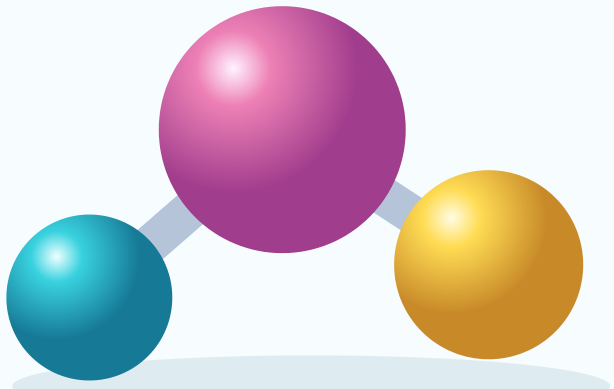
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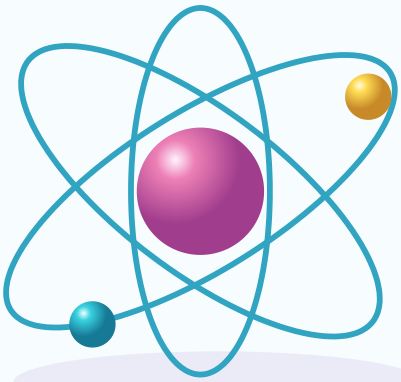
THE CHAPTER NOTEBOOK EDITION

Physical Chemistry

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Physical Chemistry

Your chapter route · 9 chapters
Tap a chapter to jump to its opening page.

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Space to pause. Space to revise.
One completely blank buffer page follows every chapter, including the final chapter. Use it for quick recall, your own examples or extra notes.

Chapter opening numbers and the page numbers below match this separate volume.

Mole Concept

Mass • particles • composition

01

01 SI prefixes and length conversion

Prefix	Symbol	Multiplier
femto	f	10^{-15}
pico	p	10^{-12}
nano	n	10^{-9}
micro	μ	10^{-6}
milli	m	10^{-3}
centi	c	10^{-2}
deci	d	10^{-1}
deca	da	10^{1}
hecto	h	10^{2}
kilo	k	10^{3}
mega	M	10^{6}
giga	G	10^{9}
tera	T	10^{12}
peta	P	10^{15}

$$1\,\text{Å} = 10^{-10}\,\text{m}$$

02 Classification of matter

- A mixture contains more than one chemical substance. Sugar solution is homogeneous; a dry mixture of sugar and salt is heterogeneous.

- A pure substance has a fixed chemical identity. Elements include $H_2(g)$ and $O_2(g)$; compounds include H_2O and CO_2.

03 Electrons, protons and neutrons

- For a neutral atom or molecule, the number of protons equals the number of electrons. In the general species A_xB_y, let x_i be the number of atoms of element i, Z_i its atomic number, A_i its isotope mass number, and N the number of molecules.

$$N_{p^+} = N_{e^-} = N\sum_i Z_i x_i$$

Mole Concept

Electrons, protons and neutrons · Moles and constituent atoms

03 Electrons, protons and neutrons

continued

$$N_n = N \sum_i (A_i - Z_i)x_i$$

$$\begin{aligned} N_A^{(\text{atoms})} &= xN \\ N_B^{(\text{atoms})} &= yN \\ N_{\text{total atoms}} &= (x+y)N \end{aligned}$$

- Only electrons are transferred during ordinary ion formation; the proton and neutron counts remain unchanged.

$$N_{p^+} = N_{\text{ions}} \sum_i Z_i x_i$$

$$N_n = N_{\text{ions}} \sum_i (A_i - Z_i)x_i$$

$$N_{e^-}(\text{cation of charge } q+) = N_{\text{ions}} \left(\sum_i Z_i x_i - q \right)$$

$$N_{e^-}(\text{anion of charge } q-) = N_{\text{ions}} \left(\sum_i Z_i x_i + q \right)$$

04 Moles and constituent atoms

$$\mathrm{A_xB_y} \longrightarrow x\mathrm{A} + y\mathrm{B}$$

Atom-counting relationship.

$$\begin{aligned} n(\text{A atoms}) &= x n(\mathrm{A_xB_y}) \\ n(\text{B atoms}) &= y n(\mathrm{A_xB_y}) \end{aligned}$$

$$n(\text{total atoms}) = (x+y)n(\mathrm{A_xB_y})$$

Mole Concept

Moles and constituent atoms · Calculating amount of substance

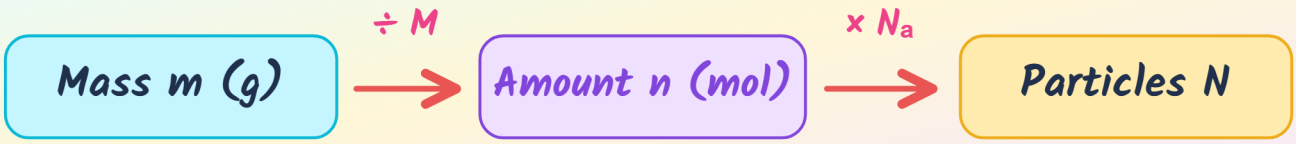
04 Moles and constituent atoms

continued

$$N(\text{A atoms}) = xnN_A$$
$$N(\text{A}_x\text{B}_y) = nN_A$$
$$N(\text{total atoms}) = (x+y)nN_A$$

05 Calculating amount of substance

Moles connect mass and particles



M = molar mass in g mol⁻¹; N_a = number of particles per mole

$$n = \frac{m}{M} = \frac{N}{N_A}$$
$$N_A = 6.02214076 \times 10^{23}\ \text{mol}^{-1}$$

Applicable to all physical states. M is molar mass; mass of one mole is numerically M grams when M is in g mol⁻¹. Mass = amount × molar mass.

$$n = \frac{V}{22.4\ \text{L mol}^{-1}}$$

Approximate ideal-gas formula at 273.15 K and 1 atm only; the source uses the 1-atm convention for STP.

$$n = \frac{PV}{RT}$$

Ideal-gas relation at any stated temperature and pressure, with consistent units.

06 Water reminder

- At 1 atm the boiling point of water is approximately 100 °C = 373 K. Below 100 °C liquid water can exist; above it the stable phase is vapour. At the boiling point, liquid and vapour may coexist. These statements concern the liquid/vapour range, not temperatures below freezing.

Mole Concept

Water reminder · Atomic mass vocabulary

06 Water reminder

continued

$$\rho = \frac{m}{V} \approx 1\,\mathrm{g\,mL^{-1}}$$

Approximate density of liquid water under ordinary conditions.

07 Atomic mass vocabulary

- An atom is the smallest unit that retains an element's chemical identity. Most of its mass lies in its protons and neutrons. Mass number counts these nucleons. Atomic mass in u is close to the mass number, but is not exactly the same.

$$1\,\mathrm{u} = \frac{1}{12} m(^{12}\mathrm{C}) \approx 1.66054 \times 10^{-24}\,\mathrm{g}$$

A proton has mass approximately 1.67 × 10^{-24} g, about 1 u.

Quantity	Meaning / relation
Actual atomic mass (AAM)	Mass of one atom in g; approximately A × 1.66054 × 10^{-24} g
Relative atomic mass (A_r / source RAM)	Dimensionless ratio of atomic mass to 1 u; approximately A for an isotope
Gram atomic mass (source GAM) / molar mass	Mass of one mole of atoms; M = AAM × N_a, in g mol^{-1}

- Atomic mass expressed in u describes one atom; the corresponding molar mass in g mol^{-1} describes one mole. One gram-atom means one mole of atoms; one gram-molecule means one mole of molecules.

08 Molecular mass and averages

$$\overline{M} = \frac{\sum_i M_i n_i}{\sum_i n_i} = \frac{M_1 n_1 + M_2 n_2}{n_1 + n_2}$$

- One molecule has mass M_r u. One mole of molecules has mass numerically M_r grams. Thus 6.022 × 10^{23} molecules have that mass; for an ideal gas, approximately 22.4 L at 273.15 K and 1 atm also has that mass.

$$\overline{A} = \frac{\sum_i A_i n_i}{\sum_i n_i}$$
$$A_{\min} \le \overline{A} \le A_{\max}$$

For an isotope mixture, the average lies closer to the isotope with the larger abundance. For two isotopes both present, the inequalities are strict.

Mole Concept

Vapour density and elemental percentage · Empirical and molecular formulae

09 Vapour density and elemental percentage

$$\mathrm{VD}_{\mathrm{H_2}} = \frac{M_{\mathrm{gas}}}{2}$$

$$\mathrm{VD}_{\mathrm{mixture}} = \frac{M}{2}$$

Vapour density relative to H_2 at the same temperature and pressure, with the school-level molar mass 2 g mol^{-1} for H_2.

$$\text{Mass \% of element} = \frac{\text{mass contribution of that element in one formula unit}}{\text{formula mass of compound}} \times 100$$

This relation can also be rearranged to find composition or formula information from a percentage.

10 Empirical and molecular formulae

- An empirical formula gives the simplest whole-number ratio of atoms. Its formula mass is the smallest formula mass consistent with that ratio.

$$\text{Molecular formula} = (\text{empirical formula})_n$$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

n is a positive integer; multiply every empirical-formula subscript by n.

11 Mass percentage, ppm and ppb

- Let w_1 be solute mass and w_2 solvent mass in the same unit. Mass percentage expresses solute mass in 100 g of solution.

$$\text{Solute mass \%} = \frac{w_1}{w_1 + w_2} \times 100$$

$$\text{solvent mass \%} = \frac{w_2}{w_1 + w_2} \times 100$$

$$\text{ppm} = \frac{w_1}{w_1 + w_2} \times 10^6 = (\text{mass \%}) \times 10^4$$

Mole Concept

Mass percentage, ppm and ppb · Percentage concentrations

11 Mass percentage, ppm and ppb

continued

$$\text{ppb} = \frac{w_1}{w_1 + w_2} \times 10^9 = (\text{mass }\%) \times 10^7 = \text{ppm} \times 10^3$$

12 Percentage concentrations

$$w_{\text{mix}}(\%) = \frac{x + y}{2}$$

Only when equal masses of x% (w/w) and y% (w/w) solutions are mixed without reaction or loss. If solution masses are supplied, use their weighted average.

- For x% (w/w): x g solute in 100 g solution, hence (100 − x) g solvent.

$$\%(w/v) = \frac{w_{\text{solute}}(\text{g})}{V_{\text{solution}}(\text{mL})} \times 100$$

x% (w/v) means x g solute in 100 mL solution, not in 100 g solution.

$$m_{\text{solution}} = \rho_{\text{solution}} V_{\text{solution}}$$

With density in g mL^{-1} and volume in mL, mass is in g.

$$\%(v/v) = \frac{V_{\text{solute}}}{V_{\text{solution}}} \times 100$$

x% (v/v) means x mL solute per 100 mL final solution. Vsolution = V_1 + V_2 only when volumes are additive.

13 Mole fraction

$$x_1 = \frac{n_1}{n_1 + n_2}$$
$$x_2 = \frac{n_2}{n_1 + n_2}$$
$$x_1 + x_2 = 1$$

$$\text{Mole }\% \text{ of solute} = \frac{n_1}{n_1 + n_2} \times 100$$
$$\frac{n_1}{n_2} = \frac{x_1}{x_2}$$

Mole Concept

Molality · Molarity

14 Molality

$$m_{\text{solvent}} = m_{\text{solution}} - m_{\text{solute}}$$

$$b = \frac{n_{\text{solute}}}{m_{\text{solvent}}(\text{kg})} = \frac{1000 n_{\text{solute}}}{m_{\text{solvent}}(\text{g})}$$

Molality is often written m in school notes; unit mol kg⁻¹. For example 2 mol kg⁻¹ = 2 m. Here b avoids confusion with mass.

$$b = \frac{1000 n_{\text{solute}}}{\rho_{\text{solution}} V_{\text{solution}} - m_{\text{solute}}}$$

Use g mL⁻¹, mL and g in the denominator.

$$\frac{x_1}{x_2} = \frac{b M_2}{1000}$$

M_2 is solvent molar mass in g mol⁻¹; 1 denotes solute and 2 solvent.

15 Molarity

Same solute moles · different denominators

Molarity C = moles of solute ÷ **litres of SOLUTION**

Molality b = moles of solute ÷ **kilograms of SOLVENT**

Solution = solute + solvent. Check what belongs in the denominator.

$$C = \frac{n_{\text{solute}}}{V_{\text{solution}}(\text{L})} = \frac{1000 n_{\text{solute}}}{V_{\text{solution}}(\text{mL})}$$

Molarity is commonly denoted M. Always use final solution volume; solvent volume is only an approximation in sufficiently dilute solutions.

$$C = \frac{1000 n_{\text{solute}} \rho_{\text{solution}}}{m_{\text{solution}}}$$

Density in g mL⁻¹, solution mass in g.

- For complete dissociation of A_xB_γ at molarity C, the formal constituent-ion concentrations are xC for A and yC for B; actual free-ion concentrations depend on dissociation and subsequent reactions.

Mole Concept

Molarity · Conversion between concentration scales

15 Molarity

continued

$$n_{\text{solute}} = C\,V_{\text{solution}}(\text{L})$$

16 Conversion between concentration scales

$$b = \frac{1000C}{1000\rho - CM_1}$$

ρ in g mL⁻¹; solute molar mass M_1 in g mol⁻¹. Taking 1 L of solution makes the derivation convenient; the resulting relation is general.

$$C = \frac{x\rho_{\text{g/L}}}{100M_1} = \frac{10x\rho_{\text{g/mL}}}{M_1}$$

For a solution of x mass percent.

$$C = \frac{10x}{M_1}$$

For x% (w/v), because x g occurs in 100 mL solution.

17 Mixing and dilution

$$C_1V_1 + C_2V_2 = C_f(V_1 + V_2)$$

For mixing solutions of the same conserved solute, without reaction and with additive volumes. For different acids or bases, distinguish concentration of each species from total acid/base equivalents.

$$C_1V_1 = C_f(V_1 + V_2)$$

Dilution by adding solvent volume V_2, assuming additive volumes; generally $C_1V_1 = CfVfinal$.

18 Stoichiometric calculation

$$\nu_1\text{A} \longrightarrow \nu_2\text{B} + \nu_3\text{C}$$

- 1. Balance the reaction. 2. Convert the given quantities to moles. 3. Use the stoichiometric coefficients to relate moles consumed and formed.

Mole Concept

Stoichiometric calculation · Percentage purity

18 Stoichiometric calculation

continued

$$\frac{n_{\text{A,consumed}}}{\nu_1} = \frac{n_{\text{B,formed}}}{\nu_2} = \frac{n_{\text{C,formed}}}{\nu_3}$$

19 Percentage purity

$$\%\ \text{purity} = \frac{m_{\text{pure substance}}}{m_{\text{sample}}} \times 100$$

The total sample mass is usually given; calculate the mass of the pure reacting component.

20 Percentage yield

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

Calculate the theoretical mass of the same product whose actual mass is supplied.

$$\%\ \text{yield} = \frac{m_{\text{reactant equivalent to actual product}}}{m_{\text{available limiting reactant}}} \times 100$$

This is the source's reactant-based method: infer, stoichiometrically, the reactant mass corresponding to the actual product. It is not a general statement that reactant conversion always equals product yield.

21 Limiting reagent

Find the reactant that runs out first

Initial moles of each reactant → **Divide by its** balanced coefficient → **Smallest ratio** = limiting reagent

The limiting reagent fixes the maximum possible amount of product.

- *For each reactant, divide its initial moles by its balanced coefficient. The smallest ratio identifies the limiting reagent: it is used up first.*

$$\xi_{\max} = \min_i \left(\frac{n_{i,0}}{\nu_i} \right)$$

$$\frac{n_{\text{LR},0}}{\nu_{\text{LR}}} = \frac{n_{\text{desired,formed or consumed}}}{\nu_{\text{desired}}}$$

Use the limiting-reagent ratio to calculate the requested quantity.

Atomic Structure

Models • spectra • quantum numbers

02

01 Fundamental particles

Particle / associated discovery	Charge (C)	Relative charge	Approx. mass (kg)	Relative mass	Relative |charge/mass|
Electron — J. J. Thomson	-1.602×10^{-19}	-1	9.109×10^{-31}	1/1836	1836
Proton — Rutherford	$+1.602 \times 10^{-19}$	$+1$	1.673×10^{-27}	1	1
Neutron — Chadwick	0	0	1.675×10^{-27}	≈ 1	0
α particle (^{4}He nucleus)	$+2 \times 1.602 \times 10^{-19}$	$+2$	$\approx 4 \times 1.67 \times 10^{-27}$	≈ 4	$\approx 1/2$

- The last column is the magnitude of specific charge relative to the proton, not an SI charge-to-mass value.

$$1\,\text{fm} = 10^{-15}\,\text{m}$$
$$1\,\text{pm} = 10^{-12}\,\text{m}$$
$$1\,\text{Å} = 10^{-10}\,\text{m}$$

$$1\,\text{nm} = 10^{-9}\,\text{m}$$
$$1\,\mu\text{m} = 10^{-6}\,\text{m}$$
$$1\,\text{eV} = 1.602 \times 10^{-19}\,\text{J}$$

02 Thomson and Rutherford models

- Thomson's plum-pudding / watermelon model: positive charge is uniformly distributed and negative electrons are embedded in it. It cannot account for the observed nuclear structure; the source also notes its failure to explain atomic stability.

- Rutherford model: most of an atom is empty space. Almost all mass and all positive nuclear charge occupy a tiny central nucleus.

$$R_{\text{atom}} \sim 10^{-10}\,\text{m}$$
$$R_{\text{nucleus}} \sim 10^{-15}\,\text{m}$$
$$R_{\text{atom}} \sim 10^{5} R_{\text{nucleus}}$$

$$R = R_0 A^{1/3}$$
$$R_0 \approx 1.33 \times 10^{-15}\,\text{m} = 1.33 \times 10^{-13}\,\text{cm} = 1.33\,\text{fm}$$

Source's approximate radius constant; nuclear density is approximately independent of mass number.

$$N(\theta) \propto \frac{1}{\sin^4(\theta/2)}$$

Rutherford angular scattering dependence under fixed experimental conditions.

Atomic Structure

Nuclear notation · Related nuclides

03 Nuclear notation

Read the nuclear symbol

$^{A}_{Z}\mathrm{X}$



Z protons

A = protons + neutrons



A − Z neutrons

Z electrons if neutral

Ordinary ion formation changes electrons; the nucleus stays unchanged.

$$^{A}_{Z}\mathrm{X}$$

$$A = Z + N$$

X is element symbol, A mass number = protons + neutrons, Z atomic number = number of protons = number of electrons for a neutral atom.

04 Related nuclides

Family	What stays equal?	Examples
Isotopes	Same Z; different A	^{12}C, ^{13}C, ^{14}C; ^{1}H, ^{2}H (D), ^{3}H (T); ^{16}O, ^{17}O, ^{18}O; ^{35}Cl, ^{37}Cl
Isobars	Same A; different Z	^{40}Ar, ^{40}K, ^{40}Ca; ^{14}C and ^{14}N
Isotones	Same N = A − Z	^{3}H and ^{4}He; ^{39}K and ^{40}Ca
Isodiaphers	Same neutron excess N − Z	^{11}B and ^{13}C; ^{15}N and ^{19}F

$$(N - Z)_1 = (N - Z)_2$$

Condition for isodiaphers.

05 Isosteres and isoelectronic species

- Isosteres have the same number of atoms and electrons in the source's introductory definition: CO_2/N_2O and CaO/KF. Isoelectronic species have the same number of electrons: Cl^-/Ar, NO^+/CO, H_2O/NH_3.

06 Wave quantities

$$\lambda = \frac{c}{\nu}$$

$$c = \nu\lambda$$

$$c \approx 3.00 \times 10^{8}\,\mathrm{m\,s^{-1}}$$

- Wavelength λ is the distance between successive crests or troughs. Amplitude A is the maximum displacement from equilibrium. Frequency ν is the number of oscillations per second, measured in hertz (Hz).

Atomic Structure

Wave quantities · Electromagnetic spectrum

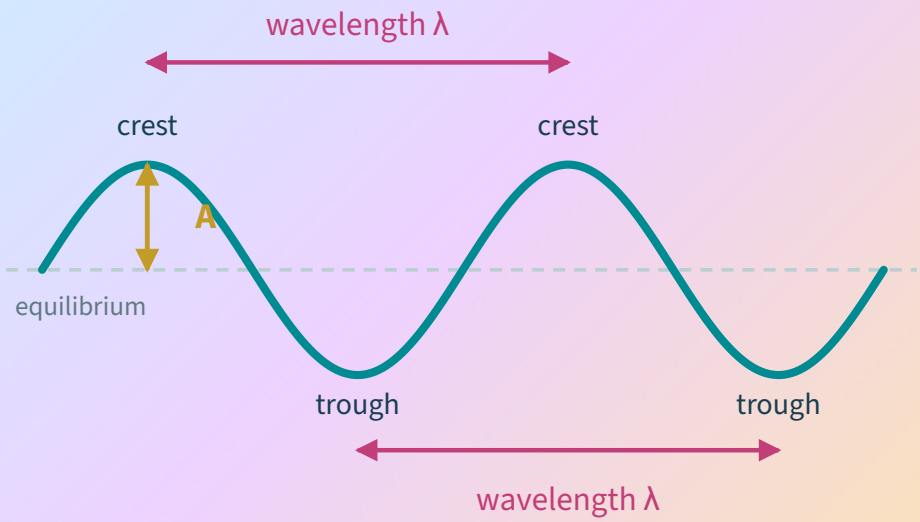
06 Wave quantities

continued

$$\tilde{\nu} = \frac{1}{\lambda}$$

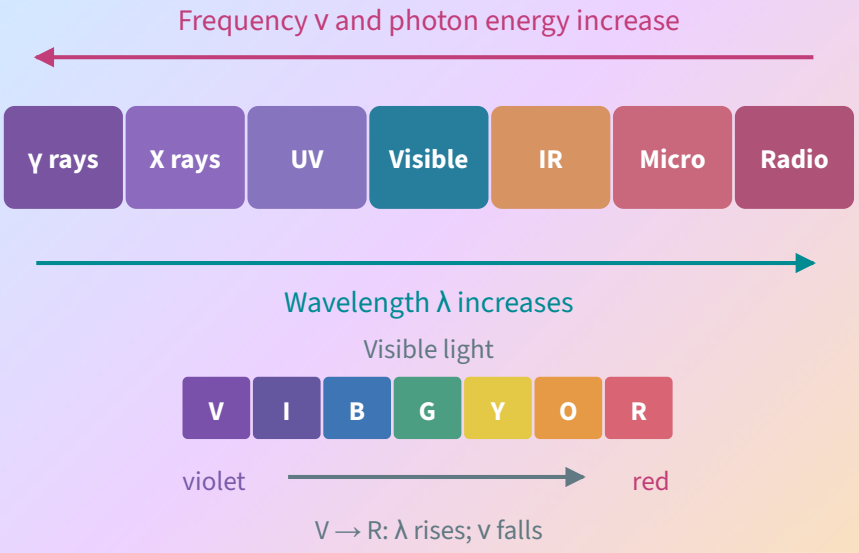
$$T = \frac{1}{\nu}$$

Wavenumber and time period, respectively.



Wavelength joins consecutive crests or troughs; amplitude is measured from the equilibrium line.

07 Electromagnetic spectrum



From gamma rays to radio waves, wavelength increases while frequency and photon energy decrease.

Atomic Structure

Electromagnetic spectrum · Planck's quantum theory

07 Electromagnetic spectrum

continued

- The source's recall phrase is 'Classic Gaadi X U V In My Range'. Its initial 'cosmic rays' entry is not an electromagnetic band; cosmic rays are predominantly high-energy particles. Retain the useful band initials G–X–U–V–I–M–R.

08 Planck's quantum theory

- Radiant energy is emitted or absorbed in discrete packets, or quanta; a light quantum is a photon. Photon energy is proportional to frequency.

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$
$$E_{n\ \text{photons}} = nh\nu = \frac{nhc}{\lambda}$$

$$E_{n\ \text{photons}}(\text{eV}) \approx \frac{12400n}{\lambda(\text{Å})}$$

$$h = 6.626 \times 10^{-34}\,\text{J s} = 6.626 \times 10^{-27}\,\text{erg s}$$
$$1\,\text{eV} = 1.602 \times 10^{-19}\,\text{J}$$

n is the number of photons.

09 Photoelectric effect

- Electrons are ejected from a metal surface when suitable light falls on it. This surface phenomenon demonstrates the particle nature of light. In the elementary one-photon process, one absorbed photon transfers energy to one electron; emission has no appreciable time lag when the threshold condition is met.

$$h\nu = \phi + K_{\max}$$
$$\phi = h\nu_0 = \frac{hc}{\lambda_0}$$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + K_{\max}$$
$$K_{\max} = h(\nu - \nu_0)$$

φ (also W_0) is work function; ν is incident frequency; ν_0 threshold frequency; λ_0 threshold wavelength.

Condition	Result
$\nu > \nu_0$; $\lambda < \lambda_0$	Emission with positive maximum kinetic energy
$\nu = \nu_0$; $\lambda = \lambda_0$	Threshold emission; maximum kinetic energy is zero
$\nu < \nu_0$; $\lambda > \lambda_0$	No photoelectric emission in the one-photon model

Atomic Structure

Black-body radiation reminder · Stopping potential and Einstein equation

10 Black-body radiation reminder

- As temperature rises, the wavelength at maximum emission decreases (Wien displacement trend).

11 Stopping potential and Einstein equation

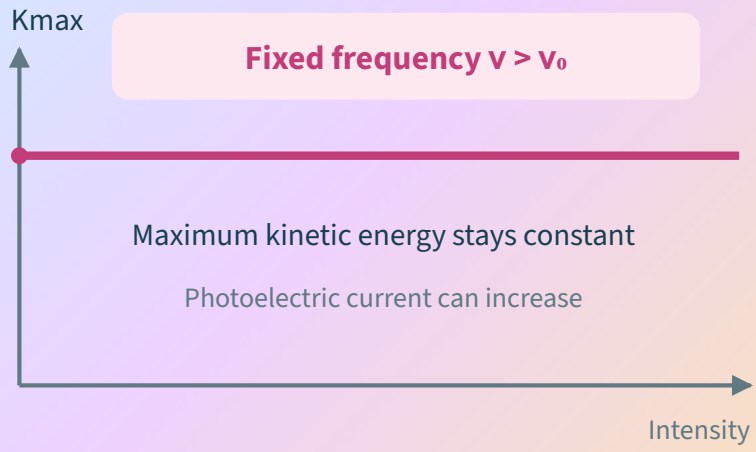
$$K_{\max} = eV_0$$

$$V_0 = \frac{h\nu - h\nu_0}{e}$$

$$h\nu = h\nu_0 + \frac{1}{2}m_e v_{\max}^2$$

12 Intensity of light

- Photon flux is the number of photons incident per unit area per unit time. Intensity is their energy per unit area per unit time. At fixed frequency above threshold, increasing intensity increases photon flux, the number of emitted photoelectrons and the photoelectric current, but does not change maximum kinetic energy.



At a fixed frequency above threshold, light intensity does not change the maximum photoelectron kinetic energy.

13 Bohr postulates

- The Bohr model applies to hydrogen-like one-electron species such as H, He^+ and Li^{2+}. Allowed electron orbits have angular momentum equal to an integer multiple of $h/(2\pi)$.

Atomic Structure

Bohr postulates · Radius, speed, period and frequency

13 Bohr postulates

continued

$$m_e v_n r_n = \frac{nh}{2\pi}$$
$$n = 1, 2, 3, \ldots$$

- *These are stationary orbits: the electron does not radiate energy while it remains in one. Photon absorption or emission occurs only on transition between stationary states.*

$$\frac{m_e v_n^2}{r_n} = \frac{kZe^2}{r_n^2}$$
$$k = \frac{1}{4\pi\varepsilon_0}$$

$$E_{\text{photon}} = E_{\text{higher}} - E_{\text{lower}}$$

For emission this is the positive energy carried by the photon; the atom loses that energy.

14 Radius, speed, period and frequency

$$r_n = 0.529\frac{n^2}{Z}\ \text{Å}$$
$$r_n \propto \frac{n^2}{Z}$$
$$\frac{r_1}{r_2} = \frac{n_1^2}{n_2^2}\frac{Z_2}{Z_1}$$

$$v_n = 2.18 \times 10^6 \frac{Z}{n}\ \text{m s}^{-1}$$
$$v_n \propto \frac{Z}{n}$$
$$\frac{v_1}{v_2} = \frac{Z_1}{Z_2}\frac{n_2}{n_1}$$

$$T_n = \frac{2\pi r_n}{v_n} \approx 1.52 \times 10^{-16}\frac{n^3}{Z^2}\ \text{s}$$
$$T_n \propto \frac{n^3}{Z^2}$$

$$f_n = \frac{1}{T_n} \propto \frac{Z^2}{n^3}$$

This is orbital frequency, distinct from the frequency of an emitted photon.

Atomic Structure

Bohr energy and transitions · Hydrogen energy levels

15 Bohr energy and transitions

$$E_n = -13.6\frac{Z^2}{n^2}\,\text{eV atom}^{-1} = -313.6\frac{Z^2}{n^2}\,\text{kcal mol}^{-1}$$

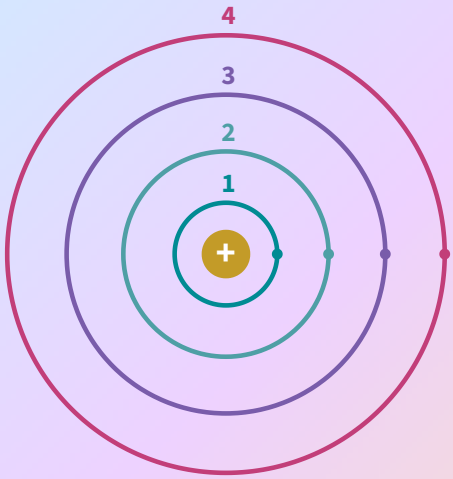
$$\begin{aligned} 1\,\text{eV} &\approx 3.83 \times 10^{-23}\,\text{kcal} \\ &= 1.602 \times 10^{-12}\,\text{erg} \\ &= 1.602 \times 10^{-19}\,\text{J} \end{aligned}$$

$$E_{n_2} - E_{n_1} = 13.6Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\,\text{eV}$$

For $n_2 > n_1$, this is the positive energy gap; use its magnitude for a photon.

16 Hydrogen energy levels

Shell / n	Energy (eV)	Adjacent upward gap
K / 1	−13.6	$E_2 - E_1$ = 10.2 eV
L / 2	−13.6/4 = −3.40	$E_3 - E_2 \approx$ 1.89 eV
M / 3	−13.6/9 ≈ −1.51	$E_4 - E_3 \approx$ 0.66 eV
N / 4	−13.6/16 = −0.850	$E_5 - E_4 \approx$ 0.31 eV



K · n = 1 · E_1

L · n = 2 · E_2

M · n = 3 · E_3

N · n = 4 · E_4

Higher n: energy approaches 0 from below

K, L, M and N correspond to n = 1, 2, 3 and 4. The shell radii here are schematic; energy approaches zero as n rises.

Atomic Structure

Kinetic, potential and total energy · Hydrogen spectral series

17 Kinetic, potential and total energy

$$E_{\mathrm{T}} = -13.6\frac{Z^2}{n^2}\ \mathrm{eV}$$
$$K = +13.6\frac{Z^2}{n^2}\ \mathrm{eV}$$
$$U = -27.2\frac{Z^2}{n^2}\ \mathrm{eV}$$

Bohr energy accounting: K + U = E

+1 **Kinetic K** positive + −2 **Potential U** negative = −1 **Total E** bound state

Ratio K : U : E = 1 : −2 : −1 for a hydrogen-like bound electron.

$$U = -2K = 2E_{\mathrm{T}}$$
$$K = -E_{\mathrm{T}} = -\frac{U}{2}$$
$$K : U : E_{\mathrm{T}} = 1 : -2 : -1$$

$$E_{\mathrm{ionization}} = -E_{\mathrm{T}} = 13.6\frac{Z^2}{n^2}\ \mathrm{eV}$$

Energy needed to remove the electron from level n to infinity.

18 Hydrogen spectral series

Series	Final n_1	Initial n_2	Region
Lyman	1	2, 3, 4, 5, …	Ultraviolet
Balmer	2	3, 4, 5, 6, …	Visible lines; series limit in near UV
Paschen	3	4, 5, 6, 7, …	Near infrared
Brackett	4	5, 6, 7, 8, …	Infrared
Pfund	5	6, 7, 8, 9, …	Infrared, longer wavelengths

$$N_{\mathrm{lines,max}} = \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

Maximum number of distinct transitions among all levels n_1 through n_2 when all are populated in an ensemble.

$$N_{\mathrm{lines,max}} = \frac{n(n-1)}{2}$$

For transitions among levels 1 through n. A single atom in one cascade does not emit every possible line.

Atomic Structure

Hydrogen spectral series · de Broglie hypothesis

18 Hydrogen spectral series

continued

$$\tilde{\nu} = \frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$n_2 > n_1$$

Rydberg formula; $R \approx 109678\ \text{cm}^{-1}$ for hydrogen ($\approx 1.09678 \times 10^7\ \text{m}^{-1}$).

19 de Broglie hypothesis

- Matter has both particle and wave properties.

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2mK}} = \frac{h}{\sqrt{2m|q|V}}$$

Nonrelativistic particle accelerated from rest through a potential difference of magnitude V; $|q|$ is its charge magnitude.

$$\lambda_{\text{electron}} \approx \frac{12.27}{\sqrt{V(\text{V})}}\ \text{Å} \approx \sqrt{\frac{150}{V(\text{V})}}\ \text{Å}$$

$$2\pi r_n = n\lambda$$

Exactly n de Broglie wavelengths fit around the nth Bohr orbit.

20 Heisenberg uncertainty principle

- The position and momentum of a particle cannot both be specified with arbitrarily small uncertainties. Δx and Δp denote their standard deviations; Δv is velocity uncertainty, m particle mass and h Planck's constant.

$$\Delta x\,\Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2}$$

$$\Delta x\, m\Delta v \geq \frac{h}{4\pi}$$

$$\Delta x\,\Delta v \geq \frac{h}{4\pi m}$$

$$\Delta E\,\Delta t \gtrsim \frac{\hbar}{2}$$

$$\frac{h}{4\pi} \approx 5.27 \times 10^{-35}\ \text{J s}$$

Energy–time is a related uncertainty relation; Δt is an appropriate characteristic timescale, not a position-like observable.

Atomic Structure

Principal quantum number n · Azimuthal quantum number ℓ

21 Principal quantum number n

- n identifies the shell and largely controls orbital size and energy. n = 1, 2, 3, 4 correspond to K, L, M, N. For a hydrogen-like atom, energy increases with n.

$$N_{\text{orbitals in shell}} = n^2$$
$$N_{\text{electrons,max}} = 2n^2$$
$$N_{\text{subshells}} = n$$

- Allowed ℓ values are 0 through n − 1: n = 3 permits ℓ = 0, 1, 2; n = 4 permits ℓ = 0, 1, 2, 3.

22 Azimuthal quantum number ℓ

- ℓ specifies the subshell and orbital angular-momentum magnitude and is associated with orbital shape. Allowed values: ℓ = 0, 1, ..., n − 1.

$$L = \sqrt{\ell(\ell+1)}\,\frac{h}{2\pi} = \sqrt{\ell(\ell+1)}\,\hbar$$
$$\hbar = \frac{h}{2\pi}$$

ℓ	Subshell	Name
0	s	sharp
1	p	principal
2	d	diffuse
3	f	fundamental

$$N_{\text{orbitals in subshell}} = 2\ell + 1$$
$$N_{\text{electrons,max}} = 2(2\ell + 1)$$

23 Magnetic quantum number mℓ

- mℓ distinguishes orbital angular-momentum orientation; its integer values run from −ℓ to +ℓ, including zero.

ℓ	Allowed mℓ
0	0
1	−1, 0, +1
2	−2, −1, 0, +1, +2

Atomic Structure

Electron spin · Nodes and radial plots

24 Electron spin

- An electron has intrinsic spin $s = 1/2$. Its spin projection quantum number is $m_s = +1/2$ or $-1/2$, represented by ↑ and ↓. These labels do not mean literal clockwise or anticlockwise mechanical rotation.

$$S = \frac{N_{\text{unpaired}}}{2}$$

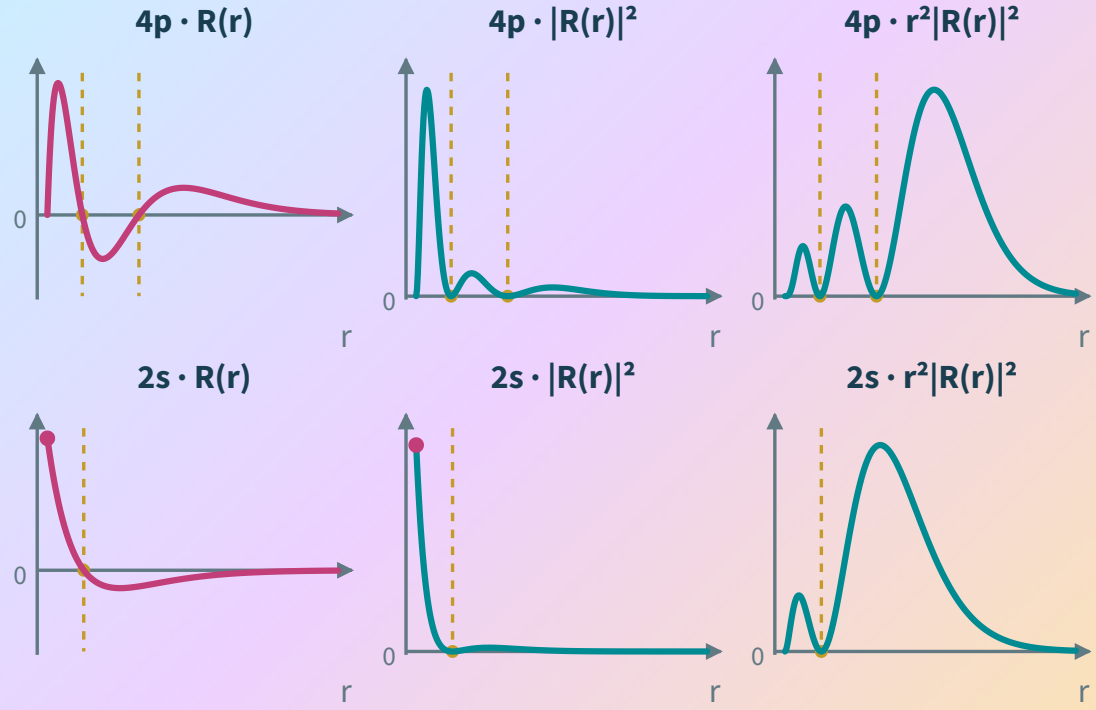
Total spin for parallel unpaired electrons; the two signs in the source correspond to spin projections, not a negative spin magnitude.

$$|\mathbf{S}| = \sqrt{S(S+1)}\,\hbar = \sqrt{S(S+1)}\,\frac{h}{2\pi}$$

25 Nodes and radial plots

$$N_{\text{radial}} = n - \ell - 1$$
$$N_{\text{angular}} = \ell$$
$$N_{\text{total}} = n - 1$$

- Find radial nodes using $n - \ell - 1$. On the graph, count the finite positive radii where the radial wavefunction is zero. For 4p, $n = 4$ and $\ell = 1$, giving two radial nodes.



Gold guides: radial nodes at r > 0; vertical scales normalized

Hydrogenic radial shapes: 4p has two radial nodes and 2s has one. The gold guides mark nodes at positive radius; vertical scales are normalized separately.

Atomic Structure

Aufbau principle and energy ordering · (n + ℓ) rule

26 Aufbau principle and energy ordering

- In the ground-state Aufbau approximation, electrons fill lower-energy orbitals before higher-energy orbitals.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p$$

- Subshell capacities: s^2, p^6, d^{10} and f^{14}. A 3f subshell is impossible because $\ell = 3$ requires $n \geq 4$.

- Some atoms gain stability through half-filled d^5 or filled d^{10} arrangements, giving common exceptions to a simple d^4 or d^9 prediction (for example, promotion from a nearby s subshell). This is a useful pattern, not a universal promotion rule.

CHECK THE LOWER SUBSHELL FIRST



lower-energy s higher-energy p

An s vacancy remains while p is occupied.

Not the ordinary Aufbau ground-state filling.

The ordinary Aufbau ground state fills the lower-energy s subshell before the higher-energy p subshell.

27 (n + ℓ) rule

- A subshell with lower $n + \ell$ usually fills first. For equal $n + \ell$, lower n fills first. This empirical rule gives a filling order, not a numerical orbital energy.

Atomic Structure

(n + ℓ) rule · Pauli exclusion and Hund's rule

27 (n + ℓ) rule

continued

$$0 \le \ell \le n - 1$$

A proposed subshell with $n \le \ell$ is not possible; ℓmin = 0 and ℓmax = n − 1.

28 Pauli exclusion and Hund's rule

- Pauli exclusion principle: no two electrons in an atom have the same set of all four quantum numbers. Each orbital holds at most two electrons, with opposite spin projections.
- Hund's rule: fill the degenerate orbitals of a subshell singly with parallel spins before pairing electrons.

3d⁸: fill all five orbitals before extra pairing

Correct



two parallel unpaired electrons

Incorrect



one empty orbital despite extra pairing

For 3d⁸, the Hund arrangement leaves two parallel unpaired electrons across the five d orbitals.

29 Spin-only magnetic moment

$$\mu_{so} = \sqrt{N(N+2)}\,\mu_B$$

N is the number of unpaired electrons; μB is the Bohr magneton. This is the spin-only approximation.

NEW CHAPTER PHYSICAL CHEMISTRY

Thermodynamics

Heat • work • energy

03

01 Thermodynamics and its scope

- Thermodynamics describes energy changes and exchanges between a system and its surroundings, including changes accompanying reactants → products. Bond breaking requires energy (endothermic); bond formation releases energy (exothermic).

$$\text{Universe} = \text{system} + \text{surroundings}$$

- System: the part of the universe being studied. Surroundings: everything outside it. Boundary: the real or imaginary surface between them.

02 Types of systems

System	Matter exchange	Energy exchange
Open	Yes	Yes
Closed	No	Yes
Isolated	No	No

03 State and path functions

- A state-function change depends only on initial and final states. Examples: U, H, G, S, P, T and V, and their changes. Path functions depend on how the process is carried out: heat q and work w.

04 Intensive and extensive properties

Type	Definition	Examples
Intensive	Independent of system amount at fixed state	Density, temperature, pressure, molar heat capacity, specific heat, viscosity, surface tension, melting point, boiling point, freezing point
Extensive	Scales with amount of material	Mass, volume, amount n, entropy S, Gibbs energy G, enthalpy H, internal energy U (or E), heat capacity C

- For a homogeneous system, an extensive property divided by mass is a specific, intensive property. A ratio of two extensive properties that scale together is intensive.

05 Heat and chemistry sign convention

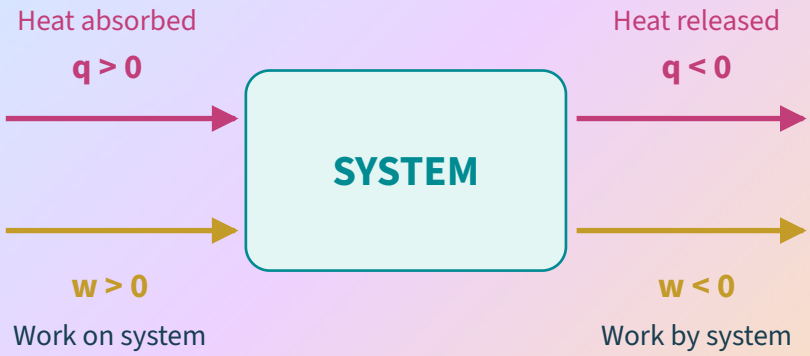
- Heat q is energy transfer caused by a temperature difference between system and surroundings. Heat absorbed by the system is positive; heat released by the system is negative. Work done on the system is positive; work done by the system is negative.

Thermodynamics

Heat and chemistry sign convention · Energy conversions

05 Heat and chemistry sign convention

continued



Chemistry convention: ΔU = q + w

Energy entering the system is positive; energy leaving the system is negative in the chemistry sign convention.

06 Energy conversions

$$1\,\text{cal} = 4.184\,\text{J} \approx 4.2\,\text{J}$$
$$1\,\text{L atm} = 101.325\,\text{J}$$

$$1\,\text{L bar} = 100\,\text{J}$$
$$1\,\text{J} = 10^{7}\,\text{erg}$$

07 Pressure–volume work

$$w = -\int_{V_i}^{V_f} P_{\text{ext}}\,dV$$
$$w = -P_{\text{ext}}\Delta V = -P_{\text{ext}}(V_f - V_i)$$

The second form requires constant external pressure; work is the signed area associated with the external-pressure–volume path.

- *Expansion: $\Delta V > 0$, so $w < 0$; the system does work. Compression: $\Delta V < 0$, so $w > 0$; work is done on the system.*

Thermodynamics

Reversible and irreversible processes · Thermodynamic process vocabulary

08 Reversible and irreversible processes

Reversible ideal limit	Irreversible process
Infinitesimal driving differences; proceeds through equilibrium states	Finite driving differences; does not pass through equilibrium at every stage
Can be reversed without net change to system and surroundings	Cannot restore both system and surroundings exactly by simple reversal
Quasistatic; external pressure changes to track gas pressure in expansion	May be fast; constant-external-pressure expansion is a common example
Ideal limiting process	Natural spontaneous processes are irreversible

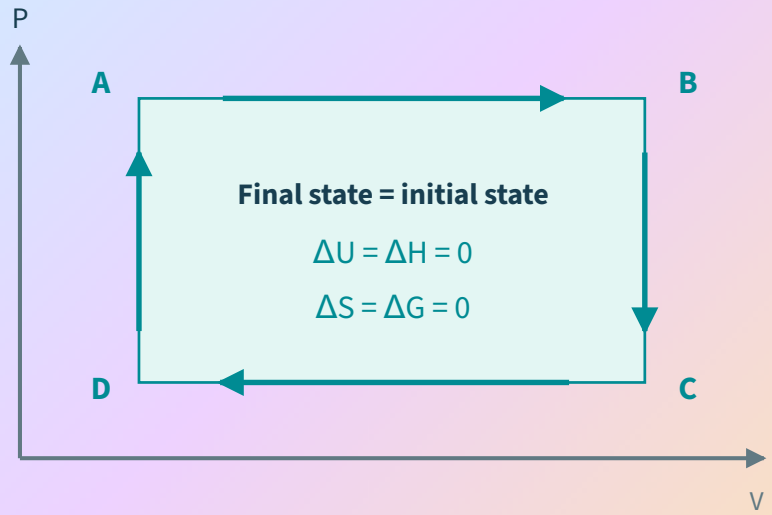
- Speed alone does not determine reversibility, and not every irreversible process has constant external pressure.

09 Thermodynamic process vocabulary

Process	Constraint
Isothermal	$\Delta T = 0$; constant temperature
Isobaric	$\Delta P = 0$; constant pressure
Isochoric	$\Delta V = 0$; constant volume
Adiabatic	$q = 0$; no heat transfer
Cyclic	Final state equals initial state

$$\Delta U = \Delta H = \Delta S = \Delta G = 0$$
(complete cycle)

State-function changes vanish; net heat and work need not vanish.



Net heat and work can be nonzero over a cycle.

A complete cycle returns every state function to its initial value; net heat and work can still be nonzero.

Thermodynamics

Internal energy · Zeroth and first laws

10 Internal energy

- Internal energy U (or E) is the sum of microscopic forms of energy, including kinetic, intermolecular/electrostatic, chemical and nuclear contributions. For an ideal gas U depends only on temperature; for a real gas it generally depends on temperature and volume.

$$U = U_{\text{microscopic kinetic}} + U_{\text{potential}} + U_{\text{nuclear}} + \cdots$$

11 Zeroth and first laws

- Zeroth law: if A is in thermal equilibrium with B, and B with C, then A is in thermal equilibrium with C.

- First law: energy is conserved. It can be transformed, but cannot be created or destroyed; the total energy of an isolated universe remains constant.

$$\Delta U = q + w$$

Use the chemistry sign convention consistently.

12 Isothermal ideal-gas process

$$\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow q = -w$$

$\Delta U = 0$ here requires an ideal gas.

- In reversible isothermal expansion/compression, gas pressure varies as volume changes.

$$w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -2.303nRT \log_{10} \frac{V_2}{V_1}$$

$$w_{\text{rev}} = -nRT \ln \frac{P_1}{P_2} = -2.303nRT \log_{10} \frac{P_1}{P_2}$$

13 Irreversible isothermal expansion or compression

$$w = -P_{\text{ext}}(V_2 - V_1) = -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$$

Constant external pressure; P_1 and P_2 are equilibrium gas pressures at the endpoints. Gas pressure itself need not remain constant.

Thermodynamics

Irreversible isothermal expansion or compression · Adiabatic ideal-gas relations

13 Irreversible isothermal expansion or compression

continued

- *Expansion into a vacuum has Pext = 0, so w = 0. Between the same isothermal endpoints, reversible expansion gives the greatest work magnitude, while reversible compression needs the least work input.*

$$w_{\text{rev}} < w_{\text{irrev}}$$

(expansion, signed chemistry work)

Equivalently |wrev| > |wirrev| for expansion. For compression, wrev < wirrev with both works positive.

14 Adiabatic ideal-gas relations

$$q = 0$$
$$w = \Delta U$$

$$PV^{\gamma} = \text{constant}$$
$$TV^{\gamma-1} = \text{constant}$$
$$T^{\gamma}P^{1-\gamma} = \text{constant}$$

These relations require a reversible adiabatic ideal-gas process and approximately constant heat capacities.

Mayer relation · ideal gas

$C_{p,m}$ (constant pressure) = $C_{V,m}$ (constant volume) + R

Per mole: $C_{p,m} - C_{V,m} = R$. For n moles: $C_p - C_V = nR$.

$$C_{P,m} - C_{V,m} = R$$
$$C_P - C_V = nR$$
$$\gamma = \frac{C_{P,m}}{C_{V,m}} = \frac{C_P}{C_V}$$

Mayer relation and heat-capacity ratio (Poisson ratio); molar and total heat capacities must not be mixed.

Ideal gas model	$C_{V,m}$	$C_{p,m}$	γ
Monatomic: He, Ne	3R/2	5R/2	5/3 ≈ 1.67
Diatomic: O_2, N_2	5R/2	7R/2	7/5 = 1.40
Linear triatomic: CO_2	5R/2	7R/2	7/5 = 1.40
Nonlinear triatomic: SO_2	3R	4R	4/3 ≈ 1.33

Thermodynamics

Adiabatic ideal-gas relations · Isochoric process

14 Adiabatic ideal-gas relations

continued

- The tabulated polyatomic values assume rotations are active and vibrations are not thermally excited.

$$w_{\text{ad}} = \Delta U = nC_{V,m}(T_2 - T_1)$$
$$= \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

Ideal gas, constant Cv; the equality w = −PextΔV additionally requires constant Pext, but w = −Δn_gRT is not a general adiabatic-work formula.

15 Isochoric process

$$V = \text{constant}$$
$$\Delta V = 0$$
$$w_{PV} = 0$$
$$q_V = \Delta U = nC_{V,m}\Delta T$$

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T}\right)_V$$

For one mole, ΔUm = Cv,mΔT when heat capacity is constant; qV = ΔU requires only PV work.

16 Isobaric process and enthalpy

$$\Delta U = q + w = q - P\Delta V$$
$$q_P = \Delta U + P\Delta V = \Delta H$$

Constant pressure and only PV work.

$$\Delta H = nC_{P,m}\Delta T$$
$$C_{P,m} = \left(\frac{\partial H_m}{\partial T}\right)_P$$

$$H = U + PV$$
$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$$

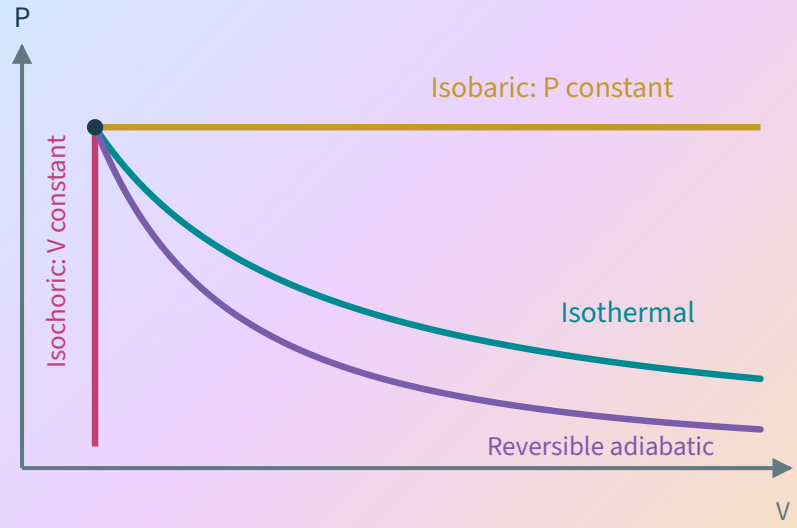
Thermodynamics

Isobaric process and enthalpy · Enthalpy versus internal energy

16 Isobaric process and enthalpy

continued

- $\Delta H > 0$: endothermic. $\Delta H < 0$: exothermic.



Same initial state; ideal-gas expansion curves

From a common starting point, reversible adiabatic expansion lowers pressure more steeply than isothermal expansion.

17 Enthalpy versus internal energy

$$\Delta H = \Delta U + P\Delta V \quad (P \text{ constant})$$

$$\Delta_r H = \Delta_r U + \Delta n_g RT$$

For ideal gaseous reactants and products at the same temperature; condensed-phase PV contributions are usually negligible.

$$\Delta n_g = \sum \nu_{\text{gaseous products}} - \sum \nu_{\text{gaseous reactants}}$$

Δn_g	Comparison
0	$\Delta H = \Delta U$
> 0	$\Delta H > \Delta U$
< 0	$\Delta H < \Delta U$

Thermodynamics

Free expansion · Heat capacity definitions

18 Free expansion

- Free expansion is irreversible expansion against zero external pressure, so $w = 0$. For an insulated ideal gas, $q = 0$, $\Delta U = 0$ and $\Delta T = 0$. Neither $q = 0$ nor $\Delta T = 0$ follows from free expansion alone for all systems.

19 Heat capacity definitions

$$C = \frac{q}{\Delta T}$$
$$c = \frac{q}{m\Delta T}$$
$$C_m = \frac{q}{n\Delta T}$$

Heat capacity, specific heat capacity and molar heat capacity for a specified process and approximately constant capacities.

$$C_{P,m} = \frac{q_P}{n\Delta T}$$
$$\Delta H = q_P = nC_{P,m}\Delta T$$

$$C_{V,m} = \frac{q_V}{n\Delta T}$$
$$\Delta U = q_V = nC_{V,m}\Delta T$$

- The first law alone cannot tell us whether a process is feasible or spontaneous under the given conditions.

20 Second law and entropy

- The second law determines the allowed direction of spontaneous change, including heat flow. A spontaneous irreversible process increases total entropy of system plus surroundings.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Total entropy change	Interpretation
> 0	Spontaneous irreversible direction
< 0	Nonspontaneous proposed direction for an isolated total system
$= 0$	Reversible limit; equilibrium has no net change

Thermodynamics

Second law and entropy · Entropy trends and reversibility

20 Second law and entropy

continued

- Entropy is often introduced as a measure of dispersal or disorder. Greater energy dispersal and a larger number of accessible microstates correspond to greater entropy.

$$dS = \frac{\delta q_{\text{rev}}}{T}$$

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

(T constant)

Entropy has unit J K^{-1}; molar entropy has unit J mol^{-1} K^{-1}.

21 Entropy trends and reversibility

- For a gas of fixed amount: lowering pressure generally increases entropy; raising temperature increases entropy. Increasing the amount increases total entropy. Mixing distinguishable ideal components and dilution generally increase entropy.

$$\Delta S_{\text{universe}} = 0 \Rightarrow \Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

(reversible)

$$\Delta S_{\text{universe}} > 0$$

(irreversible spontaneous process)

$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

Typical molar-entropy order for the same substance under comparable conditions.

22 Entropy change of an ideal gas

$$\Delta S = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = nC_{P,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

Ideal gas and constant heat capacities. Entropy is a state function, so these endpoint formulas also apply to irreversible paths between the same equilibrium states.

Thermodynamics

Entropy change of an ideal gas · Phase changes and chemical reactions

22 Entropy change of an ideal gas

continued

Special process	Entropy change
Isothermal ideal gas	$\Delta S = nR\ \ln(V_2/V_1) = nR\ \ln(P_1/P_2)$
Isochoric ideal gas	$\Delta S = nC_{v,m}\ \ln(T_2/T_1)$
Isobaric ideal gas	$\Delta S = nC_{p,m}\ \ln(T_2/T_1)$
Reversible adiabatic	$q_{rev} = 0;\ \Delta S = 0$

23 Phase changes and chemical reactions

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_m}$$
$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$$
$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T_{\text{sub}}}$$

At the relevant equilibrium phase-transition temperature; use kelvin.

$$\Delta_{\text{r}} S^\circ = \sum_{\text{products}} \nu_i S_i^\circ - \sum_{\text{reactants}} \nu_i S_i^\circ$$

24 Spontaneous and nonspontaneous processes

- A spontaneous direction is thermodynamically favoured under the stated conditions and can proceed without continuous external work, although activation energy may still be needed. A nonspontaneous direction requires suitable external driving or coupling. Spontaneity reflects both entropy change and enthalpy change; exothermicity alone is insufficient.

25 Gibbs free energy

$$G = H - TS$$
$$\Delta G = \Delta H - T\Delta S$$
$$(T \text{ constant})$$

$$\Delta G_{\text{system}} = -T\Delta S_{\text{universe}}$$

For a system at constant T and P exchanging heat with a reservoir, with the standard conditions for the Gibbs spontaneity criterion.

Thermodynamics

Gibbs free energy · Reaction quotient, equilibrium and useful work

25 Gibbs free energy

continued

Condition at constant T, P	Total entropy	Gibbs criterion
Spontaneous	$\Delta S_{total} > 0$	$\Delta G < 0$
Nonspontaneous forward direction	$\Delta S_{total} < 0$	$\Delta G > 0$
Equilibrium	$\Delta S_{total} = 0$	$\Delta_r G = 0$

$$\Delta G = \Delta H - T\Delta S$$

Spontaneity at fixed T, P

$\Delta H < 0; \Delta S > 0$	Spontaneous at all temperatures
$\Delta H > 0; \Delta S < 0$	Nonspontaneous at all temperatures
$\Delta H < 0; \Delta S < 0$	Spontaneous at low T
$\Delta H > 0; \Delta S > 0$	Spontaneous at high T

ΔH	ΔS	Temperature dependence
−	+	Spontaneous at all T ($\Delta G < 0$)
−	−	Spontaneous at low T; nonspontaneous at high T
+	+	Nonspontaneous at low T; spontaneous at high T
+	−	Nonspontaneous at all T ($\Delta G > 0$)

- When ΔH and ΔS have the same sign, the crossover is $T = \Delta H/\Delta S$ if those quantities can be treated as constant.

26 Reaction quotient, equilibrium and useful work

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q = \Delta_r G^\circ + 2.303RT \log_{10} Q$$

Q is the reaction quotient. The ° symbol denotes standard states at the specified temperature, not necessarily STP.

$$\Delta_r G = 0,\ Q = K \Rightarrow \Delta_r G^\circ = -RT \ln K = -2.303RT \log_{10} K$$

$$w_{\text{useful,max,by system}} = -\Delta G$$

At constant T and P, the maximum reversible non-expansion work obtainable equals $-\Delta G$. In chemistry's 'work on the system' sign convention, $w_{non\text{-}PV,rev} = \Delta G$.

$$\Delta_r G = -nFE_{\text{cell}}$$
$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$$

n is moles of electrons transferred per mole of reaction; F is Faraday constant.

NEW CHAPTER PHYSICAL CHEMISTRY

Chemical Equilibrium

Equilibrium constants • shifts • dissociation

04

01 Basic equilibrium ideas

- At equilibrium, macroscopic properties such as temperature, pressure, colour and concentrations stay constant under fixed conditions. Chemical equilibrium is dynamic, can be reached from either direction, and occurs in both homogeneous and heterogeneous systems.

- A catalyst speeds up both forward and reverse processes, so equilibrium is reached sooner. It does not change the equilibrium composition or equilibrium constant.

02 Reversible and effectively irreversible reactions

Reversible reaction	Effectively irreversible reaction under the stated conditions
Forward and reverse reactions both occur	Reverse reaction is negligible on the observed timescale
A closed system permits equilibrium composition to become established	Product removal or other conditions can drive near-complete conversion
Reactants and products coexist at equilibrium	May proceed nearly to completion
Products can regenerate reactants	Products do not appreciably regenerate reactants under those conditions

- Open versus closed container is not a universal definition of reversibility; effectively irreversible reactions can also occur in closed containers.

03 What is equal at equilibrium?

$$r_{\mathrm{f}} = r_{\mathrm{b}}$$
$$\Delta_{\mathrm{r}} G = 0$$

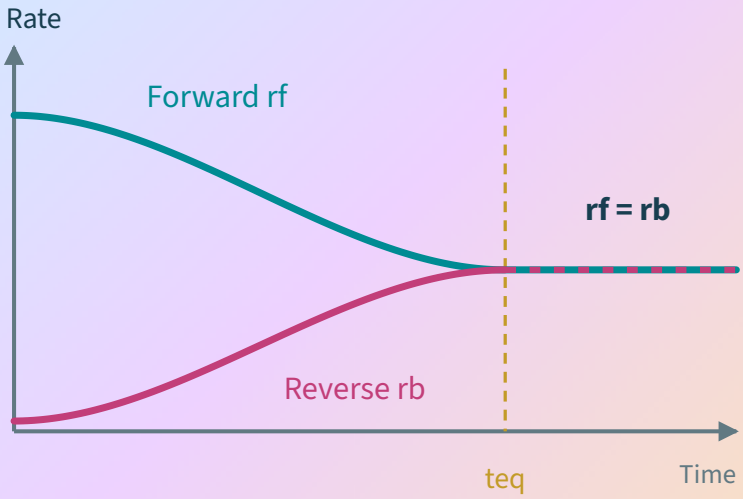
- Reactant and product concentrations are constant, but need not equal one another. Depending on the reaction and starting amounts, the equilibrium reactant concentration may be larger, equal to or smaller than the product concentration.

Chemical Equilibrium

What is equal at equilibrium?

03 What is equal at equilibrium?

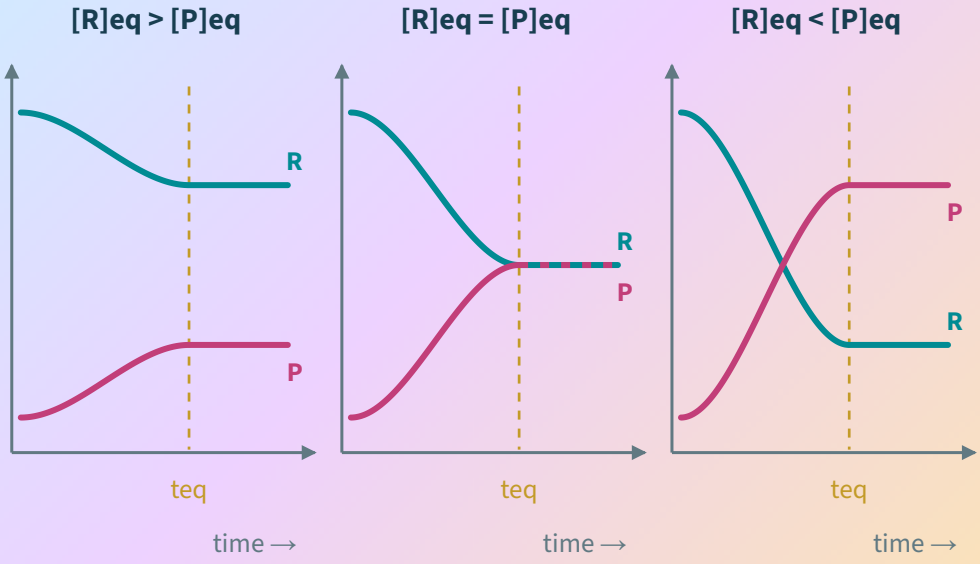
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Equal rates; both reactions continue.

At equilibrium, the forward and reverse rates are equal and remain nonzero.

Concentration at equilibrium



Teal: reactant R · Magenta: product P

Equilibrium concentrations are constant, but the reactant and product concentrations can differ.

- *A catalyst shortens the time needed to attain equilibrium. The equilibrium remains dynamic even though the net reaction rate is zero.*

Chemical Equilibrium

Law of mass action: scope · Activities and the elementary rate-law illustration

04 Law of mass action: scope

- The equilibrium law of mass action expresses the equilibrium constant as a product of activities raised to stoichiometric powers. For an elementary reaction, its rate is proportional to the product of reactant activities or concentrations raised to the corresponding elementary-step powers; this rate rule cannot automatically be applied to an overall multistep reaction.

05 Activities and the elementary rate-law illustration

- Pure solids and pure liquids have activity 1 and are omitted from equilibrium-constant expressions. Gases and dissolved species can contribute; the rule is not restricted to gaseous elements.

$$2\mathrm{A(g)} + \mathrm{B(g)} \longrightarrow 2\mathrm{C(g)}$$
$$r = k[\mathrm{A}]^2[\mathrm{B}]$$

Rate law shown in the source; valid as written only for the stated elementary-step model.

$$\mathrm{A(s)} + 2\mathrm{B(g)} \longrightarrow 4\mathrm{C(g)}$$
$$a_{\mathrm{A(s)}} = 1$$

The source writes r = k[B]². Treat that as an assumed rate model, not something deduced from an overall heterogeneous equation.

$$a\mathrm{A(g)} + b\mathrm{B(g)} \rightleftharpoons c\mathrm{C(g)} + d\mathrm{D(g)}$$

$$r_f = k_f[\mathrm{A}]^a[\mathrm{B}]^b$$
$$r_b = k_b[\mathrm{C}]^c[\mathrm{D}]^d$$

For an elementary forward/reverse pair with these rate laws.

$$r_f = r_b \Rightarrow K_c = \frac{k_f}{k_b} = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

06 Kc, Kp and Kx

Symbol	Expressed using
Kc	Equilibrium concentrations
Kp	Equilibrium partial pressures
Kx	Equilibrium mole fractions

Chemical Equilibrium

Kc, Kp and Kx · Relation of pressure and concentration constants

06 Kc, Kp and Kx

continued

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

$$K_x = \frac{x_C^c x_D^d}{x_A^a x_B^b}$$

$$\Delta n_g = (c+d) - (a+b)$$

Sum of stoichiometric coefficients of gaseous products minus that of gaseous reactants; do not count solids or liquids.

- In the source's dimensional school convention, units of Kc are (mol L⁻¹)^Δn_g and of Kp are (atm)^Δn_g for this all-gas equation; Kx is dimensionless. Thermodynamic equilibrium constants formed from dimensionless activities are themselves dimensionless.

07 Relation of pressure and concentration constants

$$K_p = K_c(RT)^{\Delta n_g}$$

$$R \approx 0.082057\,\mathrm{L\,atm\,mol^{-1}\,K^{-1}}$$

Ideal gases, using the source's dimensional Kp/Kc convention; T in kelvin. The mnemonic R ≈ 1/12 is a rough approximation.

- If Δn_g = 0, Kp = Kc numerically in matched conventions. If the numerical value RT > 1 in the chosen L–atm units, positive Δn_g gives Kp > Kc and negative Δn_g gives Kp < Kc. These comparisons depend on units.

$$T \approx \frac{1}{0.0821}\,\mathrm{K} \approx 12.18\,\mathrm{K} \Rightarrow (RT)_{\text{numerical}} = 1$$

This reproduces the source's numeric shortcut; it is not a universal physical equality temperature independent of units.

08 Changing the written reaction

Reaction	Equilibrium constant
A ⇌ B	K
B ⇌ A	1/K
nA ⇌ nB	Kⁿ
A/n ⇌ B/n	K^(1/n)

Chemical Equilibrium

Combining equilibrium reactions · Extent of reaction

09 Combining equilibrium reactions

$$\mathrm{A} \rightleftharpoons \mathrm{B}$$
$$K_1 = \frac{[\mathrm{B}]}{[\mathrm{A}]};$$
$$\mathrm{B} \rightleftharpoons \mathrm{C}$$
$$K_2 = \frac{[\mathrm{C}]}{[\mathrm{B}]}$$

$$\mathrm{A} \rightleftharpoons \mathrm{C}$$
$$K_3 = K_1 K_2 = \frac{[\mathrm{C}]}{[\mathrm{A}]}$$

Add reactions → multiply constants; subtract a reaction → divide by its constant.

10 Extent of reaction

Magnitude of K	Usual interpretation
$K > 10^3$	Products strongly favoured; reaction often nearly complete
$K < 10^{-3}$	Reactants strongly favoured; little conversion in the simple initial-reactant case
$10^{-3} < K < 10^3$	Both sides appreciably represented

For a simple A ⇌ B equilibrium, K = [B]/[A], making the comparison direct. For a general reaction, K includes powers and activities; its magnitude is a qualitative guide and must be interpreted with stoichiometry and initial composition. Larger K corresponds to more favourable standard Gibbs energy of products relative to reactants, not a literal universal proportionality to 'stability'.

11 Reaction quotient and direction

$$Q_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$
at any instant;
$$K_c = Q_c$$
at equilibrium

Chemical Equilibrium

Reaction quotient and direction · Temperature dependence of K

11 Reaction quotient and direction

continued

Compare Q with K to predict the direction

$Q < K$	$Q = K$	$Q > K$
Forward favoured →	Dynamic equilibrium	← Reverse favoured

$\Delta_r G = RT \ln(Q/K)$. At equilibrium: $\Delta_r G = 0$; forward rate = reverse rate.

Comparison	Net direction
$Q < K$	Forward, toward products
$Q = K$	Equilibrium
$Q > K$	Backward, toward reactants

12 Temperature dependence of K

- For a fixed written reaction and standard-state convention, the equilibrium constant depends on temperature. Initial concentrations and catalysts do not change it.

$$\log_{10}\frac{K_2}{K_1} = \frac{\Delta_r H^\circ}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Integrated van 't Hoff equation; assumes ΔrH° approximately constant over the interval.

- If $T_2 > T_1$: for an endothermic reaction ($\Delta H° > 0$), $K_2 > K_1$; for an exothermic reaction ($\Delta H° < 0$), $K_2 < K_1$.

13 Degree of dissociation

$$\alpha = \frac{\text{initial reactant moles that dissociate}}{\text{initial reactant moles}}$$

$$\nu_1 \mathrm{A} \rightleftharpoons \nu_2 \mathrm{B} + \nu_3 \mathrm{C}$$
$$\Delta\nu = (\nu_2 + \nu_3) - \nu_1$$

$$\alpha = \frac{\nu_1}{\Delta\nu}\left(\frac{D_T - D_O}{D_O}\right)$$

Initially pure gaseous A, ideal behaviour, $\Delta\nu \neq 0$. DT is theoretical vapour density of undissociated A ($M_A/2$ relative to H_2); DO is observed equilibrium vapour density.

Chemical Equilibrium

K and Gibbs energy · Le Chatelier's principle

14 K and Gibbs energy

$$\Delta_r G^\circ = -RT \ln K = -2.303RT \log_{10} K$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$
$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

- At equilibrium ΔrG = 0 and Q = K. A more negative ΔrG° means larger K. Negative ΔrG means forward change is spontaneous at the current composition; positive ΔrG means the reverse direction is favoured. Product dominance is linked to K and ΔrG°, not to the sign of ΔrG alone.

15 Le Chatelier's principle

- When an equilibrium is disturbed, the composition shifts in a direction that tends to oppose the change. A new equilibrium forms under the new conditions. This principle applies to chemical and physical equilibria.

16 Concentration, temperature and pressure

Change	Favoured direction
Add reactant or remove product	Forward
Remove reactant or add product	Backward
Increase temperature	Endothermic direction
Decrease temperature	Exothermic direction
Increase volume / decrease pressure	Side with more gas moles
Decrease volume / increase pressure	Side with fewer gas moles

$$\mathrm{R} \rightleftharpoons \mathrm{P} + \text{heat}$$

Forward direction exothermic; reverse direction endothermic. Pressure/volume rules concern gaseous equilibria at fixed temperature, with no shift from this cause if gas-mole counts are equal.

17 Adding an inert gas

- At constant volume and temperature, adding an ideal inert gas does not change reacting gases' partial pressures, so it does not shift equilibrium. At constant total pressure and temperature, the volume increases and equilibrium shifts toward the side with more gaseous moles, if the gas-mole counts differ.

Chemical Equilibrium

Physical equilibrium and phase volume · Ice–water equilibrium

18 Physical equilibrium and phase volume

- Different phases of a substance can coexist in dynamic equilibrium: solid ⇌ liquid ⇌ gas, with sublimation/deposition linking solid and gas. Increased pressure favours the phase of lower molar volume. For many substances $V_{solid} < V_{liquid} \ll V_{gas}$, but ice has a larger molar volume than liquid water.

$$\rho = \frac{m}{V}$$

For a fixed mass, density and volume vary inversely.

19 Ice–water equilibrium

$$\mathrm{H_2O(s)} \rightleftharpoons \mathrm{H_2O(l)}$$
$$\Delta H_{\mathrm{fus}} > 0$$

- Ice: lower density, larger volume. Liquid water: higher density, smaller volume. Raising pressure favours melting and lowers the ordinary melting point of ice.

20 Boiling of water

$$\mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_2O(g)}$$
$$\Delta H_{\mathrm{vap}} > 0$$

- Liquid has much smaller volume than vapour. Raising temperature favours vaporization; raising pressure favours condensation, forms more liquid and raises the boiling point.

21 Solubility of a gas in a liquid

$$\text{gas} + \text{liquid solvent} \rightleftharpoons \text{solution}$$

- Dissolution of many gases is exothermic and reduces the volume associated with the gas. For such cases, increasing gas partial pressure or lowering temperature increases solubility; decreasing pressure or raising temperature decreases it. The temperature rule follows the actual dissolution enthalpy and is not universal for every gas/solvent pair.

Ionic Equilibrium

Acids & bases • pH • solubility

05

01 Common logarithms and natural logarithms

$$\log \equiv \log_{10}$$
$$\ln \equiv \log_e$$
$$\ln e = 1$$
$$\log_{10} 10 = 1$$
$$\log 1 = 0$$

$$\ln x = 2.303 \log_{10} x$$

x	$\log_{10} x$ (approx.)
2	0.30
3	0.48
4	0.60
5	0.70
6	0.78
7	0.84
8	0.90
9	0.95
10	1.00
20	1.30
30	1.48
200	2.30
500	2.70
1000	3.00

$$\log(ab) = \log a + \log b$$
$$\log \frac{a}{b} = \log a - \log b$$
$$\log(a^n) = n \log a$$

02 The p notation

$$pX = -\log_{10} X$$
$$\mathrm{pH} = -\log_{10} a_{\mathrm{H^+}} \approx -\log_{10}[\mathrm{H^+}]$$
$$\mathrm{pOH} \approx -\log_{10}[\mathrm{OH^-}]$$

Ionic Equilibrium

The p notation · Antilogarithms

02 The p notation

continued

$$pK_a = -\log_{10} K_a$$
$$pK_b = -\log_{10} K_b$$

Concentration expressions are the usual dilute-solution approximation, with concentrations numerically in mol L^{-1}.

03 Antilogarithms

$$\text{antilog}_{10}(x) = 10^x$$
$$\text{antilog}_{10}(-x) = 10^{-x}$$

$$\ln x = y \Rightarrow x = e^y$$
$$\log_{10} x = y \Rightarrow x = 10^y$$

Log statement	Equivalent antilog
log 100 = 2	antilog 2 = 10^2 = 100
log 0.01 = −2	antilog(−2) = 10^{-2} = 0.01
log 2 ≈ 0.30	antilog 0.30 ≈ $10^{0.30}$ ≈ 2
log 1000 = 3	antilog 3 = 10^3 = 1000
antilog(log 2)	2
log x = 4	x = 10^4

04 Worked log and pH examples

$$\log x = 4.84 \Rightarrow x = 10^{4.84} = 10^4 \times 10^{0.84} \approx 7 \times 10^4$$

This is the source's antilog calculation, presented as a mathematical x example; it is not a realistic dilute-aqueous $[H^+]$.

$$[\mathrm{H^+}] = 1.2 \times 10^{-5}\,\mathrm{mol\,L^{-1}} \Rightarrow \mathrm{pH} = 5 - \log(1.2) \approx 4.92$$

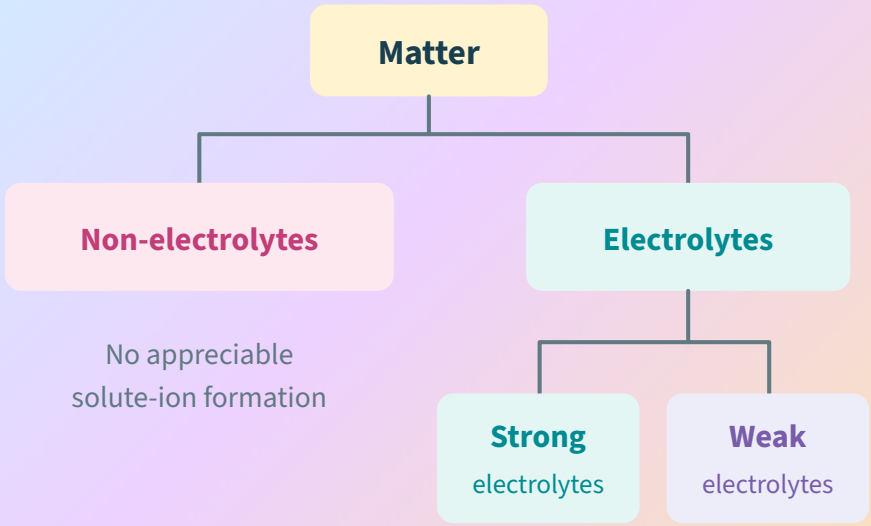
$$-\log(1.2 \times 10^{-5}) = -[\log 12 + \log 10^{-6}] = 6 - \log 6 - \log 2$$

Alternative decomposition used in the handwritten working.

Ionic Equilibrium

Electrolyte classification · Electrolytes

05 Electrolyte classification



Electrolytes form conducting ions and are classified as strong or weak according to their degree of ionization.

- *Non-electrolytes have essentially no ionization into solute ions in the stated solvent ($\alpha \approx 0$), so they do not contribute appreciable ionic conduction. Examples in the source: benzene (C_6H_6), diethyl ether, urea, glucose and fructose. Benzene/ether have limited water solubility; their classification does not imply high aqueous solubility.*

06 Electrolytes

- *Electrolytes produce ions in a suitable solvent or molten state and thereby conduct electricity. Acids, bases and salts are common examples. Strong electrolytes are nearly completely ionized/dissociated in dilute solution ($\alpha \approx 1$); weak electrolytes are partially ionized ($0 < \alpha < 1$). Conductivity also depends on concentration and ion mobility, so strength alone does not fix it.*

$$\mathrm{HCl(aq)} \longrightarrow \mathrm{H^+(aq) + Cl^-(aq)}$$

$$\mathrm{CH_3COOH(aq)} \rightleftharpoons \mathrm{CH_3COO^-(aq) + H^+(aq)}$$

Ionic Equilibrium

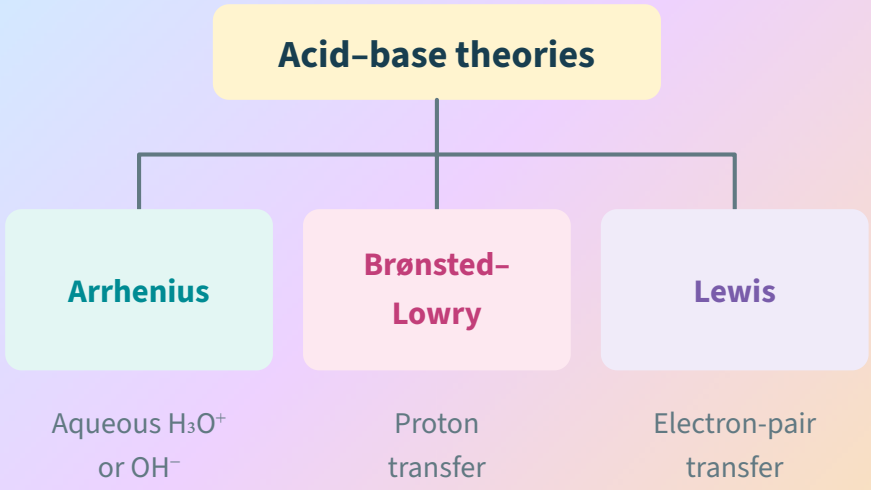
Acid and base examples · Three acid–base frameworks

07 Acid and base examples

Category	Examples / qualification
Strong acids	$HClO_4$, HI, HBr, HCl, HNO_3; H_2SO_4 has a strong first ionization; $HClO_3$ is also usually treated as strong
Weak acids	H_2CO_3, HF, HCN, HNO_2, HCOOH, CH_3COOH, H_3PO_4 and other common phosphorus oxyacids such as H_3PO_2, $HClO_2$, HClO, H_2S, H_2SO_3
Strong bases in water	Group-1 hydroxides including LiOH, NaOH, KOH, RbOH; dissolved $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$ are strongly dissociated
Weak molecular bases	$NH_3(aq)$, traditionally written NH_4OH in elementary notes; many organic bases
Sparingly soluble / amphoteric hydroxides mentioned in source	$Be(OH)_2$, $Mg(OH)_2$, $Zn(OH)_2$, $Al(OH)_3$, $Fe(OH)_2$, $Cu(OH)_2$; distinguish low solubility and amphoterism from weak-base ionization

- Many common carboxylic acids are weak; 'almost all organic compounds are weak acids' is not a valid generalization. Soluble salts are strong electrolytes in the usual introductory classification, but 'all salts dissolve completely' is false.

08 Three acid–base frameworks



Arrhenius, Brønsted–Lowry and Lewis describe aqueous ions, proton transfer and electron-pair transfer, respectively.

Common aqueous acid properties	Common aqueous base properties
Increase H_3O^+ (often written H^+)	Increase OH^-
Turn blue litmus red	Turn red litmus blue
Described as sour	Described as bitter
pH < 7 at 25 °C	pH > 7 at 25 °C

- Taste descriptions are traditional properties, not a laboratory identification test; never taste chemicals.

Ionic Equilibrium

Arrhenius theory and hydrated ions · Limits of Arrhenius and next theory

09 Arrhenius theory and hydrated ions

- An Arrhenius acid increases aqueous H_3O^+; examples HNO_3 and $HClO_4$. An Arrhenius base increases aqueous OH^-; examples $NaOH$ and $Ca(OH)_2$.

$$H^+ + H_2O \rightarrow H_3O^+$$
$$H_3O^+ + H_2O \rightarrow H_5O_2^+$$
$$H_5O_2^+ + H_2O \rightarrow H_7O_3^+$$

$$H_7O_3^+ + H_2O \rightarrow H_9O_4^+$$
$$H_{2n+1}O_n^+$$

Formal hydrated-proton cluster stoichiometries; H^+ in water is solvated, not a free bare proton.

$$OH^- + H_2O \rightarrow H_3O_2^-$$
$$H_3O_2^- + H_2O \rightarrow H_5O_3^-$$

$$H_5O_3^- + H_2O \rightarrow H_7O_4^-$$
$$H_7O_4^- + H_2O \rightarrow H_9O_5^-$$
$$H_{2n-1}O_n^-$$

Formal hydroxide hydrate series.

10 Limits of Arrhenius and next theory

- The strict Arrhenius framework is tied to aqueous solutions and does not describe every acid–base reaction without water. It is too narrow for substances without an obvious ionizable H or OH group; the source lists $AlCl_3$, NH_3, BF_3 and Na_2O. Their acid/base behaviour can be understood through broader theories or reaction with water.

- Brønsted–Lowry theory is the proton-transfer / conjugate acid–base theory and is not restricted to aqueous solution.

11 Brønsted–Lowry acids and bases

- A Brønsted acid donates H^+; a Brønsted base accepts H^+. Add H^+ to get a conjugate acid. Remove H^+ to get a conjugate base.

$$OH^- + H^+ \rightarrow H_2O$$
$$NH_4^+ \rightarrow NH_3 + H^+$$

H_2O is the conjugate acid of OH^-; NH_3 is the conjugate base of NH_4^+.

Ionic Equilibrium

Brønsted–Lowry acids and bases · Lewis theory

11 Brønsted–Lowry acids and bases

continued

- A stronger acid has a weaker conjugate base, and vice versa. An acid–base equilibrium favours the side containing the weaker acid and weaker base.

- Amphiprotic species can donate or accept a proton; examples H_2O and HCO_3^-. The source uses the broader word amphoteric for this proton-transfer behaviour.

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$H_2O + H^+ \rightleftharpoons H_3O^+$$

- The proton-transfer definition alone does not describe nonprotic Lewis acidity. Source examples of substances without hydrogen that may show acid behaviour are BF_3, $AlCl_3$, SO_2 and $COCl_2$.

12 Lewis theory

- A Lewis acid accepts an electron pair; a Lewis base donates an electron pair. Acids include electron-deficient BF_3 and $AlCl_3$ and cations such as H^+, Fe^{2+} and Na^+ when they accept donor coordination. Bases include anions O^{2-}, SO_4^{2-}, Cl^-, CO_3^{2-} and neutral lone-pair donors NH_3, $R–NH_2$ and H_2O.

- The handwritten 'vacant orbital' examples SF_4 and PF_3 should not be memorized as a universal Lewis-acid list: Lewis behaviour depends on the reaction, and PF_3 is commonly an electron-pair donor ligand. The defining test is acceptance or donation of an electron pair.

- A Brønsted base donates an electron pair to H^+ and is a Lewis base; proton-transfer acid–base reactions fit within Lewis theory. Many Lewis acids, such as BF_3, are not Brønsted acids. Arrhenius acid/base behaviour in water is compatible with the corresponding proton-transfer description. Avoid treating all substances as belonging exclusively to one category.

13 Ostwald dilution law for a weak acid

$$HA \rightleftharpoons H^+ + A^-$$

Stage	[HA]	[H⁺]	[A⁻]
Initially	C	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Ionic Equilibrium

Ostwald dilution law for a weak acid · Ionic product of water

13 Ostwald dilution law for a weak acid

continued

$$\alpha < 0.05 \Rightarrow 1 - \alpha \approx 1$$
$$K_a \approx C\alpha^2$$
$$\alpha \approx \sqrt{\frac{K_a}{C}}$$

Check the 5% approximation; water autoionization must also be negligible.

$$\alpha \approx \sqrt{K_a V_m}$$
$$V_m = \frac{1}{C}$$

Here V_m is dilution volume per mole (L mol⁻¹ if C is mol L⁻¹), not arbitrary total solution volume.

- Increasing C reduces α; dilution lowers C and increases α. At equal concentration, a larger dissociation constant gives larger α and stronger acid behaviour; comparing α at different concentrations does not by itself compare intrinsic acid strengths.

14 Ionic product of water

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_w \approx [H^+][OH^-] = 1.0 \times 10^{-14}$$
$$(25\,^\circ C)$$

Kw is the water autoionization / ionic-product constant; dilute-solution concentration form.

15 Water, temperature and neutrality

$$pK_w = pH + pOH$$
$$pH_{neutral} = pOH_{neutral} = \frac{pK_w}{2}$$

- At a fixed pressure, Kw varies with temperature. In the ordinary liquid-water range, ionization is endothermic: increasing temperature increases Kw and lowers neutral pH. The water remains neutral because $[H^+] = [OH^-]$.

Given Kw	pH + pOH	Neutral pH
10^{-14} (usual 25 °C approximation)	14	7
10^{-12} (hypothetical supplied value)	12	6
10^{-16} (hypothetical supplied value)	16	8

Ionic Equilibrium

Water, temperature and neutrality · p notation and strength trends

15 Water, temperature and neutrality

continued

- The source labels the last two examples 90 °C and 0 °C; those are not reliable physical values. Near 0.1 MPa, published NIST data give pKw ≈ 14.95 at 0 °C and ≈13.99 at 25 °C. For an exam calculation at any temperature, use the supplied Kw. Reference: https://srd.nist.gov/JPCRD/jpcrd696.pdf (Table 4).

At 25 °C	Meaning
pH = pOH = 7	Neutral
pH < 7; pOH > 7	Acidic
pH > 7; pOH < 7	Basic

Conventional aqueous scale at 25 °C



7 = neutral

[H⁺] > [OH⁻] [OH⁻] > [H⁺]

The possible pH range is not limited to 0–14.

At 25 °C, dilute aqueous solutions are acidic below pH 7 and basic above pH 7. The full pH range extends beyond 0–14.

16 p notation and strength trends

$$pX = -\log X$$
$$\mathrm{pH} = \log \frac{1}{[\mathrm{H^+}]}$$
$$\mathrm{pOH} = \log \frac{1}{[\mathrm{OH^-}]}$$

$$\mathrm{p}K_a = -\log K_a$$
$$\mathrm{p}K_b = -\log K_b$$
$$\mathrm{p}K_w = -\log K_w$$

- More H^+ means lower pH and greater acidity. Larger Ka means a stronger acid and lower pKa. More OH^- means lower pOH and greater basicity; larger Kb means a stronger base and lower pKb. These are monotonic trends, not literal inverse proportionalities to pH or pKa.

Ionic Equilibrium

Single strong-acid calculations · Single strong-base calculations

17 Single strong-acid calculations

$$\mathrm{HCl} \rightarrow \mathrm{H^+} + \mathrm{Cl^-}$$
$$C = 0.10\,\mathrm{M} \Rightarrow [\mathrm{H^+}] \approx 0.10\,\mathrm{M} \Rightarrow \mathrm{pH} = 1$$

$$C(\mathrm{HCl}) = 2.0\,\mathrm{M} \Rightarrow \mathrm{pH_{ideal}} = -\log 2 \approx -0.30$$

pH is not undefined above 1 M. Actual concentrated-solution pH requires activity rather than concentration.

$$\mathrm{H_2SO_4} \rightarrow 2\mathrm{H^+} + \mathrm{SO_4^{2-}}$$
$$C = 10^{-3}\,\mathrm{M} \Rightarrow [\mathrm{H^+}] \approx 2 \times 10^{-3}\,\mathrm{M}$$

$$\mathrm{pH} \approx 3 - \log 2 \approx 2.70$$

Source's approximation assumes both protons are fully released. The second ionization is an equilibrium and gives a small correction if Ka2 is supplied.

18 Single strong-base calculations

$$\mathrm{NaOH} \rightarrow \mathrm{Na^+} + \mathrm{OH^-}$$
$$C = 2 \times 10^{-4}\,\mathrm{M} \Rightarrow [\mathrm{OH^-}] = 2 \times 10^{-4}\,\mathrm{M}$$

$$\mathrm{pOH} = 4 - \log 2 \approx 3.70$$

$$C(\mathrm{NaOH}) = 10^{-2}\,\mathrm{M} \Rightarrow [\mathrm{OH^-}] = 10^{-2}\,\mathrm{M}$$
$$\Rightarrow \mathrm{pOH} = 2 \Rightarrow \mathrm{pH} = 12$$

This example continues at the top of the next source page.

19 Dilution and concentration

- *Dilution adds solvent; concentration by evaporation removes solvent. The amount of solute stays constant if none is lost or reacted.*

$$C_1V_1 = C_2V_2$$

- *For a strong acid sufficiently above the water-ionization level, a tenfold dilution raises pH by 1, a hundredfold by 2 and a thousandfold by 3. Strong-base dilution lowers pH toward neutral; all dilution rules eventually require water autoionization.*

Ionic Equilibrium

Dilution and concentration · pH of a weak monoprotic acid

19 Dilution and concentration

continued

Source example · dilute a strong acid 100-fold

$[H^+] = 10^{-2}$ M, pH = 2 → Volume × 100, $[H^+] \div 100$ → $[H^+] = 10^{-4}$ M, pH = 4

The amount of acid stays the same; water autoionization is negligible here.

$$\mathrm{pH}_i = 2 \Rightarrow [\mathrm{H}^+]_i = 10^{-2}\,\mathrm{M};$$
$$V_f = 100V_i \Rightarrow [\mathrm{H}^+]_f = 10^{-4}\,\mathrm{M} \Rightarrow \mathrm{pH}_f = 4$$

The source's 100-fold dilution example, assuming strong acid and negligible water contribution.

20 pH of a weak monoprotic acid

$$K_a = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2$$
$$\alpha \approx \sqrt{\frac{K_a}{C}}$$

$$[\mathrm{H}^+] = C\alpha \approx \sqrt{K_a C}$$
$$\mathrm{pH} \approx \frac{1}{2}(\mathrm{p}K_a - \log C)$$

- Ka is the acid dissociation constant and C the initial acid concentration. On dilution C decreases, α increases, but $[H^+]$ decreases. Apply the small-dissociation approximation only when justified.

21 pH of a weak base

$$K_b = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2$$
$$\alpha \approx \sqrt{\frac{K_b}{C}}$$

$$[\mathrm{OH}^-] = C\alpha \approx \sqrt{K_b C}$$
$$\mathrm{pOH} \approx \frac{1}{2}(\mathrm{p}K_b - \log C)$$

Ionic Equilibrium

pH of a weak base · Nonreacting mixtures

21 pH of a weak base

continued

$$\mathrm{pH} = \mathrm{p}K_w - \mathrm{pOH} = 14 - \mathrm{pOH} \quad (25\,^\circ\mathrm{C})$$

22 Nonreacting mixtures

$$[\mathrm{H^+}] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

Mixture of strong acids: N is acid equivalent concentration, with full release of the counted protons and additive volumes.

$$[\mathrm{OH^-}] = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

Mixture of strong bases: N is hydroxide equivalent concentration.

$$N_i = C_i f_i$$

$$C_{\text{ion,total}} = \frac{C_1V_1f_1 + C_2V_2f_2}{V_1 + V_2}$$

f is the number of the same ion produced per formula unit. This additive expression cannot be used for mixing an acid with a base; they neutralize.

- For strong acid + weak acid, or strong base + weak base, common-ion suppression often makes the weak component's contribution negligible compared with the strong component. Check the concentrations and constants before using this approximation.

23 Reacting mixture: strong acid plus strong base

$$\text{strong acid} + \text{strong base} \longrightarrow \text{salt} + \mathrm{H_2O}$$

- Compare acid equivalents N_1V_1 and base equivalents N_2V_2 after converting volumes to compatible units. If $N_1V_1 = N_2V_2$, neutralization is complete; the salt of a strong acid and strong base gives neutral solution, pH ≈ 7 at 25 °C.

$$n_{\text{excess equivalents}} = |N_1V_1 - N_2V_2|$$

For unequal amounts, the excess acid or base controls pH; continuation on the next source page.

Ionic Equilibrium

Strong acid–strong base mixtures: remaining cases · Weak polyprotic acids

24 Strong acid–strong base mixtures: remaining cases

$$N_1V_1 > N_2V_2 \Rightarrow [\mathrm{H^+}] \approx \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

Acid excess; pH < 7 at 25 °C. N_1,V_1 denote acid and N_2,V_2 denote base.

$$N_1V_1 < N_2V_2 \Rightarrow [\mathrm{OH^-}] \approx \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

Base excess; pH > 7 at 25 °C. Use additive volumes and equivalent concentrations; include water ionization if excess is extremely small.

25 Weak polyprotic acids

$$\mathrm{H_2S} \rightleftharpoons \mathrm{H^+} + \mathrm{HS^-}$$
$$K_{a1} = 10^{-7}$$

$$\mathrm{HS^-} \rightleftharpoons \mathrm{H^+} + \mathrm{S^{2-}}$$
$$K_{a2} = 10^{-14}$$

Use these as the source's supplied school-example constants.

- *When successive constants are well separated (Ka1 ≫ Ka2 ≫ Ka3), the first ionization often dominates the pH of a weak polyprotic acid.*

$$[\mathrm{H^+}] \approx \sqrt{K_{a1}C}$$
$$\mathrm{pH} \approx \frac{1}{2}(\mathrm{p}K_{a1} - \log C)$$

$$[\mathrm{HS^-}] \approx \sqrt{K_{a1}C}$$
$$[\mathrm{S^{2-}}] \approx K_{a2}$$
$$[\mathrm{H_2S}] \approx C - \sqrt{K_{a1}C}$$

The sulfide simplification uses [HS⁻] ≈ [H⁺], first-ionization dominance and negligible water contribution.

26 Common-ion effect

- *Adding a source of an ion already present in a weak-electrolyte equilibrium suppresses its ionization (Le Chatelier's principle). A weak acid is suppressed by added H^+ or its conjugate anion; an analogous rule holds for a weak base.*

Ionic Equilibrium

Common-ion effect · Salt hydrolysis: weak acid + strong base salt

26 Common-ion effect

continued

$$\mathrm{HCOOH} \rightleftharpoons \mathrm{HCOO^-} + \mathrm{H^+}$$
$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^-} + \mathrm{H^+}$$

- Example: mixing formic acid and acetic acid introduces a shared H^+ pool. If x and y are the respective ionized concentrations, $[H^+] \approx x + y$. Each acid's degree of ionization is lower than for that acid alone at the same formal concentration.

27 Salt hydrolysis: weak acid + strong base salt

$$\text{acid} + \text{base} \rightleftharpoons \text{salt} + \mathrm{H_2O}$$

Neutralization runs toward salt/water; hydrolysis refers to reaction of salt ions with water to regenerate a weak parent acid or base.

$$\mathrm{CH_3COONa} \rightarrow \mathrm{CH_3COO^-} + \mathrm{Na^+}$$

$$\mathrm{CH_3COO^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{CH_3COOH} + \mathrm{OH^-}$$

Anionic hydrolysis gives a basic solution. Initial acetate concentration C; Na^+ is a spectator.

Stage	$[CH_3COO^-]$	$[CH_3COOH]$	$[OH^-]$
Initially	C	0	0
Equilibrium	$C(1-h)$	Ch	Ch

$$K_h = \frac{[\mathrm{CH_3COOH}][\mathrm{OH^-}]}{[\mathrm{CH_3COO^-}]} = \frac{K_w}{K_a} = \frac{Ch^2}{1-h}$$

- h is the degree of hydrolysis. Multiplying numerator and denominator by $[H^+]$ shows $K_h = K_w/K_a$.

$$h < 0.05 \Rightarrow K_h \approx Ch^2$$
$$h \approx \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a C}}$$

$$[\mathrm{OH^-}] = Ch \approx \sqrt{\frac{K_w C}{K_a}}$$

$$\mathrm{pOH} = \frac{1}{2}(\mathrm{p}K_w - \mathrm{p}K_a - \log C)$$
$$\mathrm{pH} = \frac{1}{2}(\mathrm{p}K_w + \mathrm{p}K_a + \log C)$$

Ionic Equilibrium

Salt hydrolysis: weak acid + strong base salt · Salt hydrolysis comparison

27 Salt hydrolysis: weak acid + strong base salt

continued

$$\mathrm{pH} = 7 + \frac{1}{2}(\mathrm{p}K_a + \log C)$$
$$(25\,^\circ\mathrm{C})$$

The salt solution is basic; approximation requires hydrolysis and water-ionization assumptions to hold.

28 Salt hydrolysis comparison

Salt parents	Hydrolysis	Kh	Small-h approximation	Example / nature
Strong acid + strong base	None appreciable	Not applicable	$h \approx 0$	NaCl; neutral
Strong acid + weak base	Cationic	Kw/Kb	$h \approx \sqrt{(Kw/(KbC))} = \sqrt{(Kh/C)}$	NH_4Cl; acidic
Weak acid + strong base	Anionic	Kw/Ka	$h \approx \sqrt{(Kw/(KaC))} = \sqrt{(Kh/C)}$	CH_3COONa; basic
Weak acid + weak base	Both cationic and anionic	Kw/(KaKb)	$h \approx \sqrt{Kh}$ only if $h \ll 1$	CH_3COONH_4; near neutral only if Ka ≈ Kb

$$\mathrm{pH}_{\mathrm{SA+SB}} = \frac{1}{2}\mathrm{p}K_w \approx 7$$
$$(25\,^\circ\mathrm{C})$$

$$\mathrm{pH}_{\mathrm{SA+WB}} = \frac{1}{2}(\mathrm{p}K_w - \mathrm{p}K_b - \log C) = 7 - \frac{1}{2}(\mathrm{p}K_b + \log C)$$
$$(25\,^\circ\mathrm{C})$$

$$\mathrm{pH}_{\mathrm{WA+SB}} = \frac{1}{2}(\mathrm{p}K_w + \mathrm{p}K_a + \log C) = 7 + \frac{1}{2}(\mathrm{p}K_a + \log C)$$
$$(25\,^\circ\mathrm{C})$$

$$\mathrm{pH}_{\mathrm{WA+WB}} \approx \frac{1}{2}(\mathrm{p}K_w + \mathrm{p}K_a - \mathrm{p}K_b) = 7 + \frac{1}{2}(\mathrm{p}K_a - \mathrm{p}K_b)$$
$$(25\,^\circ\mathrm{C})$$

$$K_h = \frac{h^2}{(1-h)^2}$$
$$h = \frac{\sqrt{K_h}}{1+\sqrt{K_h}}$$

For the simplified 1:1 weak-acid/weak-base salt hydrolysis model. Its degree of hydrolysis is independent of C in this model; Kh ≈ h² is only a small-h limit.

Ionic Equilibrium

Buffer solutions · Buffer capacity and range

29 Buffer solutions

A conjugate pair removes small added doses

Added H^+	→	$A^- + H^+ \rightarrow HA$	Acid consumed
Added OH^-	→	$HA + OH^- \rightarrow A^- + H_2O$	Base consumed

Both HA and A^- must remain appreciable; buffer capacity is finite.

- A buffer resists small additions of strong acid or base and keeps its pH nearly constant. Moderate dilution changes its pH little while both components remain appreciable, but reduces its buffer capacity.

- Acidic buffer: a weak acid and its conjugate base, often supplied as its salt with a strong base. Example $CH_3COOH + CH_3COONa$.

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]} \approx \mathrm{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

- Basic buffer: a weak base and its conjugate acid, often supplied as its salt with a strong acid. Source example $NH_4OH + NH_4Cl$ is more precisely $NH_3(aq) + NH_4Cl$.

$$\mathrm{pOH} = \mathrm{p}K_b + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]} \approx \mathrm{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

- A buffer requires appreciable amounts of a conjugate pair. Partial neutralization can create that pair. Merely combining an arbitrary weak acid and weak base does not guarantee an effective buffer; the final composition matters.

30 Buffer capacity and range

$$\beta \approx \frac{\text{moles of strong acid or base added per litre}}{|\Delta \mathrm{pH}|}$$

- For a fixed total buffer concentration, buffering is most effective near equal conjugate-component concentrations: [salt] ≈ [acid] for an acidic buffer, giving pH ≈ pKa. '50%' here means equal neutralized and unneutralized analytical amounts, not that the weak acid has 50% spontaneous ionization.

Ionic Equilibrium

Buffer capacity and range · Amphiprotic species

30 Buffer capacity and range

continued

$$\text{Acidic buffer range: } \mathrm{pH} \approx \mathrm{p}K_a \pm 1$$

$$\text{Basic buffer range: } \mathrm{pH} \approx (\mathrm{p}K_w - \mathrm{p}K_b) \pm 1$$

- Blood contains the carbonic acid / bicarbonate buffer system, commonly represented H_2CO_3 / $NaHCO_3$.

31 Amphiprotic species

- An amphiprotic ion can both donate and accept H^+. Source examples are bicarbonate ($NaHCO_3$) and hydrogen phosphate (correct salt formula Na_2HPO_4).

$$\mathrm{pH} \approx \frac{1}{2}(\mathrm{p}K_{a,\text{previous}} + \mathrm{p}K_{a,\text{next}})$$

Use the two dissociations adjacent to the amphiprotic species: pKa1 and pKa2 for HCO_3^-; pKa2 and pKa3 for HPO_4^{2-}. This common approximation requires appropriate concentration and well-separated constants.

32 Solubility

- Solubility is the maximum equilibrium amount of solute that can dissolve in a specified amount of solvent or solution at a stated temperature. Molar solubility s is expressed in mol L^{-1} of saturated solution. The next page develops the solubility product Ksp.

33 Solubility product Ksp

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$
$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$

- Ksp is the equilibrium constant for dissolution of a sparingly soluble solid; the solid has unit activity. In the usual fixed-pressure treatment, the thermodynamic constant depends on temperature. Concentration formulas assume sufficiently ideal behaviour.

$$\mathrm{A_xB_y(s)} \rightleftharpoons x\mathrm{A^{y+}} + y\mathrm{B^{x-}}$$

$$K_{sp} = [\mathrm{A^{y+}}]^x[\mathrm{B^{x-}}]^y = (xs)^x(ys)^y = x^x y^y s^{x+y}$$

The s relation assumes dissolution in pure solvent with no common ions, no competing equilibria and negligible relevant water-ionization contribution.

Ionic Equilibrium

Ionic product Qsp · Molar-solubility examples

34 Ionic product Qsp

$$Q_{sp} = [\mathrm{A}^{y+}]^x[\mathrm{B}^{x-}]^y$$

Use ion concentrations at any instant for Qsp; use equilibrium saturated concentrations for Ksp.

Will a precipitate form? Compare Q_{sp} and K_{sp}

$Q_{sp} < K_{sp}$	$Q_{sp} = K_{sp}$	$Q_{sp} > K_{sp}$
Unsaturated	Saturated	Precipitation favoured

Use ion concentrations after mixing; stoichiometry sets the powers in Q_{sp}.

Comparison	State / precipitation prediction
Qsp < Ksp	Unsaturated; no precipitation is thermodynamically favoured; solid can dissolve if present
Qsp = Ksp	Saturated equilibrium
Qsp > Ksp	Supersaturated; precipitation is thermodynamically favoured until saturation is restored

35 Molar-solubility examples

Dissolution	Equilibrium ion concentrations	Ksp in terms of s
$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$	s, s	s^2; $s = \sqrt{Ksp}$
$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$	2s, s	$(2s)^2 s = 4s^3$
$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$	3s, 2s	$(3s)^3(2s)^2 = 108s^5$
$Al(OH)_3(s) \rightleftharpoons Al^{3+} + 3OH^-$	s, 3s	$s(3s)^3 = 27s^4$

- The last two are formal stoichiometric exercises; real phosphate and aluminium hydroxide systems may require acid–base, hydrolysis and complex-ion equilibria for a quantitative solubility.

36 Which salt precipitates first?

- As a precipitating ion is added, the first salt precipitates when its ionic product reaches Ksp. Calculate each salt's critical added-ion concentration from the actual ion concentrations and stoichiometry. A smaller Ksp predicts earlier precipitation only when the cases are comparable.

$$[\mathrm{X}^-]_{\text{critical}} = \frac{K_{sp}}{[\mathrm{M}^+]}$$

Example criterion for $MX(s) \rightleftharpoons M^+ + X^-$. For other stoichiometries solve the appropriate Ksp expression.

- Lower solubility generally means a greater tendency to remain precipitated, but do not compare Ksp values directly across different stoichiometries. Ksp predicts equilibrium onset and extent; it does not by itself give the kinetic rate of precipitation.

NEW CHAPTER PHYSICAL CHEMISTRY

Redox Reactions

06

Oxidation numbers • balancing • equivalents

01 Redox reactions

- Oxidation and reduction occur together in a redox reaction.

$$\text{Redox} = \text{oxidation} + \text{reduction}$$

02 Recognise oxidation

Criterion	Source example
Loss of electrons	$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$
Removal of hydrogen	$H_2S + Cl_2 \rightarrow 2HCl + S$
Addition of oxygen	$2Mg + O_2 \rightarrow 2MgO$
Increase in oxidation number	$SnCl_2 \rightarrow SnCl_4$; Sn changes from +2 to +4
Increase in positive charge	$Fe^{2+} \rightarrow Fe^{3+} + e^-$

- $SnCl_2 \rightarrow SnCl_4$ shows the oxidation-number change only; it is not a balanced complete reaction.

03 Recognise reduction

Criterion	Source example
Gain of electrons; decrease in positive charge	$Fe^{3+} + e^- \rightarrow Fe^{2+}$
Addition of hydrogen	$S + H_2 \rightarrow H_2S$
Removal of oxygen	$CuO + C \rightarrow Cu + CO$
Decrease in oxidation number	$MnO_4^- \rightarrow Mn^{2+}$; Mn changes from +7 to +2

- The permanganate arrow shows the species change. Balance H, O and charge for the given medium.

04 Meaning of oxidation number

- Oxidation number (oxidation state) is an atom's formal charge after treating its bonds as ionic. Positive → formal electron loss; negative → formal electron gain. It can equal the real charge of a simple ion. In a covalent compound, it is a bookkeeping value.

Redox Reactions

Rules 1–5 · Oxygen exceptions and fluorine

05 Rules 1–5

Rule	Application
An uncombined element has oxidation number 0	Na, Cu, I_2, Cl_2
The sum for a neutral compound is 0	Add the contributions of every atom
The sum for a polyatomic ion equals its charge	In SO_4^{2-}: oxidation number of S + 4(−2) = −2
Neutral ligands have charge 0	NH_3, H_2O and CO; these are ligand charges, not oxidation numbers of every atom in them
Hydrogen is usually +I; in metal hydrides it is −I	Use the hydride exception when H is bonded to an electropositive metal

- The notation NO = +I applies to a nitrosyl ligand represented as NO^+ in suitable complexes. NO is not always a +I ligand.

06 Oxygen exceptions and fluorine

Species/class	Oxidation number of O
Most oxygen compounds	−2
Peroxides: H_2O_2, Li_2O_2	−I
Superoxides: KO_2, RbO_2	−½ (average)
Ozonides: KO_3	−⅓ (average), since I + 3x = 0
O_2F_2	+I
OF_2	+2
$O_2^+[AsF_6]^-$	+½ in O_2^+ (average)

- Fluorine is −I in every compound. In HOF, H = +I, F = −I and O = 0; HOF is not an exception to the fluorine rule.

Redox Reactions

Rules 8–13 · Bond-electron bookkeeping

07 Rules 8–13

Element or situation	Source rule, with necessary scope
Halogens other than F	Common oxidation numbers span −1 to +7; HCl (−1), $HClO_4$ (+7)
Group 1 metals	+1 in their ordinary compounds
Group 2 metals	+2 in their ordinary compounds
Group 13: B, Al	+3 is the common school-level state
Group 15: N, P	Typical range −3 to +5
Group 16: O, S	Sulfur commonly ranges from −2 to +6; oxygen requires the exceptions on page 28
An oxidation number	May be negative, zero, positive, or fractional as an average
Chromium	Common states +3 and +6
Manganese	Common states +2, +4, +6, +7
Osmium and ruthenium	+8 occurs; this is the highest state highlighted in the source's usual school-level list
Metal amalgams	Assign 0 to the uncombined metal and Hg; examples Na–Hg and Zn–Hg

08 Bond-electron bookkeeping

Bond	Assignments
Nonpolar homonuclear bonds H–H, O=O, N≡N	Both atoms: 0
Polar A–B with $\chi A < \chi B$	For one bond: A +1, B −1
Polar A=B with $\chi A < \chi B$	A +2, B −2
Polar A≡B with $\chi A < \chi B$	A +3, B −3
Coordinate A→B with $\chi A < \chi B$	Assign both bonding electrons to B, as for a covalent bond; donor-arrow origin does not override electronegativity
Coordinate bond between identical atoms	Split the bonding electrons equally for oxidation-state assignment

- The notes sketch A→A, A→B and B→A as a "back bond" memory cue. Assign electrons using electronegativity in these diagrams too. The arrow alone does not justify +2/−2 or 0/0 oxidation numbers.

$$\chi_F > \chi_O > \chi_N > \chi_C > \chi_H$$

Redox Reactions

Bond-electron bookkeeping · Atom-specific and average values

08 Bond-electron bookkeeping

continued

Structure	Oxidation numbers
H–C≡N	H +1, C +2, N −3
H–N≡C (isocyanide connectivity)	H +1, N −3, C +2

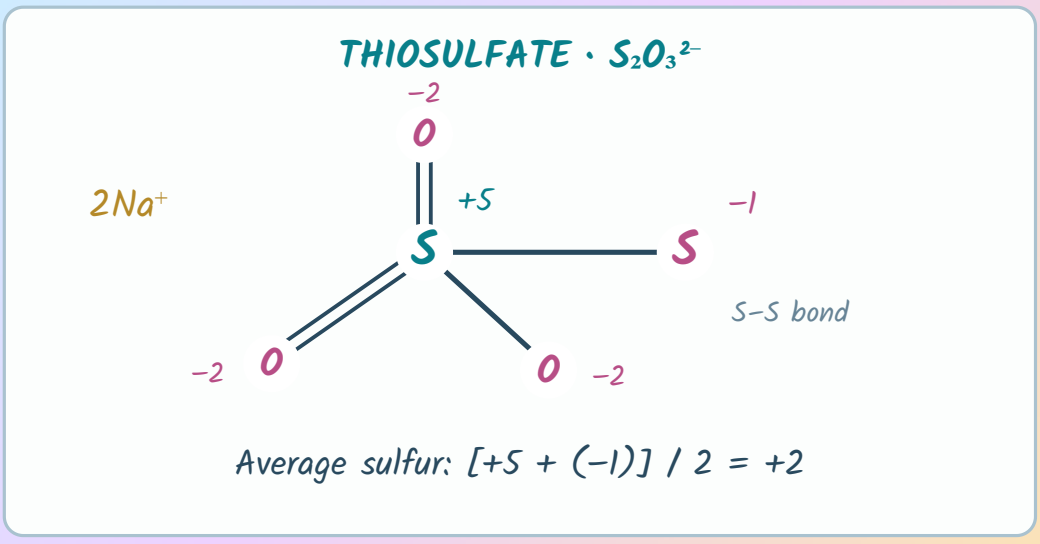
09 Atom-specific and average values

- Oxidation state and oxidation number usually mean the same thing. Different atoms of one element can have different values in the same molecule. The overall formula may give only their average.

$$\text{Average oxidation number} = \frac{\text{sum of oxidation numbers of those atoms}}{\text{number of those atoms}}$$

$$\begin{gathered}\mathrm{Na_2S_2O_3}: \\ 2(+1) + 2x + 3(-2) = 0 \\ \Rightarrow \\ x = +2\end{gathered}$$

- Thiosulfate contains a central sulfur at +5 and a terminal sulfur at −1; their average is +2.



Thiosulfate: inequivalent sulfur atoms, average oxidation number +2.

Redox Reactions

Find the requested average oxidation number · More oxidation-number examples

10 Find the requested average oxidation number

Compound or ion	Calculation	Answer
$KClO_3$ (Cl)	$1 + x + 3(-2) = 0$	+5
$Fe_{0.94}O$ (Fe)	$0.94x - 2 = 0$	$200/94 = 100/47 \approx +2.128$
$S_4O_6^{2-}$ (S)	$4x - 12 = -2$	+2.5
$Na_2S_2O_3$ (S)	$2 + 2x - 6 = 0$	+2
H_5IO_6 (I)	$5 + x - 12 = 0$	+7
HN_3 (N)	$1 + 3x = 0$	$-\frac{1}{3}$ (average)
$[Ni(CO)_4]$ (Ni)	$x + 4(0) = 0$	0
$[Co(NH_3)_4(H_2O)Cl]SO_4$ (Co)	$x + 4(0) + 0 - 1 - 2 = 0$	+3

11 More oxidation-number examples

Species	Calculation	Result
$YBa_2Cu_3O_7$ (Cu)	$3 + 4 + 3x - 14 = 0$	Cu average +7/3
$(N_2H_5)_2SO_4$ (S)	$2(+1) + x - 8 = 0$	S +6
NH_4NO_3 (N in NH_4^+)	$x + 4 = +1$	N −3
NH_4NO_3 (N in NO_3^-)	$x - 6 = -1$	N +5
$[Fe(CN)_6]^{4-}$ (Fe)	$x + 6(-1) = -4$	Fe +2

12 Peroxide linkage: O–O

- Each oxygen in a peroxide O–O link has oxidation number −1. Other oxygen atoms can still be −2. P.L. = number of peroxide O–O links.

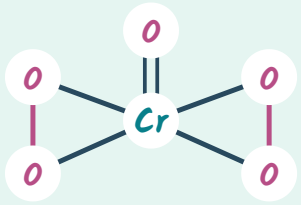
Species	Oxidation numbers	P.L.
CrO_5	Cr +6; four peroxide O at −1 and one oxo O at −2	2
K_3CrO_8	K +1; Cr +5; all eight O at −1	4
Br_3O_8	Two terminal Br at +6, central Br +4; O −2	0
C_3O_2	Terminal C +2, central C 0; O −2	0
H_2SO_5 (Caro's acid)	H +1, S +6; peroxide O −1, other O −2	1
$H_2S_2O_8$ (Marshall's acid)	H +1, both S +6; peroxide O −1, other O −2	1

Redox Reactions

Structures to remember · Recognising a hidden O–O linkage

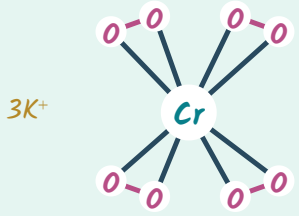
13 Structures to remember

CrO_5



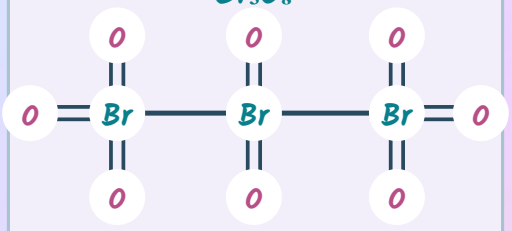
Cr +6 · two O–O links

K_3CrO_8



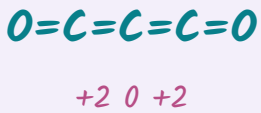
Cr +5 · four O–O links

Br_3O_8



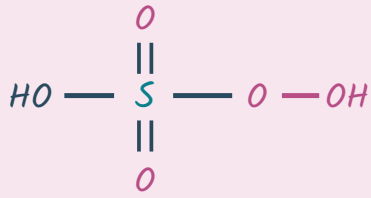
Br: +6, +4, +6 · no O–O

C_3O_2



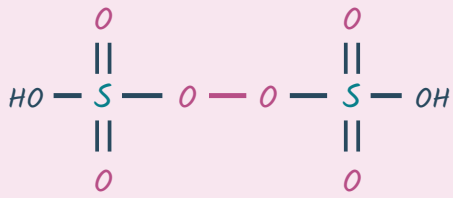
C: +2, 0, +2 · no O–O

H_2SO_5 · Caro's acid



S +6 · one O–O link

$H_2S_2O_8$ · Marshall's acid



S +6 · one O–O link

Peroxide O–O links change oxygen's oxidation number to −1.

14 Recognising a hidden O–O linkage

- *Shortcut: if O = −2 forces the central atom above a plausible oxidation number, check for peroxide oxygen. This is a warning to inspect the structure; it does not prove that the central atom has its maximum oxidation state.*

Assuming all O = −2	Implausible result	Correct structural result
CrO_5: $x - 10 = 0$	Cr +10, above +6	Cr +6 with two peroxide links
H_2SO_5: $2 + x - 10 = 0$	S +8, above +6	S +6 with one peroxide link

Redox Reactions

Counting O–O links by charge balance · Oxidising and reducing agents

15 Counting O–O links by charge balance

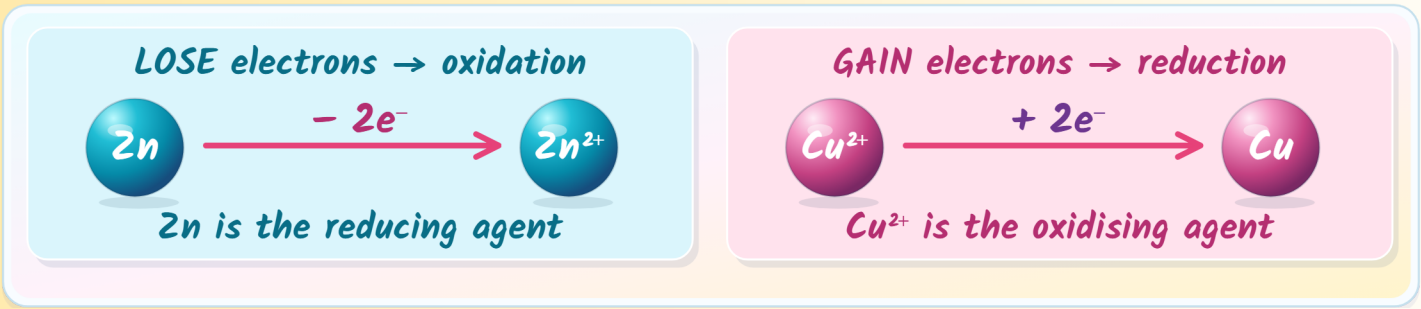
- Each peroxide link makes the total oxygen contribution 2 units less negative than the all-O(−2) estimate. If the actual central-atom oxidation-state sum is known, divide the excess formal positive charge by 2 to count the links.

$$N_{O-O} = \frac{\Sigma_{\text{central, all O}=-2} - \Sigma_{\text{central, actual}}}{2}$$

Example	Calculation
CrO_5	(10 − 6)/2 = 2
K_3CrO_8	All-O(−2) calculation: 3 + x − 16 = 0 gives x = 13; actual Cr = +5, so (13 − 5)/2 = 4
$H_2S_2O_8$	All-O(−2) gives average S = +7; actual S = +6, so [2(7 − 6)]/2 = 1

- One central atom: links = (formal value − actual value)/2. Two equivalent central atoms: links = formal average − actual average. Never round a result obtained using the wrong actual oxidation state.

16 Oxidising and reducing agents



- An oxidising agent is itself reduced. A reducing agent is itself oxidised.

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

- Zn: 0 → +2 (oxidised; reducing agent). Cu^{2+}: +2 → 0 (reduced; $CuSO_4$ is the oxidising reagent).

17 Oxidation state as a guide

Starting state	Possible role for that element	Source examples
Highest accessible oxidation state	Can be reduced; may act as an oxidising agent	$KMnO_4$, $K_2Cr_2O_7$, HNO_3, H_2SO_4, $HClO_4$
Low oxidation state	Can be oxidised; may act as a reducing agent	H_2S, $FeSO_4$, $Na_2S_2O_3$, $SnCl_2$
Intermediate oxidation state	May undergo either oxidation or reduction	H_2O_2, H_2SO_3, HNO_2, SO_2

- These are guides to possible changes, not guarantees of reaction. Some listed low-state species can also reach lower states. Check the reacting redox centre and the conditions.

Redox Reactions

Combination redox · Displacement redox

18 Combination redox

- A combination reaction joins two or more reactants into one product. It is redox if oxidation numbers change. The standard examples include at least one elemental reactant.

$$C + O_2 \rightarrow CO_2$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The source also lists this combustion example; it is redox, but it is not a combination reaction because there are two products.

19 Displacement redox

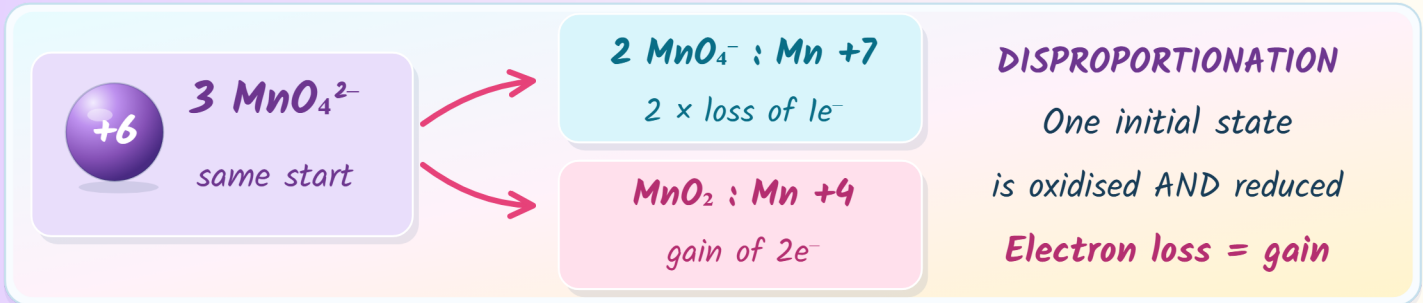
$$AB + C \rightarrow AC + B$$

- Displacement: one element replaces another in a compound. In metal displacement, a metal atom reduces another metal ion. In nonmetal displacement, the stronger oxidising nonmetal displaces another nonmetal from its ion.

$$CuSO_4 + Zn \rightarrow Cu + ZnSO_4$$

$$Cl_2 + 2KI \rightarrow 2KCl + I_2$$

20 Disproportionation



- The same element in one initial oxidation state is simultaneously oxidised and reduced.

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Mn: +6 → +7 and +4.

$$X_2 + 2NaOH \rightarrow NaX + NaOX + H_2O$$

For suitable halogens in cold dilute alkali: X 0 → −1 and +1. Fluorine does not undergo this disproportionation.

Redox Reactions

Comproportionation · n-factor (valence factor): acids

21 Comproportionation

- The same element in two different oxidation states forms a common intermediate oxidation state.

$$X^- + XO^- + 2H^+ \rightarrow X_2 + H_2O$$

X −I and +I → 0; the source writes the sodium salts.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

N −3 and +3 → 0.

22 n-factor (valence factor): acids

- For the specified acid–base reaction, n-factor = H^+ equivalents donated or OH^- equivalents consumed per formula unit.

Acid	n-factor for the indicated extent of neutralisation
$HCl \rightarrow H^+ + Cl^-$	1
$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$	2 for complete neutralisation
HNO_3	1
H_3PO_4	1, 2 or 3
H_3PO_3	1 or 2
H_3PO_2	1
H_3BO_3	1 in its usual aqueous acid–base reaction

23 Acid–base, salt, ion and element n-factors

Category	Rule and examples
Base	Number of OH^- equivalents supplied or H^+ equivalents accepted: NaOH 1; $Ca(OH)_2$ 2; $Al(OH)_3$ 3 for complete neutralisation
Salt in complete ion-exchange accounting	Total positive or total negative charge per formula unit: NaCl 1; $CaCl_2$ 2; $Ca_3(PO_4)_2$ 6; $AlPO_4$ 3
Ion for a charge-equivalent calculation	Magnitude of its charge: Na^+ 1; Al^{3+} 3; O^{2-} 2
Element in a specified reaction	Number of electrons exchanged: Na → Na^+ gives 1; Mg → Mg^{2+} gives 2; Al → Al^{3+} gives 3; O → O^{2-} gives 2

- n-factor belongs to a particular reaction. Do not automatically use an acid–base or charge-equivalent value in a redox reaction.

Redox Reactions

One changing element · More than one element changes in the same direction

24 One changing element

Oxidant and product	Oxidation-number change	n-factor
$KMnO_4 \rightarrow K_2MnO_4$ in strongly alkaline conditions	Mn +7 → +6	1
$KMnO_4 \rightarrow Mn^{2+}$ in acid	Mn +7 → +2	5
$KMnO_4 \rightarrow MnO_2$ in neutral / weakly alkaline conditions	Mn +7 → +4	3
$K_2Cr_2O_7 \rightarrow Cr^{3+}$ in acid	2 Cr atoms, each +6 → +3	2 × 3 = 6

B · strongly BASIC

$MnO_4^- \rightarrow MnO_4^{2-}$

+7 → +6 Mn change

n = 1

A · ACIDIC

$MnO_4^- \rightarrow Mn^{2+}$

+7 → +2 Mn change

n = 5

N · NEUTRAL / weak alkali

$MnO_4^- \rightarrow MnO_2$

+7 → +4 Mn change

n = 3

- Remember B–A–N = 1–5–3 for the listed basic, acidic and neutral permanganate products.

25 More than one element changes in the same direction

$$FeS_2 \rightarrow Fe^{3+} + 2SO_2$$

Species-change skeleton: Fe +2 → +3 loses 1 electron; two S atoms −1 → +4 lose 2 × 5 = 10 electrons.

$$n_f(FeS_2) = 1 + 10 = 11$$

$$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2$$

Fe +2 → +3: 1 electron; each C +3 → +4: 1 electron.

$$n_f(FeC_2O_4) = 1 + 2 = 3$$

26 Disproportionation n-factor

- Let n_1 and n_2 be the electron changes if one whole formula unit followed only the reduction branch or only the oxidation branch. Its effective n-factor in disproportionation is:

$$n_f = \frac{n_1 n_2}{n_1 + n_2}$$

Source disproportionation	Branch values	Effective n-factor
X_2 (0) → X^- (−1) and XO_3^- (+5)	$n_1 = 2 \times 1 = 2$; $n_2 = 2 \times 5 = 10$	20/12 = 5/3
P_4 (0) → PH_3 (−3) and $H_2PO_2^-$ (+1)	$n_1 = 4 \times 3 = 12$; $n_2 = 4 \times 1 = 4$	48/16 = 3
S_8 (0) → S^{2-} (−2) and $S_2O_3^{2-}$ (average S +2)	$n_1 = 8 \times 2 = 16$; $n_2 = 8 \times 2 = 16$	256/32 = 8

Redox Reactions

Disproportionation n-factor · Equivalent mass

26 Disproportionation n-factor

continued

- These arrows show branch changes only. Add water, acid or alkali as needed, then balance the complete reaction for the actual medium.

27 Equivalent mass

$$E = \frac{\text{molar mass}}{n_f}$$

Substance and reaction	n-factor	Equivalent mass
H_2SO_4, complete neutralisation	2	98/2 = 49 g eq^{-1}
H_3PO_4, complete neutralisation	3	98/3 g eq^{-1}
NaCl, charge-equivalent calculation	1	58.5/1 = 58.5 g eq^{-1}

28 Normality and gram equivalents

$$N = \frac{\text{gram equivalents of solute}}{V_{\text{solution}}(\text{L})}$$

$$\text{gram equivalents} = \frac{\text{given mass}}{E} = \frac{\text{given mass}}{\text{molar mass}} n_f$$

$$N = M n_f$$

$$\text{gram equivalents} = (\text{moles}) n_f$$

29 Balancing a redox reaction

- 1. Identify oxidation and reduction.
- 2. Equalise the total increase and decrease in oxidation number.
- 3. Balance atoms other than H and O.
- 4. Balance H, O and charge for the medium. Check every atom and the total charge.

Medium	Finishing procedure
Acidic	Balance O with H_2O and H with H^+. In the half-reaction method balance charge with e^-; combine so electrons cancel.
Basic	A reliable method is to balance as acidic, add OH^- to both sides to neutralise each H^+, convert $H^+ + OH^-$ to H_2O, and cancel common H_2O. The source abbreviates this as charge with OH^- and oxygen with H_2O.

Solutions

Concentration • vapour pressure • colligative properties

07

01 Chapter roadmap

Concentration	Dilute solutions	Colligative properties
Normality, molarity, molality, formality, mole fraction, ppm, ppb, strength; percentages w/v, w/w and v/v	Vapour pressure; Dalton's law; Raoult's law for liquid–liquid and solid–liquid systems	Relative lowering of vapour pressure; boiling-point elevation; freezing-point depression; osmotic pressure

- Special-point checklist: molarity–normality relation; molality–mole-fraction relation; dilution with water; molarity versus molality; normality of mixtures; volume strength; temperature dependence. The original roadmap names formality and volume strength but gives no further detail on these Solutions pages.

02 Solution, solute and solvent

- A solution is a homogeneous mixture of two or more pure substances. Usually, the solvent is the major component and the solute the minor one. A solution has the physical state of its solvent. A binary solution has one solute and one solvent.

03 Volume-based concentration is temperature dependent

- Normality involves solution volume, so it can change when temperature changes the volume.

$$N = \frac{\text{gram equivalents of solute}}{V_{\text{solution}}(\text{L})} = \frac{w}{E\,V(\text{L})}$$

$$\text{gram equivalents} = \frac{w}{E} = NV(\text{L}) = (Mn_f)V(\text{L}) = (\text{moles})n_f$$

$$E = \frac{\text{atomic mass or molar mass}}{n_f}$$

$$\text{milliequivalents} = N\,V(\text{mL})$$

04 Choosing the n-factor

- Acid: use basicity for the specified neutralisation. Base: use acidity for that neutralisation. Salt: for complete ionic-equivalent calculations, use the total positive or total negative charge per formula unit. Always let the actual reaction decide n-factor.

Solutions

Volume-related concentration terms · Mass-related terms are temperature independent

05 Volume-related concentration terms

Term	Definition	Source example
Volume percent, % v/v	(volume of solute / volume of solution) × 100	30% v/v = 30 mL solute in 100 mL solution
Mass by volume percent, % w/v	(mass of solute in g / volume of solution in mL) × 100	30% w/v = 30 g solute in 100 mL solution
Volume by mass percent, % v/w	(volume of solute in mL / mass of solution in g) × 100	20% v/w = 20 mL solute in 100 g solution

$$S = \frac{w_{\text{solute}}(\text{g})}{V_{\text{solution}}(\text{L})} = NE$$

Strength S has units g L^{-1}.

$$M = \frac{n_{\text{solute}}}{V_{\text{solution}}(\text{L})} = \frac{1000 n_{\text{solute}}}{V_{\text{solution}}(\text{mL})}$$

Molarity has units mol L^{-1}. These volume-related concentration terms are temperature dependent.

06 Mass-related terms are temperature independent

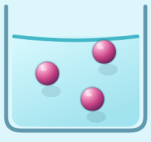
$$\%\,(w/w) = \frac{w_{\text{solute}}}{w_{\text{solution}}} \times 100$$

30% w/w = 30 g solute in 100 g solution.

$$x_A = \frac{n_A}{n_A + n_B}$$
$$x_B = \frac{n_B}{n_A + n_B}$$
$$x_A + x_B = 1$$

Mole fractions are dimensionless.

MOLARITY M



$$\frac{\text{solute moles}}{\text{solution litres}}$$

Volume → temperature dependent

MOLALITY m



$$\frac{\text{solute moles}}{\text{solvent kilograms}}$$

Mass → temperature independent

$$m = \frac{n_{\text{solute}}}{w_{\text{solvent}}(\text{kg})} = \frac{1000 n_{\text{solute}}}{w_{\text{solvent}}(\text{g})}$$

Molality has units mol kg^{-1}. One molal = 1 mol kg^{-1}; semimolal = ½ mol kg^{-1}; decimolal = 1/10 mol kg^{-1}.

Solutions

Trace concentrations · Important conversion relations

07 Trace concentrations

$$\text{ppm} = \frac{w_{\text{solute}}}{w_{\text{solution}}} \times 10^{6}$$

$$\text{ppb} = \frac{w_{\text{solute}}}{w_{\text{solution}}} \times 10^{9}$$

Masses must use the same unit.

08 Important conversion relations

- *Symbols: d = solution density in g mL⁻¹; M = molarity; m = molality. M_B = solute molar mass; M_A = solvent molar mass, both in g mol⁻¹. xB and xA are solute and solvent mole fractions.*

$$\%\,(w/v) = \%\,(w/w)\,d$$

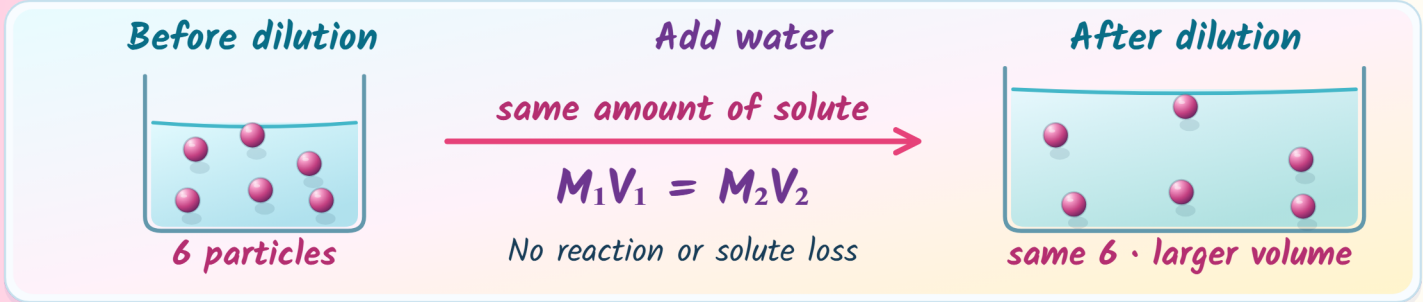
$$M = \frac{10\,\%\,(w/w)\,d}{M_B}$$

$$m = \frac{1000M}{1000d - MM_B}$$

$$m = \frac{1000x_B}{x_A M_A}$$

$$M = \frac{N}{n_f}$$

09 Dilution and mixing



- *Adding water conserves solute amount, provided there is no reaction or loss of solute.*

$$M_1V_1 = M_2V_2$$

$$M_1V_1 + M_2V_2 = M_3V_3$$

Solutions

Dilution and mixing · Vapour pressure of a pure liquid

09 Dilution and mixing

continued

$$V_3 \approx V_1 + V_2 + V_{\text{water}}$$

Use the actual final volume when volumes are not additive. For a common unchanged n-factor, the analogous relation is $N_1V_1 + N_2V_2 = N_3V_3$.

10 Vapour pressure of a pure liquid

- At a fixed temperature, equilibrium vapour pressure is the pressure of vapour in equilibrium with its liquid in a closed system.

$$\mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_2O(vapour)}$$

$$\text{rate of evaporation} = \text{rate of condensation}$$

Class	Meaning at the temperature considered	Source examples
Volatile	Appreciable vapour pressure $p^\circ \neq 0$	H_2O, CH_3OH, C_2H_5OH
Nonvolatile	Negligible vapour pressure in the intended calculation, $p^\circ \approx 0$	Urea, glucose, oil

- p° = pure-liquid vapour pressure. "Nonvolatile" means negligible volatility at the working temperature; it does not mean the substance can never become vapour.

11 Temperature dependence

- For a given liquid, vapour pressure rises as temperature rises. The relation is generally not a direct proportion.

$$\log_{10}\frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Clausius–Clapeyron approximation with nearly constant ΔH_{vap} over the interval.

12 Effect of intermolecular forces

- At the same temperature, weaker intermolecular attraction usually gives higher vapour pressure and a lower boiling point. Intermolecular H-bonding usually reduces volatility. Intramolecular H-bonding can reduce association between molecules and raise volatility in suitable comparisons.

- Comparison guide for otherwise similar molecules: H-bonding > polar–polar > polar–nonpolar > nonpolar–nonpolar attraction. Polar molecules have a nonzero dipole moment; nonpolar molecules have no permanent dipole moment. This is a guide, not a universal numerical ranking.

- In a comparable nonpolar series, greater molar mass/polarisability usually strengthens dispersion forces. Example: H_2 is much more volatile than NH_3. This is qualitative; compare vapour pressures only where the relevant equilibrium phases exist.

Solutions

Effect of intermolecular forces · Dalton's law

12 Effect of intermolecular forces

continued

Quantity	Source hydrogen-halide order
Boiling point	HF > HI > HBr > HCl
Vapour pressure at a comparable common temperature	HF < HI < HBr < HCl

- The memory cue "vapour pressure ∝ 1/boiling point" means a qualitative inverse trend. It is not an exact equation.

13 Dalton's law

$$p_T = p_A + p_B$$

$$p_A = y_A p_T$$
$$p_B = y_B p_T$$

yA and yB are mole fractions in the vapour phase, not the liquid phase.

14 Raoult's law and notation

$$p_A = x_A p_A^\circ$$
$$p_B = x_B p_B^\circ$$

For ideal liquid solutions. xA and xB are liquid-phase mole fractions; pA° and pB° are pure-liquid vapour pressures; pA and pB are partial pressures.

- Here A initially means solute and B solvent. Later nonvolatile-solute formulas use A for solvent. Follow each formula's local definitions.

15 Liquid–liquid system: both components volatile

$$p_T = x_A p_A^\circ + x_B p_B^\circ$$

$$x_A = x_B = \frac{1}{2}$$
$$\Rightarrow$$
$$p_T = \frac{p_A^\circ + p_B^\circ}{2}$$

$$p_T = (p_A^\circ - p_B^\circ)x_A + p_B^\circ$$

$$p_T = (p_B^\circ - p_A^\circ)x_B + p_A^\circ$$

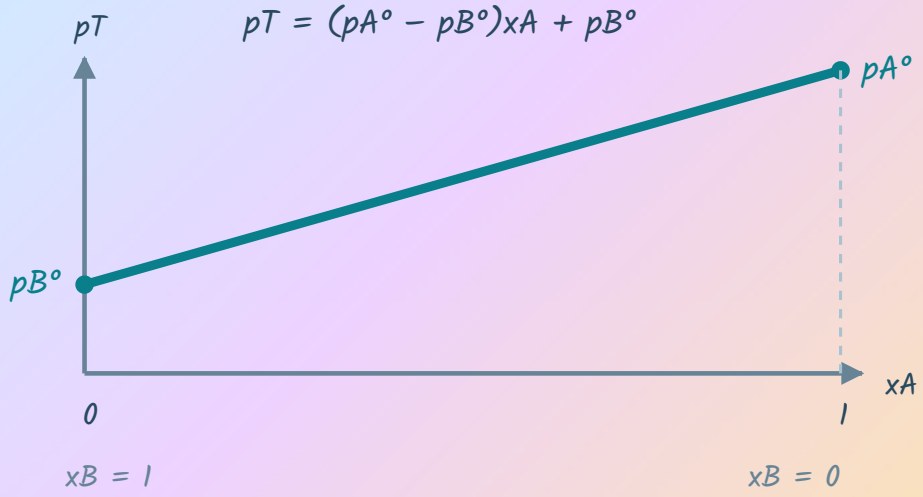
Solutions

Liquid–liquid system: both components volatile · Solid–liquid system

15 Liquid–liquid system: both components volatile

continued

- Total pressure is closer to the pure-component pressure of the component with the larger liquid mole fraction. At fixed temperature, maximise pressure by taking the more volatile component's fraction towards 1 and the other's towards 0.



Ideal total pressure varies linearly with liquid composition.

16 Solid–liquid system

- With a nonvolatile solute and volatile solvent, only the solvent contributes appreciably to vapour pressure. Relative lowering follows on the next page.

17 Nonvolatile solute: exact and dilute relations

- Here A is the volatile solvent and B the nonvolatile solute; pS is the solution vapour pressure.

$$p_S = p_A^\circ x_A$$

$$\frac{p_A^\circ - p_S}{p_A^\circ} = x_B = \frac{n_B}{n_A + n_B}$$

$$\frac{p_A^\circ - p_S}{p_S} = \frac{n_B}{n_A} = \frac{x_B}{x_A} = \frac{w_B}{w_A}\frac{M_A}{M_B}$$

$$n_B \ll n_A \Rightarrow \frac{p_A^\circ - p_S}{p_A^\circ} \approx \frac{n_B}{n_A}$$

In a dilute solution nA + nB ≈ nA and pS ≈ pA°; distinguish exact equations from dilute approximations.

Solutions

Composition of the vapour above an ideal binary liquid · Ideal solutions

18 Composition of the vapour above an ideal binary liquid

$$y_A = \frac{p_A}{p_T} = \frac{p_A^\circ x_A}{p_A^\circ x_A + p_B^\circ x_B}$$

$$y_B = \frac{p_B}{p_T} = \frac{p_B^\circ x_B}{p_A^\circ x_A + p_B^\circ x_B}$$

$$y_A + y_B = 1$$

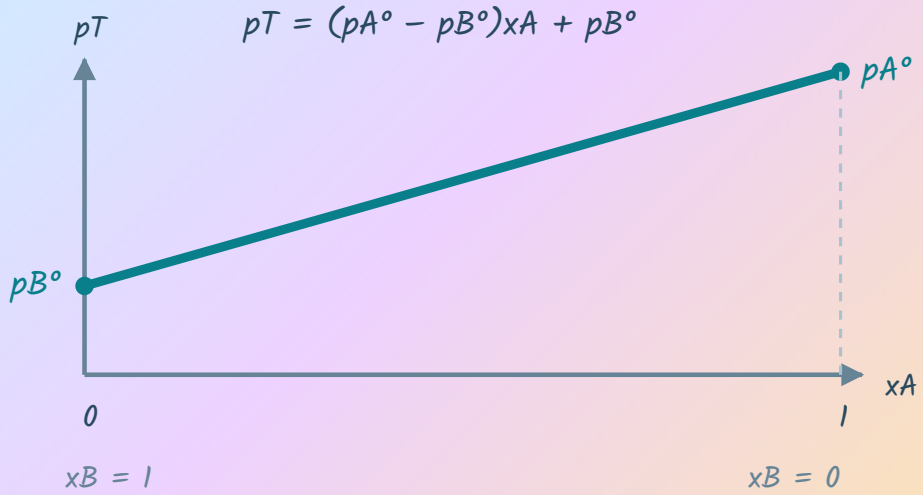
$$\frac{y_A}{y_B} = \frac{p_A}{p_B} = \frac{x_A}{x_B}\frac{p_A^\circ}{p_B^\circ} = \frac{n_A}{n_B}\frac{p_A^\circ}{p_B^\circ} = \frac{w_A}{w_B}\frac{M_B}{M_A}\frac{p_A^\circ}{p_B^\circ}$$

19 Ideal solutions

- An ideal solution obeys Raoult's law at every composition. Unlike and like intermolecular attractions are comparable: A–B ≈ A–A ≈ B–B.

$$\Delta V_{\text{mix}} = 0$$
$$\Delta H_{\text{mix}} = 0$$
$$\Delta S_{\text{mix}} > 0$$
$$\Delta G_{\text{mix}} < 0$$

Source examples	Recall guide
Benzene + toluene	Similar molecules often behave approximately ideally
Chlorobenzene + bromobenzene	Similar intermolecular interactions
Ethyl bromide + ethyl iodide	Same-family comparison; the source calls this a 'homologous series' trick



An ideal solution follows Raoult's law across the composition range.

Solutions

Positive deviation · Negative deviation

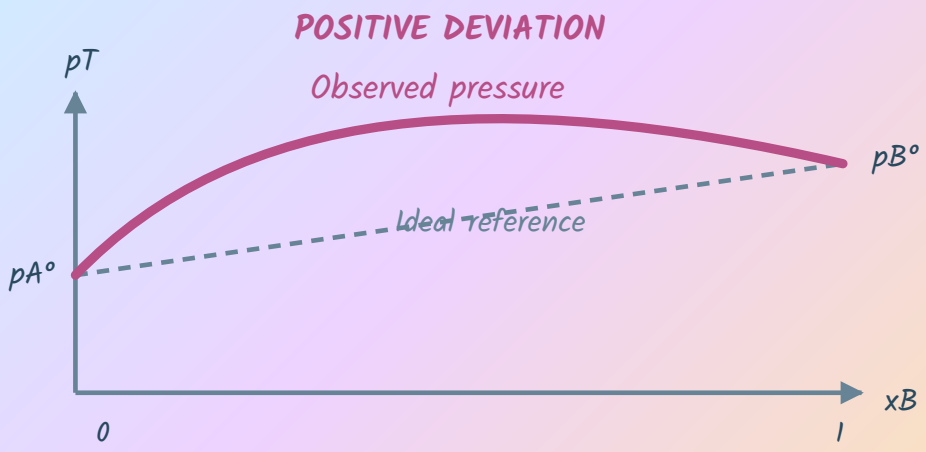
20 Positive deviation

- Positive deviation: observed total vapour pressure is above the ideal prediction. A–B attractions are weaker than the average like attractions.

$$p_T > p_{T,\text{ideal}}$$
$$\Delta H_{\text{mix}} > 0$$
$$\Delta V_{\text{mix}} > 0$$

The enthalpy/volume signs are typical for the source examples, not universal definitions.

- Examples: ethanol + water; methanol + water; CCl_4 + $CHCl_3$; CS_2 + acetone. Memory cue: the listed methyl/ethyl alcohol mixtures and CCl_4/CS_2 examples.



Weaker unlike interactions give pressure above the ideal prediction.

21 Negative deviation

- Negative deviation: observed total vapour pressure is below the ideal prediction. A–B attractions are stronger than the average like attractions.

$$p_T < p_{T,\text{ideal}}$$
$$\Delta H_{\text{mix}} < 0$$
$$\Delta V_{\text{mix}} < 0$$

Typical source-example signs. Entropy of mixing cannot be assigned the same positive sign for every nonideal mixture; spontaneous mixing at fixed T,p requires ΔGmix < 0.

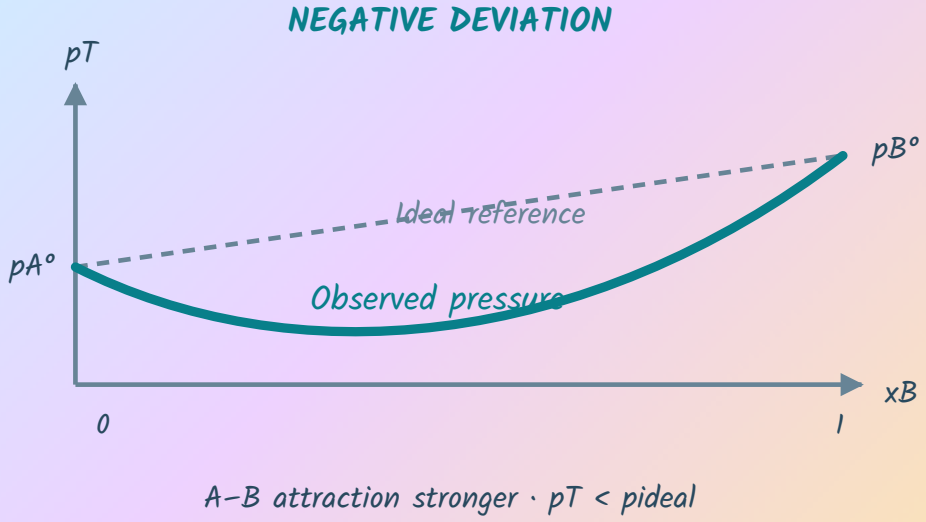
Solutions

Negative deviation · Azeotropes

21 Negative deviation

continued

- Examples: chloroform + acetic acid; chloroform + acetone; acid + water. Memory cue: an acid or chloroform component is useful only for these listed examples.



Stronger unlike interactions give pressure below the ideal prediction.

22 Azeotropes

- At a given pressure, an azeotrope boils at constant temperature and has the same liquid and vapour composition at its boiling point. Ordinary fractional distillation at that pressure cannot completely separate its components.

Type	Deviation	Source examples
Minimum-boiling azeotrope	Sufficiently strong positive deviation	Acetone + benzene; ethanol + water
Maximum-boiling azeotrope	Sufficiently strong negative deviation	HNO_3 + water; acetone + aniline; HCl + water

- Higher vapour pressure corresponds qualitatively to lower boiling temperature at a given external pressure.

23 What makes a property colligative?

- For dilute solutions under the stated assumptions, colligative properties depend on the number of dissolved solute particles, not their chemical identity. The four are relative lowering of vapour pressure, boiling-point elevation, freezing-point depression and osmotic pressure.

Solutions

1 · Relative lowering of vapour pressure · 2 · Elevation of boiling point

24 1 · Relative lowering of vapour pressure

$$\frac{\Delta p}{p_A^\circ} = \frac{p_A^\circ - p_A}{p_A^\circ} = x_B = \frac{n_2}{n_1 + n_2}$$

A/1 denotes solvent and B/2 denotes nonvolatile solute; pA° is pure-solvent pressure and pA solution pressure.

$$n_2 \ll n_1$$
$$\Rightarrow$$
$$\frac{\Delta p}{p_A^\circ} \approx \frac{n_2}{n_1}$$

25 2 · Elevation of boiling point

- A liquid boils when its vapour pressure equals external atmospheric pressure. Higher external pressure raises the boiling temperature. A nonvolatile solute lowers vapour pressure, so the solution needs a higher boiling temperature.

$$T_b(\text{solution}) > T_b^\circ(\text{solvent})$$

$$\text{solvent(l)} \rightleftharpoons \text{solvent(vapour)}$$

$$\Delta T_b = T_b(\text{solution}) - T_b^\circ(\text{solvent}) = K_b m$$

For a nonassociating, nondissociating solute.

$$\Delta T_b = i K_b m$$

i = van't Hoff factor; m = molality; Kb = ebullioscopic constant, units K kg mol⁻¹.

$$\Delta T_b = K_b \frac{1000 w_B}{M_B w_A}$$

i = 1; masses wA (solvent), wB (solute) in g and MB in g mol⁻¹.

$$K_b = \frac{R(T_b^\circ)^2 M_A}{1000 \Delta H_{\text{vap}}} = \frac{R(T_b^\circ)^2}{1000 L_{\text{vap}}}$$

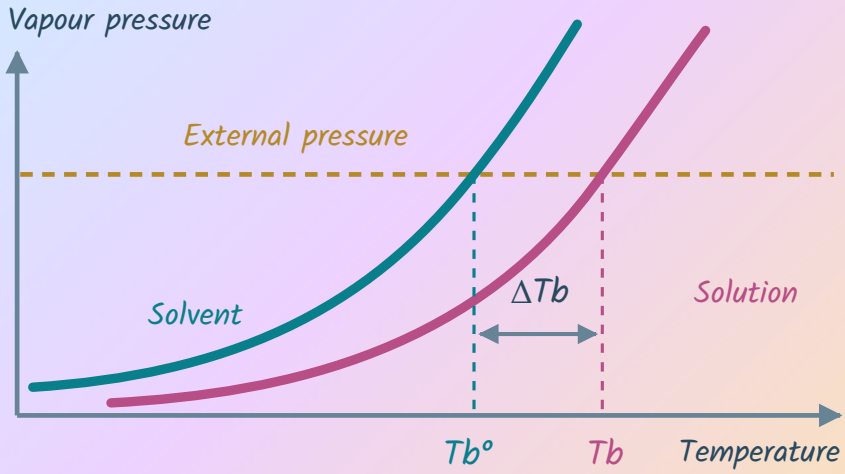
ΔHvap is molar vaporisation enthalpy in J mol⁻¹; Lvap is latent heat per gram in J g⁻¹.

Solutions

2 · Elevation of boiling point · 3 · Depression of freezing point

25 2 · Elevation of boiling point

continued



Lower vapour pressure requires a higher temperature to reach the same external pressure.

26 3 · Depression of freezing point

- At freezing equilibrium, liquid and solid solvent have matching vapour pressures (equivalently, chemical potentials). A dissolved nonvolatile solute lowers the freezing temperature, so pure solvent freezes at a higher temperature.

$$T_f^\circ > T_f$$
$$\Delta T_f = T_f^\circ - T_f > 0$$

$$\Delta T_f = iK_f m$$

$$\Delta T_f = K_f \frac{1000 w_B}{M_B w_A}$$

For $i = 1$.

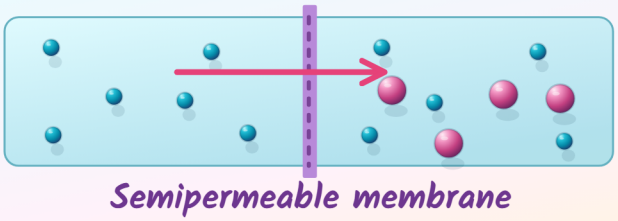
$$K_f = \frac{R(T_f^\circ)^2 M_A}{1000 \Delta H_{\text{fus}}} = \frac{R(T_f^\circ)^2}{1000 L_{\text{fus}}}$$

- Kf and Kb depend on the solvent. More solute-particle molality gives a larger freezing-point depression. An inverse relation for Tf itself is only a rough memory cue.

Solutions

4 · Osmosis and osmotic pressure · Osmotic-pressure notation and comparisons

27 4 · Osmosis and osmotic pressure



NET SOLVENT FLOW → solution

Osmotic pressure π

extra pressure that stops the net flow

Solvent passes · solute is retained

- Osmosis: solvent flows spontaneously through a semipermeable membrane from the more dilute solution (or pure solvent) towards the more concentrated solution. Osmotic pressure: the excess pressure needed to stop this net solvent flow.

$$\pi = iCRT = \frac{inRT}{V}$$

C is solute molarity; use consistent units for R, V and pressure.

28 Osmotic-pressure notation and comparisons

- In π = iCRT, i is the van't Hoff factor, C is molarity, R the gas constant and T absolute temperature in K.

Relation between two solutions	Meaning
Isotonic	$\pi_1 = \pi_2$ at the temperature considered
Hypotonic	Lower osmotic pressure relative to the other solution
Hypertonic	Higher osmotic pressure relative to the other solution

29 Definition of van't Hoff factor

$$i = \frac{\text{observed colligative property}}{\text{calculated value assuming no association/dissociation}}$$

$$i = \frac{\text{number of solute particles after association/dissociation}}{\text{number before association/dissociation}}$$

$$i = \frac{\text{normal molar mass}}{\text{apparent molar mass from the colligative measurement}}$$

Solutions

Definition of van't Hoff factor · Dissociation

29 Definition of van't Hoff factor

continued

DISSOCIATION → more particles



$i = 2$

Complete ideal example: 1 → 2

ASSOCIATION → fewer particles



$i = ½$

Complete ideal example: 2 → 1

- Dissociation → more particles → $i > 1$. Association → fewer particles → $i < 1$. No association or dissociation → $i = 1$. These ideas also apply to nonelectrolytes.

30 Dissociation

$$i = 1 + (\nu - 1)\alpha$$

α = degree of dissociation; ν = number of particles formed per formula unit.

$$\alpha = 1 \Rightarrow i = \nu$$

Source example	Formal particle count
$XePtCl_6 \rightarrow Xe^+ + [PtCl_6]^-$	2; retained as the source's formal ionic example
$K_2HgI_4 \rightarrow 2K^+ + [HgI_4]^{2-}$	3
$CsI_3 \rightarrow Cs^+ + I_3^-$	2

- Use $\alpha = 1$ when the problem assumes complete dissociation. Do not assume it for weak electrolytes or when equilibrium data show incomplete dissociation.

31 Association

$$i = 1 + \left(\frac{1}{\nu} - 1\right)\alpha$$

Here ν monomers associate to form one aggregate.

$$\alpha = 1 \Rightarrow i = \frac{1}{\nu}$$

- Listed nonelectrolytes: hydrocarbons, carbohydrates and urea. Use $i = 1$ only when the actual solute–solvent system neither associates nor dissociates.

Solutions

Colligative equations with i · Gas–liquid solubility

32 Colligative equations with i

$$\frac{p_A^\circ - p_A}{p_A^\circ} \approx i x_B$$

Dilute limit, where xB is based on undissociated formula units.

$$\Delta T_f = i K_f m$$
$$\Delta T_b = i K_b m$$
$$\pi = i C R T$$

33 Gas–liquid solubility

- Solubility is the maximum amount of solute that dissolves in a given amount of solvent at specified temperature and pressure.

Factor	Effect
Nature of gas and solvent	More favourable solute–solvent attractions generally increase solubility. The source gives polar–polar > polar–nonpolar > nonpolar–nonpolar as a comparison guide, not a universal ordering.
Temperature	Dissolution of many gases is exothermic, so their solubility falls as temperature rises. 'Always exothermic' is not a universal rule.
Pressure	At constant temperature in the Henry-law regime, increasing the gas's partial pressure increases its mole-fraction solubility.

34 Henry's law

$$p = K_H x$$

p is the gas's partial pressure, x its mole fraction in solution; KH is Henry's constant in this convention.

$$\text{At fixed } p:$$
$$K_H \uparrow \Rightarrow\ x \downarrow$$

$$x \propto \frac{1}{K_H}$$
$$(\text{fixed } p)$$

- This simple form applies to dilute dissolved gas at sufficiently low pressures. The model assumes that the gas does not react chemically with the solvent.

Electrochemistry

Cells • electrode potentials • conductance

08

01 Chemical and electrical energy

- Electrochemistry concerns conversion between chemical and electrical energy.

Cell type	Energy conversion	Reaction
Galvanic / voltaic	Chemical → electrical	Spontaneous redox under the operating conditions; $\Delta G < 0$
Electrolytic	Electrical → chemical	An externally driven nonspontaneous redox change; $\Delta G > 0$ for that direction

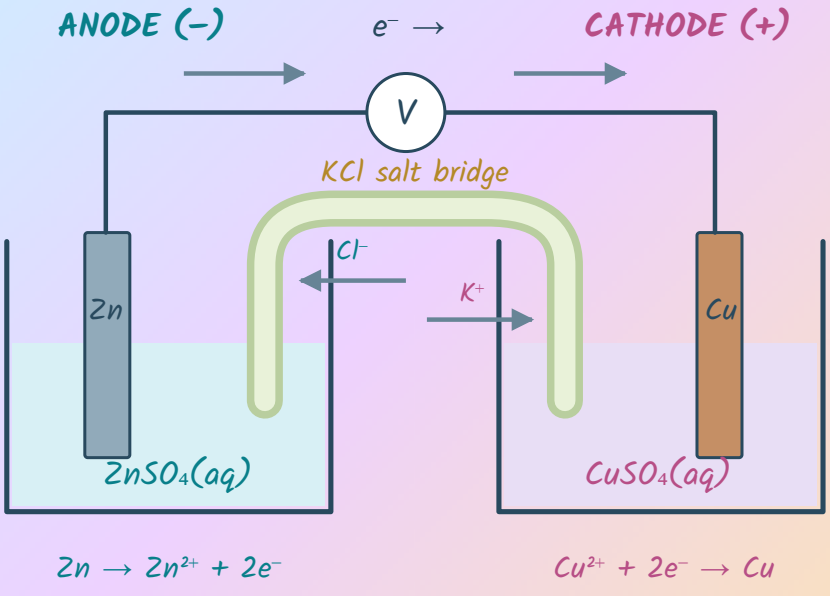
02 Working of a Daniell cell

$$\text{Anode: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$\text{Cathode: } Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

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

- Anode → oxidation; cathode → reduction. In a galvanic cell: anode negative, cathode positive. Electrons move anode → cathode through the external wire. Conventional current goes cathode → anode externally and anode → cathode through the internal ionic circuit.



Oxidation supplies electrons at Zn; reduction consumes them at Cu.

Electrochemistry

Working of a Daniell cell · Cell notation

02 Working of a Daniell cell

continued

Mnemonic	Meaning
L–O–A–N	Left, Oxidation, Anode, Negative (galvanic cell)
R–R–C–P	Right, Reduction, Cathode, Positive (galvanic cell)

03 Cell notation

$$\mathrm{Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)}$$

- One vertical line = phase boundary; double line = salt bridge. By convention, write oxidation on the left and reduction on the right.

04 Salt bridge and its functions

- A salt bridge can be a U-shaped glass tube filled with agar gel and an inert electrolyte, such as KCl, KNO_3 or NH_4NO_3. Similar ion mobilities help minimise liquid-junction potential.

- Do not use a KCl bridge when its chloride would precipitate or react with species in the cell, such as Ag^+, Pb^{2+} or Tl^+.

Function	Purpose
Completes the internal circuit	Connects the electrolyte solutions of the two half-cells
Maintains electrical neutrality	Permits compensating ion migration
Limits direct mixing	Ionic contact without bulk mixing of the solutions
Reduces liquid-junction potential	Similar cation/anion transport rates reduce charge separation

05 Cell potential and a worked example

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{red,cathode}} - E^\circ_{\mathrm{red,anode}}$$

$$\mathrm{Fe\,|\,Fe^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu}$$

- Given Fe oxidation potential +0.44 V, so $E°_{red}(Fe^{2+}/Fe) = -0.44$ V. Given $E°_{red}(Cu^{2+}/Cu) = +0.34$ V.

$$E^\circ_{\mathrm{cell}} = 0.34 - (-0.44) = 0.78\ \mathrm{V}$$

Electrochemistry

Write half-reactions: exercise continued on page 42 · Solved cell-reaction exercises

06 Write half-reactions: exercise continued on page 42

$$\mathrm{Pt\,|\,H_2(g)\,|\,H^+(aq)\,||\,Cl^-(aq)\,|\,Cl_2(g)\,|\,Pt}$$

- Identify left half-cell A as anode and right half-cell B as cathode; the next page gives the half-reactions and overall equation.

07 Solved cell-reaction exercises

Cell	Anode oxidation	Cathode reduction	Overall reaction
Pt | H_2 | H^+ || Cl^- | Cl_2 | Pt	$H_2 \rightarrow 2H^+ + 2e^-$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	$H_2 + Cl_2 \rightarrow 2H^+ + 2Cl^-$
Cr | Cr^{3+} || Fe^{2+} | Fe	$Cr \rightarrow Cr^{3+} + 3e^-$ (×2)	$Fe^{2+} + 2e^- \rightarrow Fe$ (×3)	$2Cr + 3Fe^{2+} \rightarrow 2Cr^{3+} + 3Fe$
Pt | H_2 | H^+ || Br^- | Br_2 | Pt	$H_2 \rightarrow 2H^+ + 2e^-$	$Br_2 + 2e^- \rightarrow 2Br^-$	$H_2 + Br_2 \rightarrow 2H^+ + 2Br^-$

- H_2 and Cl_2 are gases; Br_2 is liquid; metal electrodes are solids and the listed ions aqueous. Inert Pt electrodes are required for the hydrogen/halogen half-cells, even where the source abbreviates them.

08 Electrode potential

- Electrode potential is an electrode's potential relative to a reference, arising at the electrode–electrolyte interface.

$$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-} \qquad (E_{\mathrm{ox}})$$

$$\mathrm{Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)} \qquad (E_{\mathrm{red}})$$

- Tables normally list reduction potentials. Potential depends on the electrode/redox couple, temperature, ion activities (approximately dilute-solution concentrations) and gas pressures if gases take part.

09 Standard electrode potential

- Standard state: dissolved species at unit activity (often approximated by 1 M); gases at 1 bar; pure solids and liquids in their standard states. Tables commonly use 298.15 K (25 °C), but E° may be specified at other temperatures.

Electrochemistry

Standard electrode potential · Standard hydrogen electrode

09 Standard electrode potential

continued

Zinc half-reaction	Standard potential
$Zn(s) \rightarrow Zn^{2+} + 2e^-$	$E°ox = +0.76$ V
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	$E°red = -0.76$ V

$$E^\circ_{\text{red}} = -E^\circ_{\text{ox}}$$

- Multiplying all stoichiometric coefficients does not multiply the electrode potential: $2Zn^{2+} + 4e^- \rightarrow 2Zn$ still has $E°red = -0.76$ V.

10 Standard hydrogen electrode

$$\text{Pt} \,|\, \text{H}_2(\text{g},\ \text{p}^\circ) \,|\, \text{H}^+(\text{a} = 1)$$

- The standard hydrogen electrode (SHE) is the reference assigned $E° = 0$ V at every temperature. Its standard oxidation and reduction potentials are both 0 by convention.

11 Using the electrochemical series: metals

- In the listed series from very negative to very positive reduction potential, metallic reducing tendency generally decreases. Among these common metal couples, lithium has the most negative $E°red$ and is a very strong reducing metal in aqueous thermodynamic comparisons.

- More negative $E°red$ means greater metallic oxidation tendency in these comparisons. The inverse-proportionality memory cue is qualitative, not the equation reactivity $\propto 1/E°red$. Observed reactivity also depends on kinetics and passivation.

12 Nonmetals and agent strength

- In the listed order of increasing reduction potential, nonmetal oxidising power generally increases. F_2 is the strongest oxidising halogen among these standard couples.

$$\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$$
$$\text{(oxidising strength)}$$

- More negative reduction potential → stronger reducing agent. More positive reduction potential → stronger oxidising agent. Reversing the same couple changes the potential's sign, not its magnitude.

$$E^\circ_{\text{red}} = -E^\circ_{\text{ox}}$$

Electrochemistry

Source electrochemical-series recall list

13 Source electrochemical-series recall list

- Read down the listed school-level sequence as increasing standard reduction potential. Each symbol stands for its relevant redox couple; potential is not a property of the element alone. Above H: negative values. Below H: positive values. SHE: 0.

Species cue	Source mnemonic fragment
Li	Le
K	kar
Ba	barah
Sr	sardar
Ca	ka
Na	naam
Mg	mange
Al	Ali
Mn	nahan
Zn	zaan
Cr	kar
Fe	fenke
Cd	C.D.
Co	koi
Ni	neeche kahe
Sn	suno
Pb	pyaar
H	hai
Cu	kyun
I_2	aai
Ag	aaj
Hg	Hongkong me
Br_2	Britney
Pt	patai
O_2	aur
Cl_2	kilobhar
Au	sona laai
F_2	free mein

Electrochemistry

Displacement in solution · Nernst equation

14 Displacement in solution

- When Ecell is positive, a stronger reducing metal can displace a less reducing metal from its ions. A stronger oxidising halogen can oxidise the halide of a weaker oxidising halogen.

Reaction	Conclusion
$Zn + CuSO_4 \rightarrow Cu + ZnSO_4$	Occurs; Zn has the lower E°red
$Cu + ZnSO_4$	No spontaneous displacement under the stated ordinary conditions
$2KI + Cl_2 \rightarrow 2KCl + I_2$	Occurs; Cl_2 is the stronger oxidant
$2KCl + I_2$	No spontaneous displacement under the stated ordinary conditions

15 Nernst equation

- The Nernst equation relates cell potential to standard cell potential, temperature and the reaction quotient.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.05916}{n} \log_{10} Q \quad (298.15\ \text{K})$$

- Ecell = emf at the stated composition; E°cell = standard emf. R = 8.314 J K⁻¹ mol⁻¹; T = absolute temperature; n = moles of electrons per balanced reaction; F = Faraday constant. In Q = [products]/[reactants], include stoichiometric powers and the correct activities.

16 Reaction quotient and constants

- F ≈ 96500 C mol⁻¹ of electrons; more precisely, 96485 C mol⁻¹. For dilute ideal solutions, use concentration divided by standard concentration. Omit pure solids and liquids: their activities are 1. For gases, use relative partial pressures.

$$\alpha\mathrm{A(aq)} + \beta\mathrm{B(g)} \rightarrow \chi\mathrm{C(aq)} + \gamma\mathrm{D(s)}$$

$$Q = \frac{a_C^{\chi}}{a_A^{\alpha}(p_B/p^{\circ})^{\beta}}$$

$$E = E^{\circ} - \frac{0.05916}{n} \log_{10} Q \quad (298.15\ \text{K})$$

Electrochemistry

At equilibrium · Worked Mg–Ag cell

17 At equilibrium

$$E_{\text{cell}} = 0$$
$$Q = K$$

$$E^\circ_{\text{cell}} = \frac{RT}{nF}\ln K = \frac{0.05916}{n}\log_{10} K \quad (298.15\ \text{K})$$

18 Worked Mg–Ag cell

$$\text{Mg(s)}\,|\,\text{Mg}^{2+}\text{(aq)}\,||\,\text{Ag}^{+}\text{(aq)}\,|\,\text{Ag(s)}$$

$$\text{Mg(s)} + 2\text{Ag}^{+}\text{(aq)} \rightarrow \text{Mg}^{2+}\text{(aq)} + 2\text{Ag(s)}$$

- Given $E^\circ_{\text{cell}} = 3.17$ V; $[Mg^{2+}] = 10^{-1}$ M; $[Ag^{+}] = 10^{-3}$ M; $n = 2$.

$$E_{\text{cell}} = 3.17 - \frac{0.06}{2}\log_{10}\frac{10^{-1}}{(10^{-3})^2} = 3.02\ \text{V}$$

Uses the source's rounded 0.06 factor.

19 General Nernst form and concentration cells

$$a\text{A} + b\text{B} \rightarrow m\text{M} + \ell\text{N}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.05916}{n_e}\log_{10}\frac{a_M^m a_N^\ell}{a_A^a a_B^b}$$

n_e denotes electrons; use a different symbol from the product coefficient.

$$E_{\text{red}} = E^\circ_{\text{red}} - \frac{0.05916}{n_e}\log_{10}\frac{a_{\text{Red}}}{a_{\text{Ox}}}$$

Simple Ox + ne^- ⇌ Red half-reaction at 298.15 K.

$$E_{\text{concentration cell}} = \frac{0.05916}{n_e}\log_{10}\frac{c_2}{c_1}$$

For the same metal/metal-ion couple with dilute ideal solutions; positive for the chosen orientation $c_2 > c_1$.

Electrochemistry

Electrical work and Gibbs energy · Faraday's first law

20 Electrical work and Gibbs energy

ΔG = −nFEcell · follow the written reaction direction

Ecell > 0	Ecell = 0	Ecell < 0
ΔG < 0	ΔG = 0	ΔG > 0
spontaneous direction	equilibrium	nonspontaneous direction

$$\Delta G = -w_{\text{electrical,max}} = -nFE_{\text{cell}}$$

Cell potential	ΔG	Meaning for written direction
Ecell = 0	0	Equilibrium; forward and reverse rates equal
Ecell > 0	< 0	Spontaneous thermodynamic direction
Ecell < 0	> 0	Nonspontaneous thermodynamic direction

$$\Delta G^\circ = -RT\ln K = -2.303RT\log_{10} K$$

21 Faraday's first law

- The mass deposited or chemically changed at an electrode is proportional to charge passed through the electrolyte.

$$w \propto Q$$
$$Q = It$$
$$w = ZQ = ZIt$$

$$Z = \frac{E_{\text{equiv}}}{F}$$
$$E_{\text{equiv}} = \frac{M}{n_f}$$

Z is the electrochemical equivalent; M is molar mass.

$$w = \frac{E_{\text{equiv}}It}{F} = \frac{MIt}{n_f F}$$

$$\frac{w}{M} = n_{\text{substance}} = \frac{It}{n_f F}$$
$$n_{\text{substance}} n_f F = It$$

Electrochemistry

Faraday's second law · Faraday mass ratio

22 Faraday's second law

- For the same charge through different electrolytes, deposited masses are proportional to equivalent masses.

$$\frac{w}{E_{\text{equiv}}} = \frac{It}{F} = \text{constant}$$

- The ratio form continues on the next page.

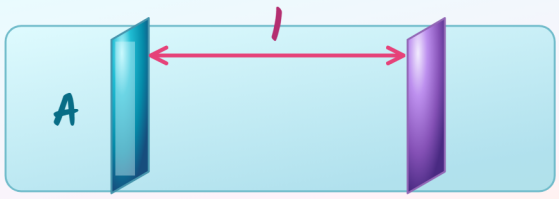
23 Faraday mass ratio

$$\frac{w_1}{w_2} = \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Same charge through both electrolytes; E here denotes equivalent mass.

24 Electrical definitions

Quantity	Relation	Common unit
Resistance R	$V = IR$; $R = V/I$	$\Omega = V\ A^{-1}$
Resistivity ρ	$R = \rho l/A$; $\rho = RA/l$	Ω cm (if l in cm and A in cm²)
Conductance G	$G = 1/R$	$S = \Omega^{-1}$; also called mho
Conductivity κ	$\kappa = 1/\rho = l/(RA)$	$S\ cm^{-1}$



A = facing electrode area

CELL GEOMETRY

$$G^* = l/A\ ;\ \kappa = G \times G^*$$

Fixed geometry → fixed cell constant

$$G^* = \frac{l}{A}$$

$$\kappa = GG^* = \frac{G^*}{R}$$

G^* is the cell constant; it is fixed for the cell geometry.

Electrochemistry

Molar and equivalent conductivity · Factors affecting electrolytic conductance

25 Molar and equivalent conductivity

$$\Lambda_m = \kappa V_m = \frac{1000\kappa}{M}$$

M in mol L^{-1} and κ in S cm^{-1} give Λm in S cm^2 mol^{-1}; Vm is the volume in cm^3 containing 1 mol.

$$\Lambda_{eq} = \kappa V_N = \frac{1000\kappa}{N}$$

N in eq L^{-1} gives Λeq in S cm^2 eq^{-1}; VN is the volume in cm^3 containing 1 equivalent.

$$\Lambda_m = n_f \Lambda_{eq}$$

26 Factors affecting electrolytic conductance

Factor	Trend or explanation
Nature of electrolyte	At comparable conditions, a strong electrolyte is largely dissociated (α ≈ 1); a weak electrolyte is only partly dissociated (α < 1). More mobile charge carriers generally increase conduction.
Interionic attraction	Lower interionic hindrance permits greater ionic mobility and generally raises molar conductivity.
Temperature	Increasing temperature generally increases ion mobility and aqueous-electrolyte conductance; viscosity and interionic hindrance decrease.
Solvation / hydration	Association of ions with solvent molecules is solvation (hydration in water). Greater effective solvated size generally lowers mobility.

- H^+ and OH^- have unusually high ionic mobility in water, with $H^+ > OH^-$. The extension "all cations > all anions" is not a general rule.

27 Effect of dilution

Quantity	Strong electrolyte	Weak electrolyte
Dissociation fraction	Already approximately 1	Increases on dilution; for a sufficiently weak 1:1 electrolyte, $\alpha \approx \sqrt{(K_a V)}$ if V = 1/c
Molar / equivalent conductivity	Increases as interionic hindrance decreases and mobility rises	Increases markedly as dissociation and mobile-ion amount per mole increase
Specific conductivity κ	Usually falls: fewer ions per unit volume	Usually falls overall in the normal dilute-solution regime despite increased dissociation

- The original rising dilution curve is labelled G. For a fixed cell, $G = \kappa/G^*$ follows conductivity κ. The quantities that normally rise on dilution are Λm and Λeq, not fixed-cell G.

Electrochemistry

Strong-electrolyte limiting law · Kohlrausch's law of independent ionic migration

28 Strong-electrolyte limiting law

$$\Lambda_m = \Lambda_m^\circ - b\sqrt{c}$$

The source calls this the Debye–Hückel–Onsager equation. It is the simple limiting concentration form for strong electrolytes in dilute solution.

- Λm = molar conductivity at concentration c; Λm° = its infinite-dilution value. b depends on ionic charge type, solvent and temperature; it is not universal.



← Dilution increases; c → 0

Molar conductivity increases on dilution; the rise is much sharper for a weak electrolyte.

29 Kohlrausch's law of independent ionic migration

INFINITE DILUTION → independent ionic contributions

$\nu_+ \lambda_+^\circ$ (cation count × share) + $\nu_- \lambda_-^\circ$ (anion count × share) = Λ_m° (electrolyte total)

Both weak and strong electrolytes

- At infinite dilution, each ion contributes independently to limiting conductivity. Kohlrausch's law applies to both weak and strong electrolytes.

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$$

ν+ and ν− are stoichiometric numbers of cations/anions per formula unit; λ° are ionic molar conductivities.

Electrochemistry

Kohlrausch's law of independent ionic migration · Alum example

29 Kohlrausch's law of independent ionic migration

continued

$$\Lambda^\circ_{\text{eq}} = \lambda^\circ_{\text{eq},+} + \lambda^\circ_{\text{eq},-}$$

$$\Lambda^\circ_{\text{eq}} = \frac{\Lambda^\circ_m}{n_f}$$

$$\Lambda^\circ_m = n_f \Lambda^\circ_{\text{eq}}$$

When ionic molar conductivities are used, $\Lambda eq° = \lambda+°/|z+| + \lambda-°/|z-|$ for a simple salt, not reciprocal stoichiometric coefficients.

30 Alum example

$$\mathrm{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O} \longrightarrow \mathrm{2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O}$$

$$\Lambda^\circ_m = 2\lambda^\circ_{\mathrm{K^+}} + 2\lambda^\circ_{\mathrm{Al^{3+}}} + 4\lambda^\circ_{\mathrm{SO_4^{2-}}}$$

$$n_f = 8$$

$$\Lambda^\circ_{\text{eq}} = \frac{\Lambda^\circ_m}{8}$$

31 Determining limiting conductivity from other electrolytes

$$\Lambda^\circ_m(\mathrm{CH_3COOH}) = \Lambda^\circ_m(\mathrm{CH_3COONa}) + \Lambda^\circ_m(\mathrm{HCl}) - \Lambda^\circ_m(\mathrm{NaCl})$$

$$\Lambda^\circ_m(\mathrm{BaCl_2}) = \Lambda^\circ_m(\mathrm{Ba(OH)_2}) - 2\Lambda^\circ_m(\mathrm{NaOH}) + 2\Lambda^\circ_m(\mathrm{NaCl})$$

- Worked symbolic data: let $\Lambda m°(Na_2C_2O_4) = x_1$, $\Lambda m°(H_2SO_4) = x_2$ and $\Lambda m°(Na_2SO_4) = x_3$.

$$\Lambda^\circ_m(\mathrm{H_2C_2O_4}) = x_1 + x_2 - x_3$$

32 Oxalic-acid limiting conductivity

$$\Lambda^\circ_m(\mathrm{H_2C_2O_4}) = \Lambda^\circ_m(\mathrm{Na_2C_2O_4}) + \Lambda^\circ_m(\mathrm{H_2SO_4}) - \Lambda^\circ_m(\mathrm{Na_2SO_4})$$

Continuation of the example on page 46.

Electrochemistry

Degree of dissociation · Dissociation constant of a weak 1:1 electrolyte

33 Degree of dissociation

$$\alpha \approx \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{\Lambda_{\text{eq}}}{\Lambda_{\text{eq}}^\circ}$$

Useful dilute weak-electrolyte approximation; numerator is the value at the specified concentration.

$$\alpha \approx \frac{1000\kappa}{M\Lambda_m^\circ}$$

34 Dissociation constant of a weak 1:1 electrolyte

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$$

Stage	HA	H^+	A^-
Initial	c	0	0
Equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

$$\alpha \leq 0.05 \Rightarrow K_a \approx c\alpha^2$$

The 5% criterion justifies $1 - \alpha \approx 1$ for this approximation.

35 Solubility from conductivity

$$\mathrm{AB(s)} \rightleftharpoons \mathrm{A^+(aq)} + \mathrm{B^-(aq)}$$
$$K_{sp} = s^2$$

For a sparingly soluble 1:1 salt, neglecting other sources of the ions.

$$\Lambda_m = \frac{1000\kappa}{M}$$

- A sufficiently sparingly soluble salt gives a very dilute saturated solution, allowing $\Lambda m \approx \Lambda m^\circ$. Put $M = s$ and subtract solvent/background conductivity before using the solution's conductivity.

$$s \approx \frac{1000\kappa_{\text{salt}}}{\Lambda_m^\circ}$$

Electrochemistry

Corrosion · Batteries and primary cells

36 Corrosion

- Corrosion changes a metal surface into compounds such as oxides or sulfides through chemical/electrochemical reaction with the environment.

Rust: $Fe_2O_3 \cdot xH_2O$

- Factors that increase corrosion: metal impurities, moisture and electrolytes. Prevention: barrier protection and sacrificial protection.

37 Batteries and primary cells

- A battery supplies electrical energy from one or more electrochemical cells; cells can be joined in series. Primary cells are designed for discharge, not for recharging after the active chemicals are used up. Examples: dry cell (Leclanché type) and mercury cell.

38 Dry cell

Part or property	Source details
Anode	Zinc container
Cathode assembly	Graphite rod current collector surrounded by MnO_2-containing cathode mixture
Paste electrolyte	$NH_4Cl + ZnCl_2$
Typical cell potential in source	About 1.25–1.5 V

$$2MnO_2 + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$$

The source gives this simplified cathode reduction equation; it is not the full cell reaction.

39 Mercury cell

Part or property	Source details
Anode	Zn–Hg amalgam
Cathode	HgO mixed with carbon
Paste	KOH and ZnO
Cell potential	About 1.35 V

$$Zn(Hg) + HgO \rightarrow ZnO + Hg$$

Electrochemistry

Secondary batteries · Lead storage battery

40 Secondary batteries

- Secondary cells can be recharged and reused by reversing the discharge reaction. Examples: lead storage and nickel–cadmium cells.

41 Lead storage battery

Component	Description
Anode during discharge	Spongy lead
Cathode during discharge	Lead grid containing PbO_2

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$$

- Recharging reverses the cell reaction. Electrode oxidation/reduction roles reverse when current is driven in the opposite direction.

42 Nickel–cadmium storage cell

Component/property	Source description
Anode	Cadmium
Cathode	Nickel-oxide active material on a metal support; written as NiO_2 in the source's simplified textbook equation
Cell potential	Approximately 1.4 V in the source's textbook description
Service-life comparison	The source notes a longer life than a lead storage cell under comparable use

$$Cd + NiO_2 + 2H_2O \rightarrow Cd(OH)_2 + Ni(OH)_2$$

Preserved as the simplified source/NCERT-style overall representation.

43 Fuel cells

- A fuel cell is a galvanic device that converts the chemical energy of continuously supplied fuel and oxidant directly into electricity. Listed fuels: H_2 and CH_4. Efficiency can be high; emissions depend on the fuel and how it is produced.

- Example: hydrogen–oxygen fuel cell. The original "H_2O_2 fuel cell" label means H_2/O_2 reactants, not hydrogen peroxide.

Chemical Kinetics

Rate laws • integrated equations • activation energy

09

01 Types by speed

Class	Source description	Example
Very fast	Completed in a fraction of a second	Many ionic / acid–base reactions
Very slow	May take years for extensive completion	Rusting of iron / corrosion
Moderate	Occurs on a measurable finite laboratory timescale	Many molecular reactions

02 Rate of reaction

$$\text{rate} = \frac{\text{change in concentration}}{\text{change in time}}$$

$$a\text{A} + b\text{B} \rightarrow x\text{X} + y\text{Y}$$

$$r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{x}\frac{d[X]}{dt} = \frac{1}{y}\frac{d[Y]}{dt}$$

- At fixed volume, use a minus sign for disappearing reactants and a plus sign for appearing products. This makes the defined forward reaction rate positive.

Rate expression	Typical unit
Concentration rate in solution or gas	mol L^{-1} s^{-1}
Gas rate expressed as pressure change	atm s^{-1} (under the stated temperature/volume conditions)

03 Average and instantaneous rates

$$\text{A} \rightarrow \text{B}$$

$$r_{\text{avg}} = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_2 - [A]_1}{t_2 - t_1}$$

Equivalently, reactant decrease = higher earlier concentration minus lower later concentration, divided by elapsed time.

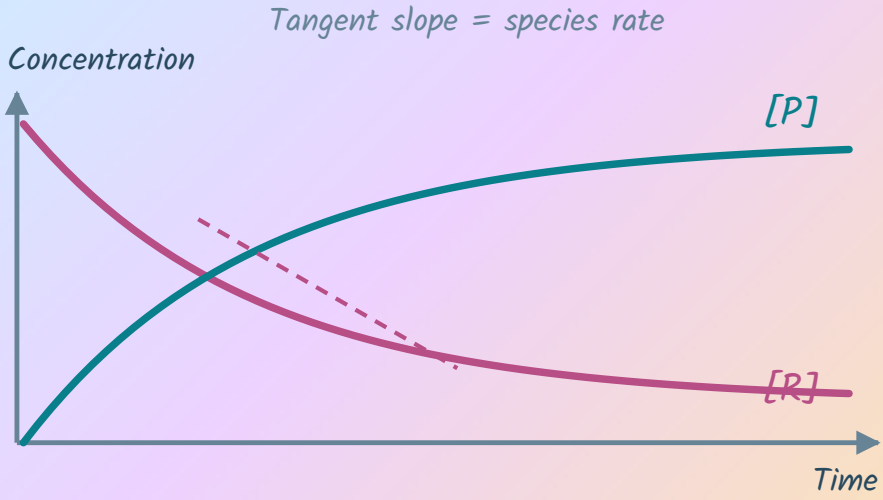
$$r_{\text{inst}} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

Chemical Kinetics

Average and instantaneous rates · Rate calculation reminders

03 Average and instantaneous rates

continued



Reactants disappear as products form; slopes give instantaneous rates.

04 Rate calculation reminders

- Relate species rates using mole/stoichiometric ratios, not mass ratios. Appearance and disappearance rates follow their stoichiometric coefficients. Divide by those coefficients to get the common reaction rate. Minus = reactant loss; plus = product formation.

05 Factors affecting rate

- Rate can depend on concentration, gas partial pressure, temperature and catalysts. For common positive-order reactions, higher concentration/pressure speeds reaction. Higher temperature commonly raises k; a suitable catalyst gives a faster pathway. These trends are conditional, not universal.

06 Rate law and rate constant

$$a\mathrm{A} + b\mathrm{B} \rightarrow \text{products}$$

Chemical Kinetics

Rate law and rate constant · Elementary and complex reactions

06 Rate law and rate constant

continued

$$r = k[A]^x[B]^y$$

The rate law's powers x,y are experimentally determined for an overall reaction. They equal a,b only for the appropriate elementary mass-action step.

$$n = x + y$$
$$[k] = (\mathrm{mol\,L^{-1}})^{1-n}\mathrm{s^{-1}} = \mathrm{L^{\,n-1}mol^{\,1-n}s^{-1}}$$

- *With the same rate-law form and concentrations, a larger k gives a faster rate. For a fixed pathway and medium, k depends on temperature. Changing the catalyst or medium can also change k. In the stated law, k does not depend on reactant concentration.*

07 Elementary and complex reactions

Elementary	Complex
One elementary step	Multiple elementary steps
Source example: an elementary SN2 substitution step	Source example: an SN1 mechanism involving multiple steps

08 Molecularity

- *Molecularity counts the atoms, ions or molecules taking part in one elementary event. It is a mechanistic/theoretical quantity assigned only to an elementary step.*

- *Molecularity is a positive integer: usually 1 or 2; rarely 3. It is never zero, negative or fractional. Simultaneous collisions of more particles are extremely unlikely. For an elementary mass-action step, molecularity equals total order.*

09 Order of reaction

$$a\mathrm{A} + b\mathrm{B} \rightarrow \text{products}$$
$$r = k[A]^x[B]^y$$

$$\text{overall order} = x + y$$

Chemical Kinetics

Order of reaction · Units of the rate constant

09 Order of reaction

continued

- a + b is molecularity only when the displayed reaction is an elementary step. Overall order is usually experimental; it can be zero, positive, negative, integral or fractional. Order applies to elementary and complex reactions. For a complex reaction, the slow step often controls rate, but earlier equilibria and intermediates may be needed to derive the observed rate law.

10 Units of the rate constant

Order	Units of k for r in mol L^{-1} s^{-1}
0	mol L^{-1} s^{-1}
1	s^{-1}
2	$L\ mol^{-1}\ s^{-1}$
n	$L^{n-1}\ mol^{1-n}\ s^{-1}$

11 Zero-order reaction

$$r = -\frac{d[A]}{dt} = k[A]^0 = k$$

- The rate is concentration-independent within the zero-order regime.

$$A_t = A_0 - kt$$

$$k = \frac{A_0 - A_t}{t} = \frac{x}{t}$$

A0 = initial concentration; At = concentration at time t; x = concentration consumed.

$$A_t = \frac{A_0}{2}$$
$$\Rightarrow$$
$$t_{1/2} = \frac{A_0}{2k}$$

$$A_t = 0$$
$$\Rightarrow$$
$$t_{100\%} = \frac{A_0}{k} = 2t_{1/2}$$

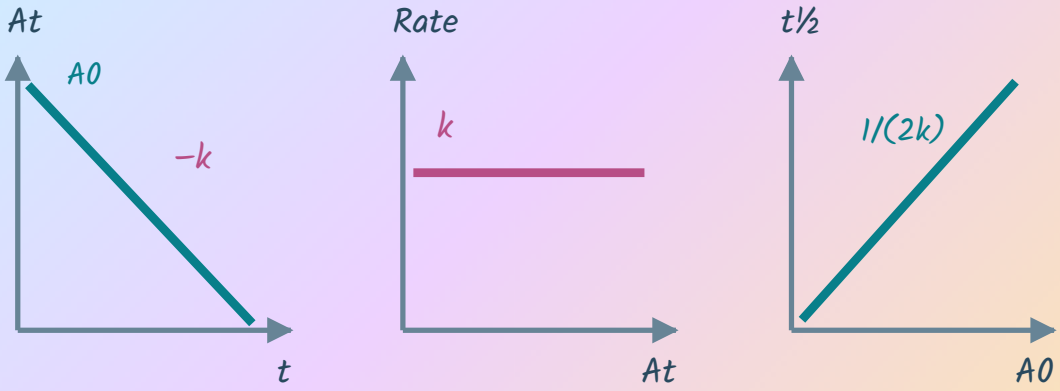
The constant-rate law ceases to apply after the reactant is exhausted.

Chemical Kinetics

Zero-order reaction · First-order reaction

11 Zero-order reaction

continued



$At = A0 - kt$ $\quad$ $Rate = k$ $\quad$ $t½ \propto A0$

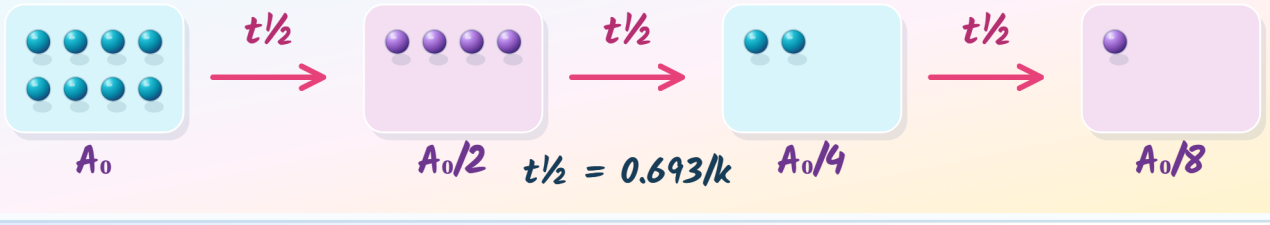
Zero order: constant rate, linear concentration loss and concentration-dependent half-life.

12 First-order reaction

$$r = kA_t$$

$$k = \frac{1}{t}\ln\frac{A_0}{A_t} = \frac{2.303}{t}\log_{10}\frac{A_0}{A_t}$$

FIRST ORDER → halve the amount in each equal time interval



$$t_{1/2} = \frac{\ln 2}{k} = \frac{2.303\log_{10}2}{k} = \frac{0.693}{k}$$

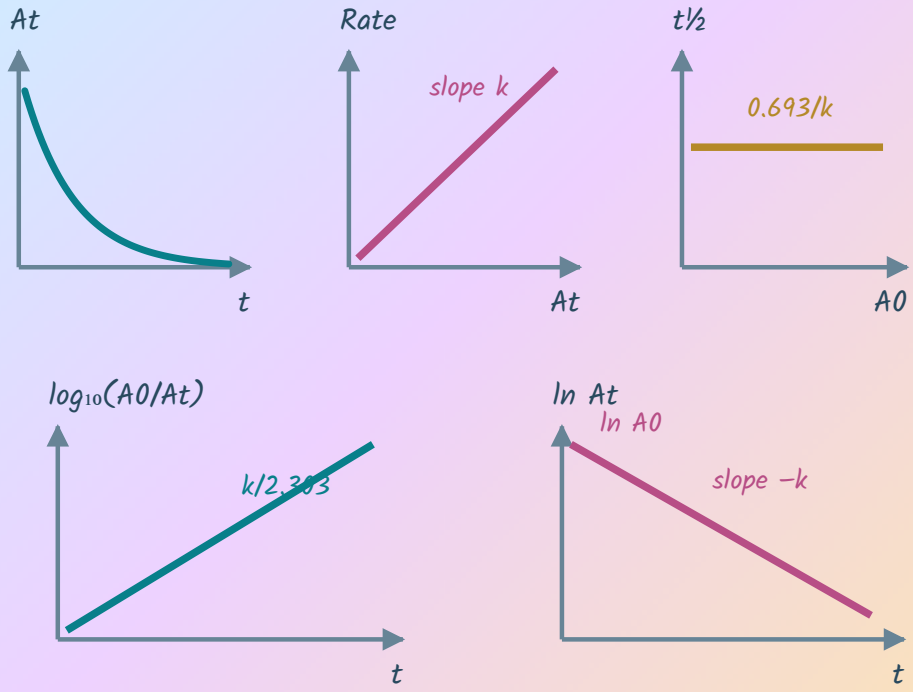
The first-order half-life is independent of A0.

Fraction completed	Elapsed time
75% (3/4)	2t½
87.5% (7/8)	3t½
93.75% (15/16)	4t½
Approximately 99.9%	Approximately 10t½; 10 half-lives gives 99.90234375% completion

Chemical Kinetics

First-order graphs · Pseudo-first-order reactions

13 First-order graphs



First-order half-life does not depend on A0

First order: exponential decay and a half-life independent of initial concentration.

14 Pseudo-first-order reactions

- A reaction with several reactants can appear first order when the other concentrations remain nearly constant, often because a reactant is in large excess. Include their constant factors in the observed rate constant.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

- Example: acid-catalysed hydrolysis of ethyl acetate in excess water. With water activity and acid concentration nearly constant, rate is first order in ester. The apparent count 1 + 0 + 0 = 1 applies to those conditions; the fundamental rate is not always independent of water or acid.

- Another example: inversion (hydrolysis) of cane sugar in acid under pseudo-first-order conditions.

15 Second order: one-reactant squared law

$$r = -\frac{dA}{dt} = kA^2$$

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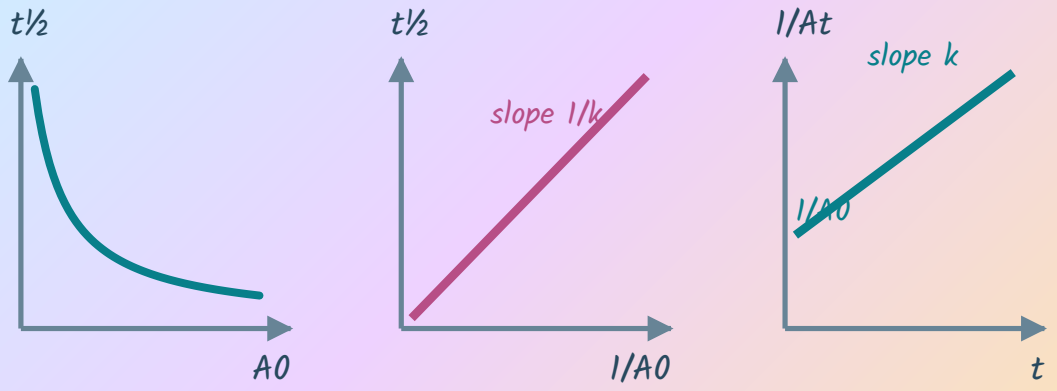
Second order: one-reactant squared law · General nth-order law

15 Second order: one-reactant squared law

continued

$$k = \frac{1}{t}\left(\frac{1}{A_t} - \frac{1}{A_0}\right)$$

$$t_{1/2} = \frac{1}{kA_0}$$



t½ = 1/(kA0)

1/At = 1/A0 + kt

Second order: 1/At is linear in time and half-life decreases with initial concentration.

16 General nth-order law

$$r = -\frac{dA}{dt} = kA^n$$

$$k = \frac{1}{(n-1)t}\left[\frac{1}{A_t^{n-1}} - \frac{1}{A_0^{n-1}}\right] \quad (n \neq 1)$$

- The notes use this for $n \geq 2$. Mathematically, it applies to the stated single-reactant power law for $n \neq 1$ wherever that model is valid.

$$t_{1/2} \propto A_0^{1-n} = \frac{1}{A_0^{n-1}}$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{(A_0)_2}{(A_0)_1}\right)^{n-1}$$

For the same rate constant.

Chemical Kinetics

Collision theory · Reactant nature, surface area and concentration

17 Collision theory

- A successful collision needs suitable orientation and enough energy. Rate depends on collision frequency, orientation and the fraction of sufficiently energetic collisions.

$$\text{rate} = PZ_{AB}e^{-E_a/(RT)}$$

- P = steric/orientation factor. ZAB = A–B collisions per unit volume per unit time. The exponential term gives the energetic factor in this simplified collision model.

18 Reactant nature, surface area and concentration

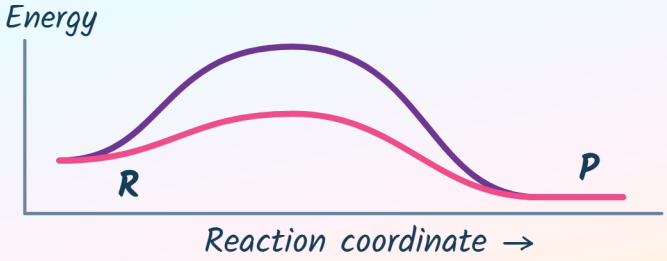
- The memory trends gas > liquid > solid and homogeneous > heterogeneous are not universal speed rankings. Phase alone cannot decide rate. In a heterogeneous reaction, more accessible surface area often raises the rate.

- The notes also link faster rate to stable products/unstable reactants. Thermodynamic stability alone cannot decide rate; consider the activation barrier and mechanism.

$$r = k[\text{reactant}]^n$$

Concentration dependence is set by the order. For a fixed pathway and medium, k changes with temperature rather than with reactant concentration.

19 Catalyst effect



Same reactants and products

— uncatalysed: higher barrier

— catalysed: lower barrier

ΔH and equilibrium unchanged

- A catalyst provides another reaction pathway with a lower effective activation barrier. It does not change reaction enthalpy or equilibrium thermodynamics.

$$\Delta E = E_{a,\text{uncat}} - E_{a,\text{cat}}$$

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{r_{\text{cat}}}{r_{\text{uncat}}} = \frac{A_{\text{cat}}}{A_{\text{uncat}}}e^{\Delta E/(RT)}$$

Rate ratio requires the same applicable concentration factors. The source labels catalysed and uncatalysed cases p ('present') and a ('absent').

Chemical Kinetics

Temperature coefficient · Activation energy and the energy profile

20 Temperature coefficient

$$\mu_T = \frac{k_{T+10}}{k_T} \approx 2 \text{ to } 3$$

Empirical rule of thumb for many reactions over a modest temperature interval; not universal.

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{E_a(T_2 - T_1)}{2.303RT_1T_2}$$

Assumes approximately constant Ea and pre-exponential factor over the interval.

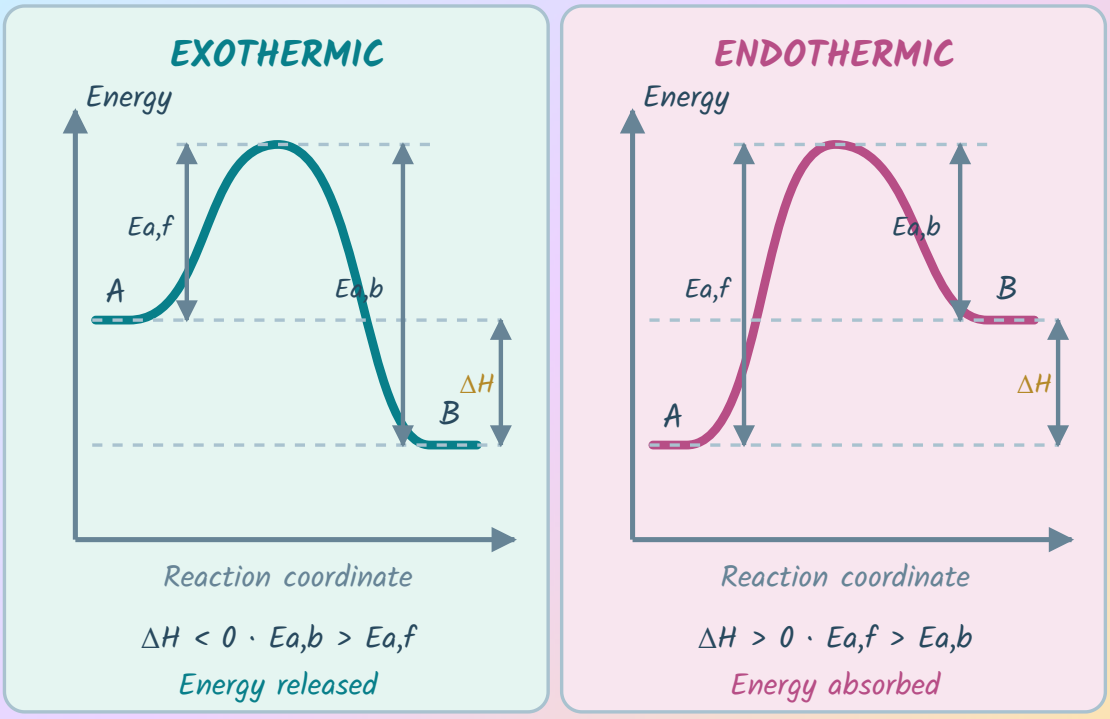
21 Activation energy and the energy profile

- *In an elementary energy-barrier diagram, activation energy is the gap from reactants to the transition state (activated complex).*

$$E_T = E_R + E_{a,\mathrm{f}}$$

$$\Delta H = E_{a,\mathrm{f}} - E_{a,\mathrm{b}}$$

Profile	Relative levels	Barrier comparison
Exothermic: energy released	Products lower than reactants; $\Delta H < 0$	$E_{a,b} > E_{a,f}$
Endothermic: energy absorbed	Products higher than reactants; $\Delta H > 0$	$E_{a,b} < E_{a,f}$



Forward and reverse barriers differ by the reaction enthalpy.

Chemical Kinetics

Activation energy and the energy profile · Arrhenius equation

21 Activation energy and the energy profile

continued

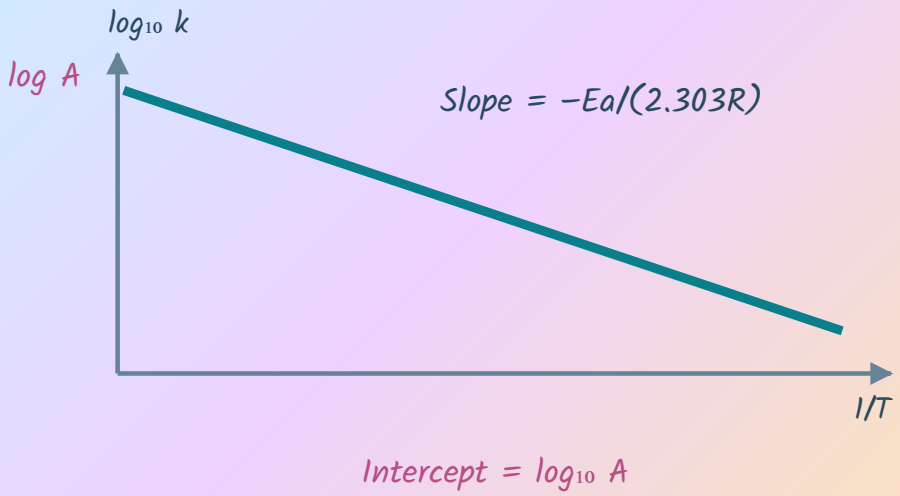
- Ea is positive in the elementary barrier diagram shown. Apparent Arrhenius activation energies for complex mechanisms can be zero or negative, so "Ea is always positive" is too broad.

22 Arrhenius equation

$$k = Ae^{-E_a/(RT)}$$

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

- A = Arrhenius pre-exponential factor; Ea = activation energy; R = gas constant; T = absolute temperature. With positive Ea and nearly constant A, a higher T increases k and commonly increases rate.



An Arrhenius plot gives activation energy from the negative slope.

23 Source recall notes with conditions

- A 10-degree rise often makes a reaction about 2–3 times faster. Exact doubling is a rough example, not a law. At the same T and equal A, larger Ea means smaller k. Ea is often treated as constant over a limited temperature range; a large temperature change or a new mechanism can invalidate this approximation.