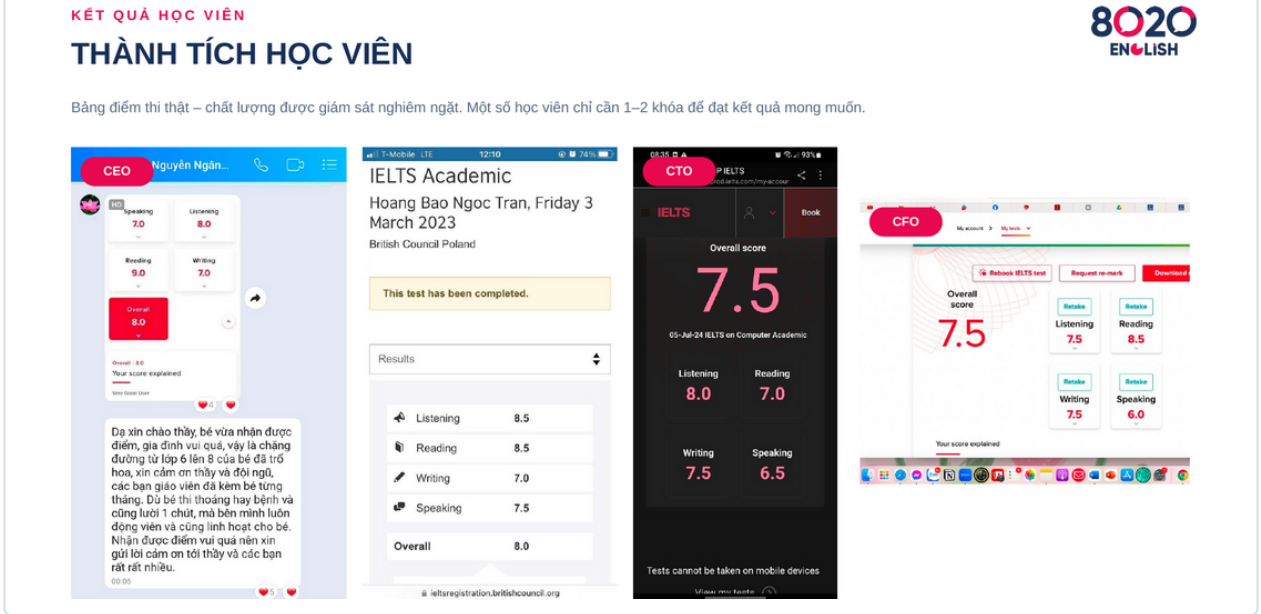
Bảng điểm AP thật — Calculus AB/BC 5/5 · Biology & Chemistry 4–5 (College Board)



Học viên 8020 — PTE Academic 90



Học viên 8020 — Duolingo English Test 110 & 100



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