Course Companion

AP Chemistry

Every topic handout in one volume

exercises.lol

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Atomic Structure and Properties

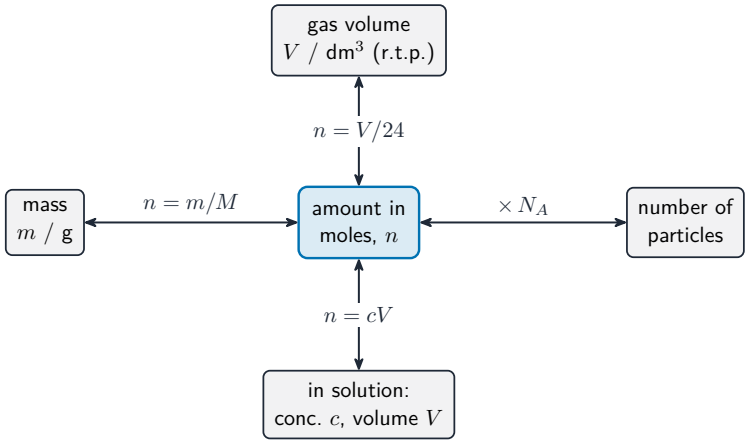
AP Chemistry

Moles and Molar Mass

Because atoms are far too small to count, chemists count in **moles** . One mole is **Avogadro's number** of particles, $N_A = 6.022 \times 10^{23}$. The **molar mass** (grams per mole, read off the periodic table) converts between mass and moles:

$$n = \frac{m}{M}.$$

Moles are the bridge between the lab (grams you weigh) and the equation (particles that react).



The mole is the hub: convert between mass, particles, gas volume, and concentration

Worked example. How many moles, and how many molecules, are in 36.0 g of water ($M = 18.0$ g/mol)?

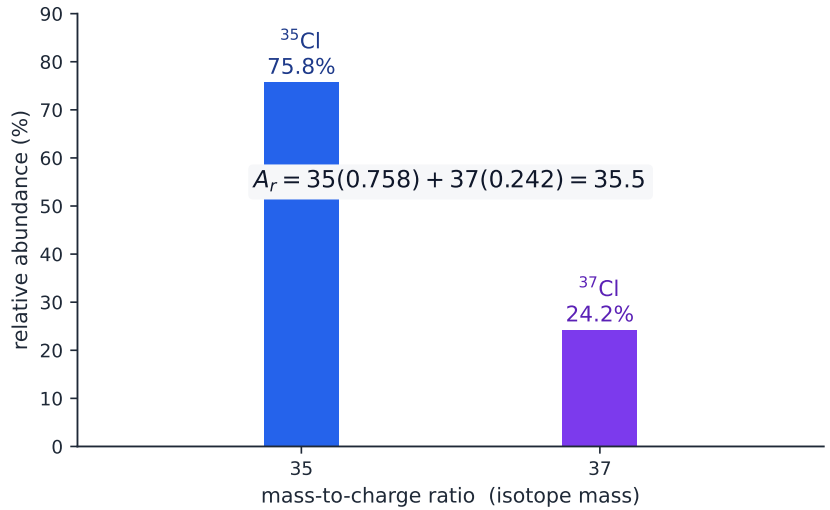
$$n = \frac{m}{M} = \frac{36.0}{18.0} = 2.0 \text{ mol}, \qquad N = n\,N_A = 2.0 \times 6.022 \times 10^{23} = 1.2 \times 10^{24} \text{ molecules}.$$

Mass Spectra of Elements

A **mass spectrometer** separates atoms by mass, giving a **mass spectrum** : peaks at each **isotope** (same element, different neutron count) with heights showing their **relative abundance** . The element's average **atomic mass** is the abundance-weighted average of its isotope masses.

$$A_r = \frac{(75 \times 35) + (25 \times 37)}{100} = 35.5$$

Relative atomic mass is the abundance-weighted average of the isotopes



The mass spectrum of chlorine: two isotopes with different abundances

Worked example. Chlorine is 75.8% chlorine-35 and 24.2% chlorine-37. Its average atomic mass is

$$A_r = (35)(0.758) + (37)(0.242) = 26.5 + 8.95 = 35.5.$$

The average lies closer to 35 because that isotope is more abundant – which is why the periodic-table value is 35.5, not a whole number.

Elemental Composition of Pure Substances

The **percent composition** of a compound is each element's mass fraction. From it you find the **empirical formula** (simplest whole-number ratio of atoms) by converting each element's mass to moles and dividing by the smallest. The **molecular formula** is a whole-number multiple of the empirical formula, found from the molar mass.

element	% by mass	$\div A_r \to$ moles	$\div$ smallest (3.33)	ratio
C	40.0	$40.0/12 = 3.33$	1.0	1
H	6.7	$6.7/1 = 6.7$	2.0	2
O	53.3	$53.3/16 = 3.33$	1.0	1

empirical formula CH_2O - if $M_r = 180$, it fits $180/30 = 6$ times: molecular formula $C_6H_{12}O_6$

Finding the empirical formula: mass to moles, divide by the smallest, read the ratio

Worked example. A compound is 40.0% C, 6.7% H, and 53.3% O by mass. Assuming 100 g, convert each mass to moles and divide by the smallest:

$$\mathrm{C} : \frac{40.0}{12} = 3.33, \quad \mathrm{H} : \frac{6.7}{1} = 6.7, \quad \mathrm{O} : \frac{53.3}{16} = 3.33 \xrightarrow{\div 3.33} 1 : 2 : 1,$$

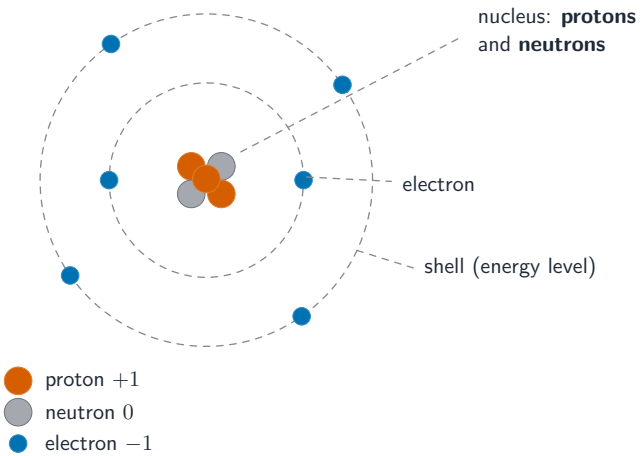
so the empirical formula is CH_2O. If the molar mass were 180 g/mol ($= 6 \times 30$), the molecular formula would be $C_6H_{12}O_6$ – glucose.

Composition of Mixtures

Unlike a pure compound, a **mixture** has variable composition – its parts keep their own identities. Describe a mixture by the mass or mole fraction of each component; these do not follow a fixed formula. Spectroscopy (like PES or absorption) can measure how much of each component is present.

Atomic Structure and Electron Configuration

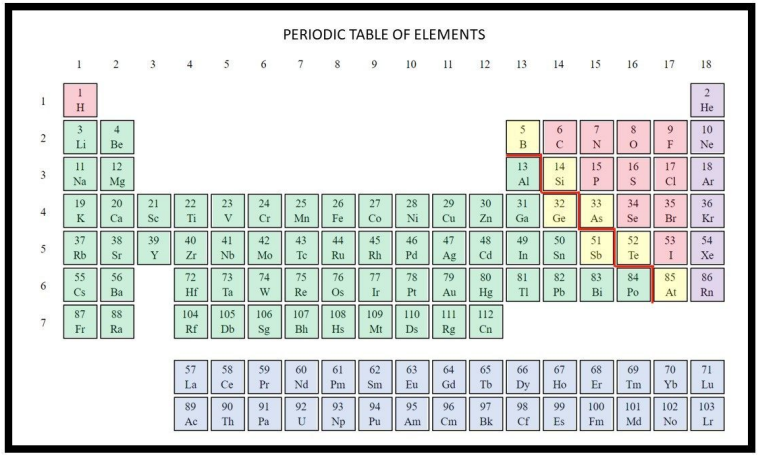
An atom is a tiny **nucleus** (protons and neutrons) surrounded by electrons in **shells** and **subshells** (s, p, d, f). The **electron configuration** lists how electrons fill these, lowest energy first (e.g. $1s^2\,2s^2\,2p^6$). The outermost, highest-energy electrons – the **valence electrons** – control chemistry. **Coulomb's law** explains their energies: electrons closer to, and less shielded from, the nucleus are held more tightly.



An atom: a tiny nucleus of protons and neutrons, with electrons in shells

Flame tests: each metal ion gives its own colour because heat excites its electrons and, as they drop back down, they emit light of specific wavelengths

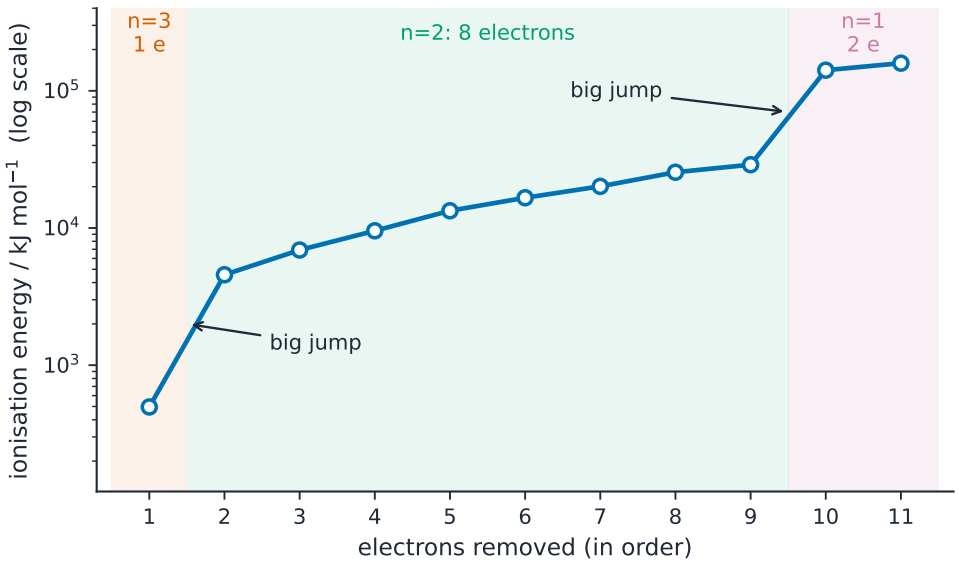
Worked example. Write the electron configuration of sulfur ($Z = 16$). Fill subshells in order until 16 electrons are placed: $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$. The $3s$ and $3p$ electrons (six in total) are the valence electrons, so sulfur tends to gain two electrons to complete its octet.



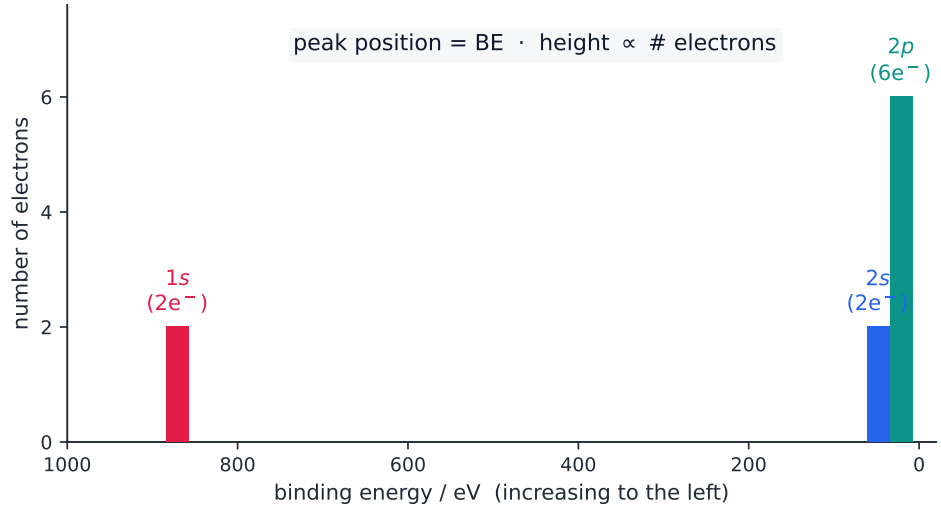
The periodic table organises elements by atomic structure — electron configuration explains the patterns

Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) measures the energy needed to remove electrons from each subshell. Each peak is a subshell: its **position** gives the binding energy (how tightly held) and its **height** gives the number of electrons in it. PES data let you read an element's electron configuration and confirm shell structure directly.



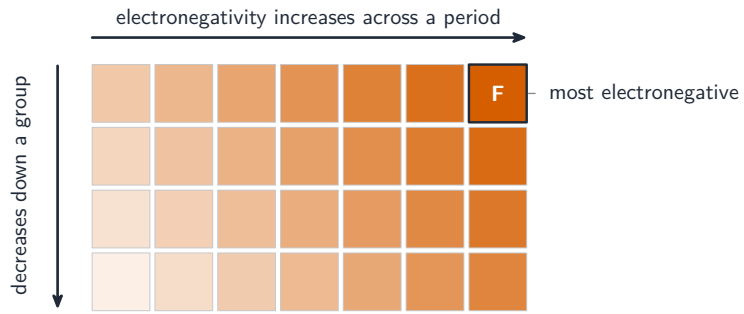
Successive ionisation energies reveal the shell structure through big jumps



The photoelectron spectrum of neon: one peak per subshell, height set by electron count

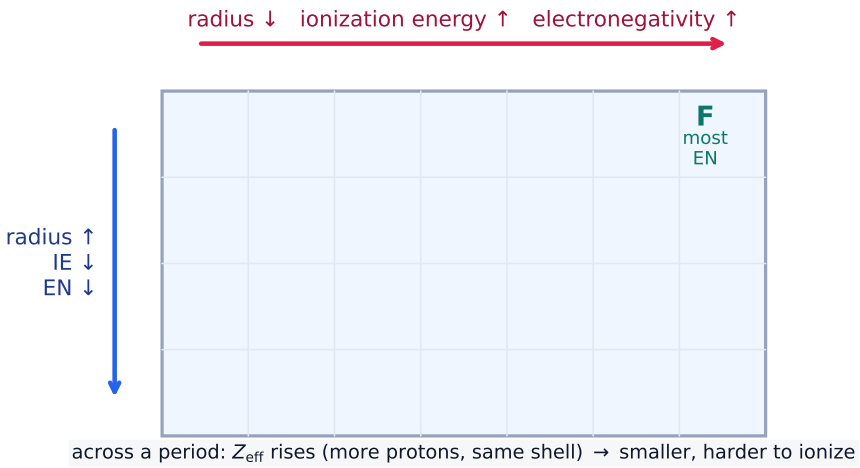
Periodic Trends

Trends across the periodic table follow from **nuclear charge** and **shielding**:



Electronegativity rises across a period and falls down a group

- **Atomic radius** decreases across a period (stronger pull) and increases down a group (more shells).
- **Ionization energy** (energy to remove an electron) increases across, decreases down – opposite to radius.
- **Electronegativity** (pull on shared electrons) increases across and up, toward fluorine.



Periodic trends: how radius, ionization energy, and electronegativity change across and down

Valence Electrons and Ionic Compounds

Atoms gain, lose, or share **valence electrons** to reach stable configurations. Metals (low ionization energy) lose electrons to form **cations** ; nonmetals gain electrons to form **anions** . Oppositely charged ions attract into an **ionic compound** , whose formula balances the charges to make the whole neutral. For example, aluminium (3+) and oxide (2−) combine as Al_2O_3 so the +6 and −6 cancel.

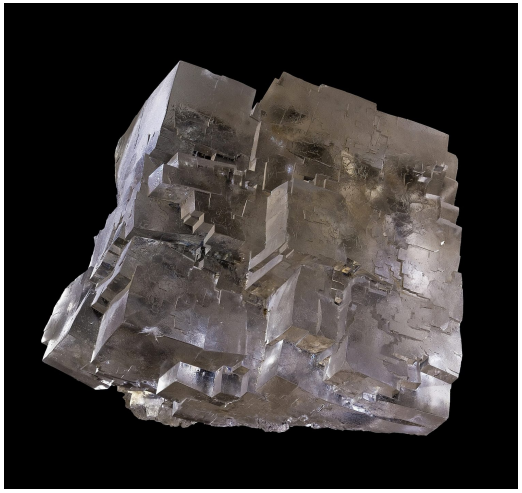
Exam tips

- Use the mole as the hub: convert grams↔moles with $n = m/M$ and moles↔particles with Avogadro's number.
- Relative atomic mass is the **abundance-weighted average** of the isotopes — it lies closer to the more abundant one, not halfway.
- For an **empirical formula**, turn each element's mass into moles and divide by the smallest; scale up to whole numbers.
- Read **periodic trends** from nuclear charge and shielding: atomic radius decreases across a period, ionisation energy and electronegativity increase across (and up).
- Fill electron configurations in energy order; the outer **valence electrons** control the chemistry.

Compound Structure and Properties

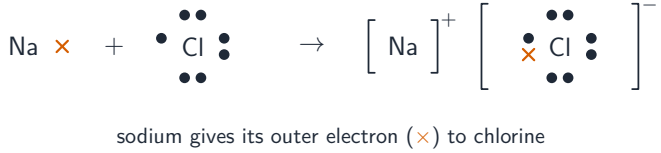
AP Chemistry

Types of Chemical Bonds



Sodium chloride crystals: ionic solids form a lattice of oppositely charged ions

A **chemical bond** is an attraction that holds atoms together. Which type forms depends on the atoms' electronegativities:



Ionic bonding: a metal transfers its outer electrons to a non-metal

- **Ionic bond** : electrons transfer from a metal to a nonmetal (large electronegativity difference).
- **Covalent bond** : nonmetals **share** electrons (small difference). A big-but-not-huge difference gives a **polar covalent** bond.
- **Metallic bond** : metal atoms share a "sea" of mobile electrons.

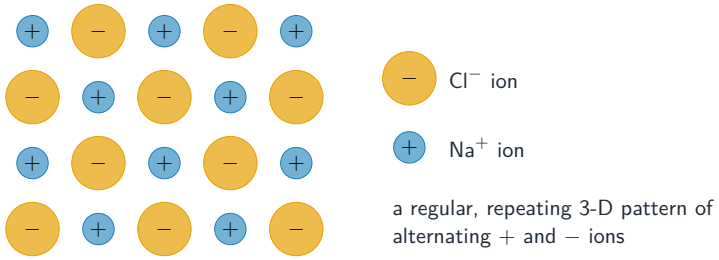
A diamond crystal: giant covalent networks explain extreme hardness and high melting points

Intramolecular Force and Potential Energy

As two atoms approach, a **potential energy** curve captures the balance of attraction and repulsion. It dips to a minimum at the **bond length** (the stable separation) whose depth is the **bond energy** . Shorter, stronger bonds sit in deeper, tighter wells; more shared pairs (double, triple bonds) give shorter, stronger bonds.

Structure of Ionic Solids

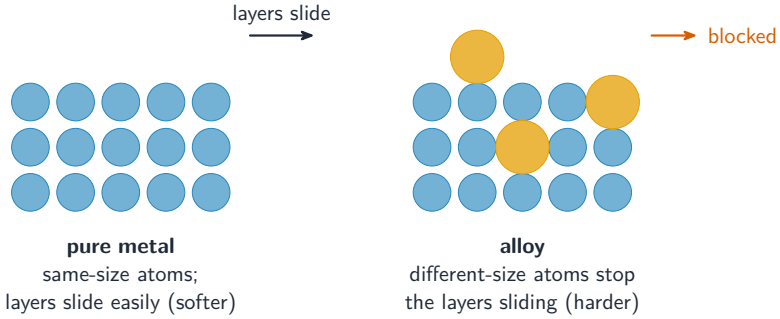
An **ionic solid** is a repeating 3-D **lattice** of alternating cations and anions, held by strong electrostatic attraction. This explains their high melting points, brittleness, and why they conduct only when molten or dissolved (ions freed to move). The **lattice energy** rises with larger ion charges and smaller ions, so MgO (both $2+/2-$) melts far higher than NaCl (both $1+/1-$).



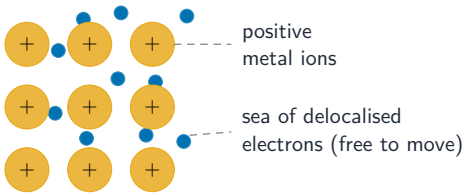
Ions pack into a giant lattice of alternating positive and negative ions

Structure of Metals and Alloys

In a metal, cations sit in a lattice bathed in **delocalized** electrons, which explains conductivity, malleability, and luster. An **alloy** mixes metals: a **substitutional** alloy swaps in similar-sized atoms; an **interstitial** alloy (like steel) fits small atoms into the gaps, making it harder.



Different-sized atoms in an alloy stop the layers sliding, so it is harder

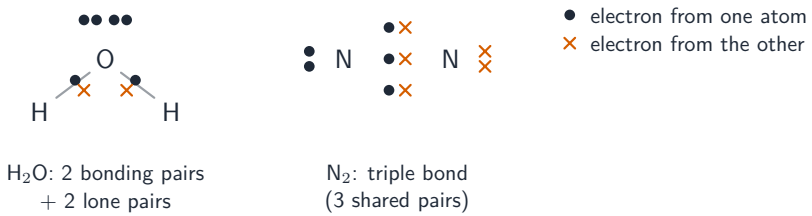


Metallic bonding: positive ions in a sea of delocalised electrons

Native copper: metallic bonding gives a shiny, malleable solid with delocalised electrons

Lewis Diagrams

A **Lewis diagram** shows valence electrons as bonding pairs and **lone pairs**, giving most atoms an **octet** (8 valence electrons; H wants 2). Steps: count total valence electrons, connect atoms with single bonds, complete octets on outer atoms, then form multiple bonds if the central atom is short.



Dot-and-cross diagrams show the bonding pairs and lone pairs in a molecule

Worked example. Draw carbon dioxide, CO_2. Total valence electrons $= 4 + 2(6) = 16$. Put C in the centre; single bonds to each O use 4 electrons and leave the outer O atoms short. Completing octets forces two **double** bonds, O = C = O: each O then has two lone pairs, C has none, and all 16 electrons are placed with every atom at an octet.

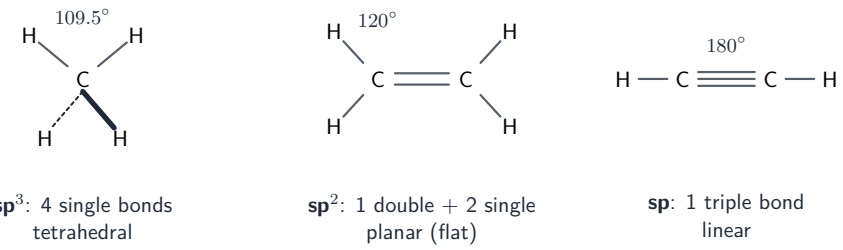
Resonance and Formal Charge

When two or more valid Lewis diagrams differ only in electron placement, the true structure is an average – **resonance**. **Formal charge** (valence electrons minus lone-pair electrons minus half the bonding electrons) picks the best structure: the one with formal charges closest to zero, and any negative charge on the most electronegative atom.

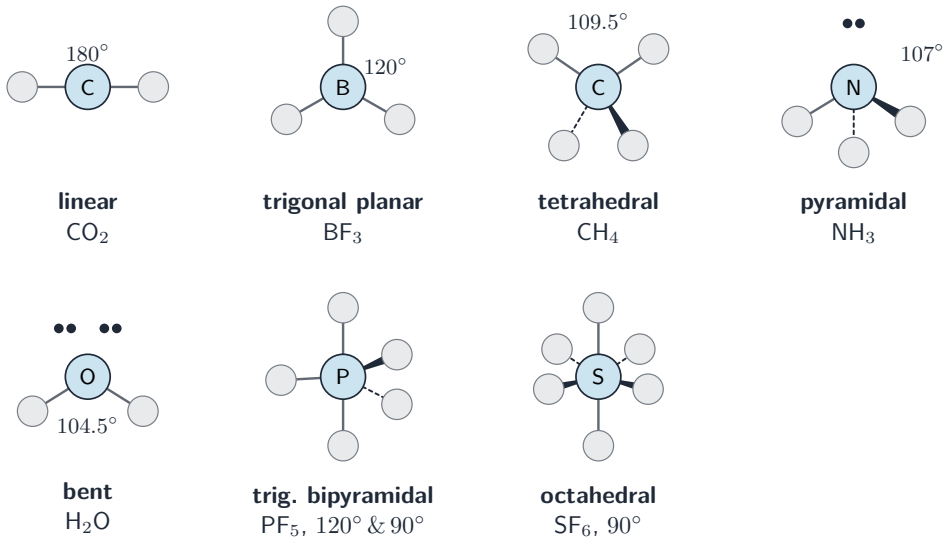
Worked example. Assign formal charges in the nitrate ion, NO_3^- (one double bond, two single bonds). For N (4 bonds, no lone pairs): $5 - 0 - 4 = +1$. For the double-bonded O (2 lone pairs): $6 - 4 - 2 = 0$. For each single-bonded O (3 lone pairs): $6 - 6 - 1 = -1$. The total is $+1 + 0 + (-1) + (-1) = -1$, matching the ion's overall charge – a good check that the structure is drawn correctly. Because the three O atoms are equivalent by resonance, the real ion has three identical bonds.

VSEPR and Bond Hybridization

VSEPR theory predicts shape: electron pairs (bonds and lone pairs) around a central atom spread out as far apart as possible. Counting electron domains gives the geometry (linear, trigonal planar, tetrahedral, …); lone pairs push bonds closer, bending the shape. **Hybridization** (sp, sp^2, sp^3) describes the mixed orbitals matching that geometry. Molecular shape and bond polarity together decide whether the whole molecule is polar.



Hybridisation and shape: sp3 tetrahedral, sp2 planar, sp linear



The common VSEPR shapes and their bond angles

Worked example. Predict the shape of ammonia, NH_3. Nitrogen has 3 bonding pairs and 1 lone pair – four electron domains, so the electron geometry is tetrahedral

and the hybridization is sp^3. The lone pair is invisible in the shape but still pushes the bonds together, so the **molecular** shape is trigonal pyramidal with a bond angle of about 107° (a little less than the ideal 109.5°). The three N–H dipoles do not cancel, so the molecule is polar.

Bonds form when atomic orbitals **overlap**. Every single bond is one **sigma bond** σ – orbitals overlapping head-on along the line joining the two atoms. A multiple bond adds a **pi bond** π, made by p orbitals overlapping sideways above and below that line: a double bond is one sigma + one pi, a triple bond one sigma + two pi. Head-on overlap is more effective, so a sigma bond is **stronger** (higher bond energy) than a pi bond – which is why a double bond is stronger than a single bond but not twice as strong. A pi bond also **locks the two atoms** so they cannot rotate about the bond; a C=C double bond therefore has fixed **cis** and **trans** forms – **geometric isomers** that a freely-rotating single bond could never show.

Worked example. Count the bonds in ethene, $H_2C = CH_2$. The four C–H bonds are single bonds (one sigma each); the C=C is one sigma plus one pi. So ethene has **5 sigma and 1 pi** bond, and that single pi bond is exactly what stops the two CH_2 ends from twisting relative to each other.

Exam tips

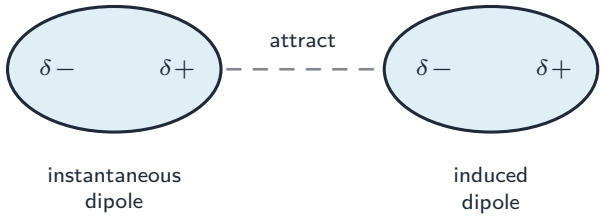
- Decide the bond type from the atoms: **ionic** (metal + non-metal, electron transfer), **covalent** (non-metals, sharing), **metallic** (sea of delocalised electrons).
- An ionic solid conducts only when **molten or dissolved** (ions free to move), never as a solid.
- Draw **Lewis structures** to satisfy the octet (H wants 2), then use **VSEPR** — electron pairs spread as far apart as possible — to predict the shape.
- **Lone pairs** take up space and push bonds closer, bending the shape (water is bent, ammonia pyramidal).
- A molecule can have polar bonds yet be **non-polar overall** if its symmetry makes the dipoles cancel (CO_2).
- A single bond is 1 **sigma** bond; a double bond is 1 sigma + 1 **pi**, a triple bond 1 sigma + 2 pi. Sigma is stronger than pi, and a pi bond blocks rotation, giving cis/trans **geometric isomers**.

Properties of Substances and Mixtures

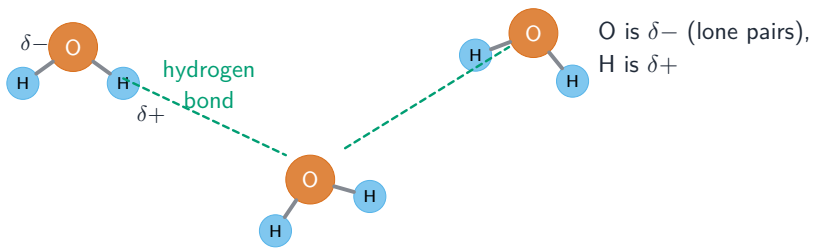
AP Chemistry

Intermolecular and Interparticle Forces

Intermolecular forces (IMFs) are attractions **between** molecules – much weaker than bonds, but they set melting/boiling points. From weakest to strongest:



London dispersion: an instantaneous dipole induces a dipole in a neighbour



Hydrogen bonding: an H on N/O/F is attracted to a lone pair on another molecule

- **London dispersion forces**: present in *all* molecules; they arise from Coulombic attraction between **temporary, fluctuating dipoles**, and are stronger for larger, more polarizable electron clouds - often the strongest net force between large molecules.
- **Dipole–dipole** - : between polar molecules. Their strength depends on the size of the dipoles **and their relative orientation** - a $\delta+$ end lining up with a neighbour's $\delta-$ end attracts, so these act *in addition* to dispersion and make polar molecules stickier than nonpolar ones of similar size.
- **Hydrogen bonding**: a strong dipole force when H is bonded to N, O, or F.

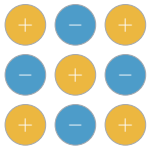
- **Ion–dipole** - : between an **ion** and a polar molecule (the ion pulls on the oppositely-charged end of the dipole). These are the **strongest** of the four here (stronger even than hydrogen bonds), and are exactly what lets water dissolve an ionic solid - each Na^+ is surrounded by the $\delta-$ oxygen ends of water molecules.

The whole ladder is understood **qualitatively** by looking at the **sign of the partial charges**: a larger or better-aligned partial charge, or a full ionic charge, gives a stronger attraction. Stronger IMFs mean higher boiling points and lower vapor pressure. This is why water (18 g/mol, hydrogen-bonded) boils at 100 °C while methane (16 g/mol, dispersion only) boils at −162 °C.

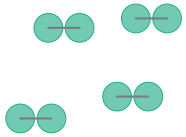
Properties of Solids

A solid's properties reflect the particles and forces holding it: **ionic**, **covalent-network** (a 3D network like diamond, very hard and high-melting; **graphite** is a layered exception — high-melting but soft, because its 2D layers slide over one another), **metallic**, and **molecular** solids (held by weak IMFs, soft, low-melting). Matching a solid's properties to its structure is a common exam task.

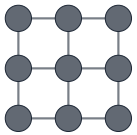
Metallic solids conduct electricity and heat and are **malleable** and **ductile**, all because their **free valence electrons** move easily and let the metal ions slide past one another without breaking the bonding. Solids are also either **crystalline** (particles in a regular, repeating 3-D arrangement) or **amorphous** (no long-range order, like glass).



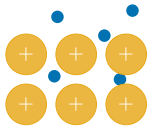
giant ionic
NaCl: high m.p.,
conducts when molten



simple molecular
I_2, ice: low m.p.,
weak forces between



giant covalent
diamond, SiO_2: very
high m.p., insulating

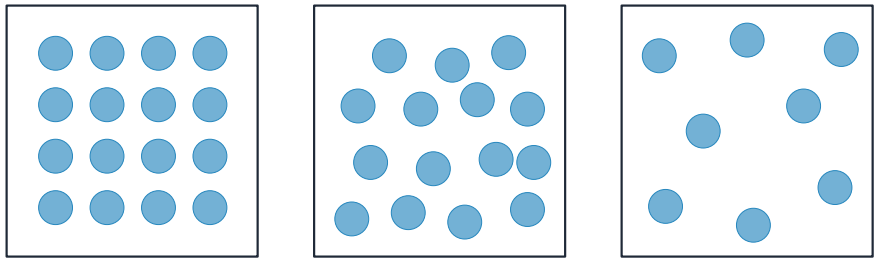


giant metallic
copper: high m.p.,
conducts (solid + molten)

The four solid structures: giant ionic, simple molecular, giant covalent, and metallic

Solids, Liquids, and Gases

The three states differ in how tightly particles are held. Rising **temperature** raises average kinetic energy; when it overcomes the attractions, the substance melts or boils. Gases are mostly empty space, so they are compressible and fill their container.



solid
regular, touching
vibrate in place

liquid
close, random
slide past each other

gas
far apart, random
move fast

Particles are packed in a solid, close but mobile in a liquid, and far apart in a gas

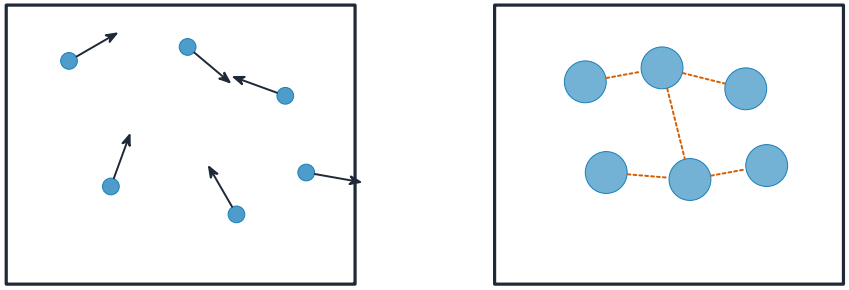
Steam rising from boiling water: gases expand to fill space and obey the ideal gas law at high T and low P

The Ideal Gas Law

An **ideal gas** obeys

$$PV = nRT,$$

linking pressure, volume, moles, and absolute temperature. Use it to find any one quantity from the others, or (holding some constant) to predict how a gas responds to a change.



ideal gas (model)
point particles, *no* forces

real gas: high p, low T
real size + attractions (dashed)

An ideal gas is a model of point particles with no forces between them

Worked example. How many moles of gas fill a 2.0 L container at 300 K and

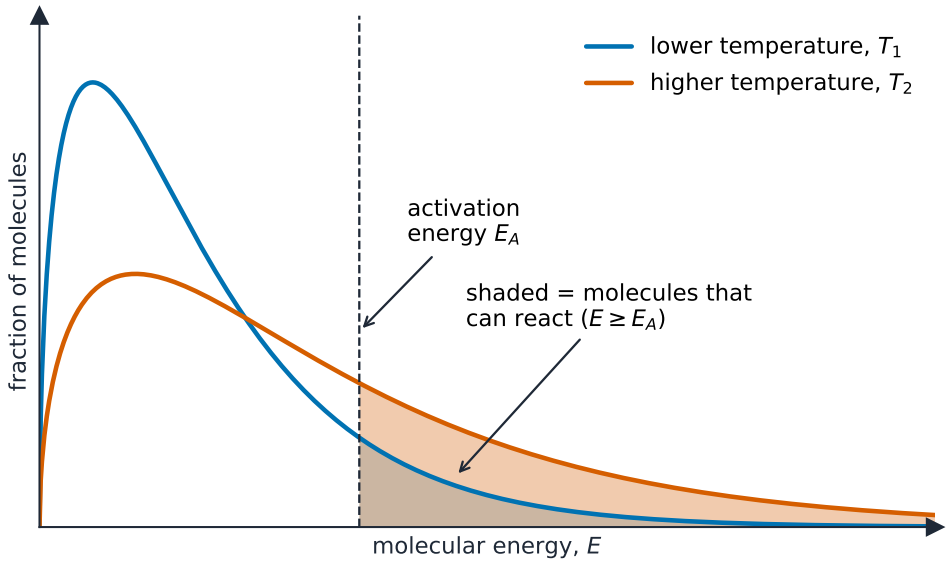
1.5 atm? Using $R = 0.0821$ L atm/(mol K),

$$n = \frac{PV}{RT} = \frac{1.5 \times 2.0}{0.0821 \times 300} = 0.12 \text{ mol.}$$

Always use **kelvin** for T and match the units of R to your pressure and volume.

Kinetic Molecular Theory

Kinetic molecular theory explains gas behavior: particles are tiny, in constant random motion, with negligible volume and no attractions, and collisions are elastic. **Temperature** is proportional to average kinetic energy, so at a given temperature lighter molecules move faster (Graham's law of effusion).



The Maxwell-Boltzmann distribution of molecular speeds shifts right when heated

Deviation from the Ideal Gas Law

Real gases deviate from ideal behavior at **high pressure** and **low temperature**, where molecules are close enough that their real volume and their attractions matter. Attractions lower the pressure below ideal; molecular volume raises it.

Solutions and Mixtures

A **solution** is a homogeneous mixture of a **solute** dissolved in a **solvent**. Concentration is usually **molarity**:

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}.$$

Dilution conserves moles: $M_1V_1 = M_2V_2$.

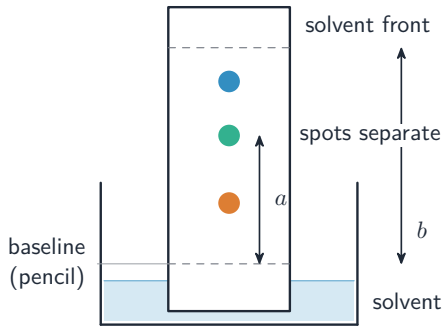
Worked example. What volume of water must you add to 50 mL of 6.0 M HCl to make it 2.0 M? The moles of HCl are unchanged, so $M_1V_1 = M_2V_2$ gives the final volume $V_2 = \frac{M_1V_1}{M_2} = \frac{6.0 \times 50}{2.0} = 150$ mL. You therefore **add** $150 - 50 = 100$ mL of water.

Representations of Solutions

A **particulate diagram** shows the solute and solvent particles. For an ionic solute, show it fully **dissociated** into separate ions surrounded by solvent; count particles to reason about concentration and conductivity.

Separation of Solutions and Mixtures

Because a mixture's components keep their properties, physical methods separate them: **filtration** (by particle size), **distillation** (by boiling point), and **chromatography** (by how strongly each component sticks to a stationary phase versus moving with a solvent).



$$R_f = \frac{a}{b} = \frac{\text{spot}}{\text{solvent}}$$

Paper chromatography separates a mixture as the solvent rises up the paper

Solubility

Solubility is how much solute dissolves. "Like dissolves like": polar (and ionic) solutes dissolve in polar solvents; nonpolar in nonpolar. Dissolving happens when solute–solvent attractions are comparable to the attractions being broken.

Blue copper(II) sulfate crystals grown from solution: a saturated solution left to evaporate deposits its dissolved solid back out as regular crystals

Spectroscopy and the Electromagnetic Spectrum

Spectroscopy studies how matter absorbs or emits light. Different regions of the **electromagnetic spectrum** probe different changes: microwaves (rotation), infrared (bond vibrations), ultraviolet–visible (electron transitions). The light absorbed reveals structure.

Properties of Photons

Light is carried by **photons**, each with energy $E = h\nu = \dfrac{hc}{\lambda}$. Higher frequency (shorter wavelength) means higher energy. A molecule absorbs a photon only when its energy matches an allowed energy gap.

The Beer-Lambert Law

The **Beer–Lambert law** - relates how much light a solution absorbs to its concentration:

$$A = \varepsilon\, b\, c,$$

where A is absorbance, ε the molar absorptivity, b the path length, and c the concentration. Since A is proportional to c, measuring absorbance is a fast way to find an unknown concentration.

Worked example. A dye has molar absorptivity $\varepsilon = 2000$ L/(mol cm); in a 1.0 cm cell a sample reads absorbance $A = 0.40$. Its concentration is $c = \dfrac{A}{\varepsilon b} = \dfrac{0.40}{2000 \times 1.0} = 2.0 \times 10^{-4}$ M. Because $A \propto c$, a solution twice as concentrated would read $A = 0.80$ – the basis of a calibration curve.

Exam tips

- **Intermolecular forces** (dispersion < dipole–dipole < hydrogen bonding) set boiling points — they are much weaker than the bonds inside a molecule.
- Boiling breaks the forces **between** molecules, not the covalent bonds within them.
- Use $PV = nRT$ with temperature in **kelvin** and R matched to your pressure/volume units.
- For solutions use molarity M = mol/L; dilution conserves moles, so $M_1V_1 = M_2V_2$.
- "Like dissolves like" — polar/ionic solutes dissolve in polar solvents, non-polar in non-polar.

Chemical Reactions

AP Chemistry

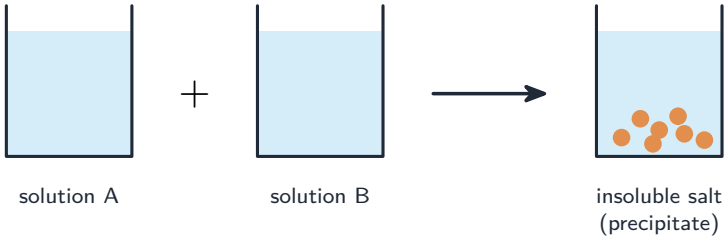
Recognizing a Chemical Reaction

Magnesium burning: a chemical reaction rearranges atoms and releases energy as light and heat

A **chemical reaction** rearranges atoms into new substances. Signs one has happened: a color change, a gas or **precipitate** forming, or a temperature change. Atoms are conserved, so an equation must be **balanced** – the same count of each element on both sides.

Net Ionic Equations

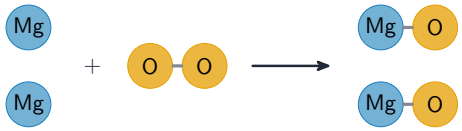
For reactions in water, ionic compounds split into ions. A **net ionic equation** shows only the species that actually change, leaving out the **spectator ions** that appear unchanged on both sides. It captures the real chemistry (e.g. $Ag^+ + Cl^- \rightarrow AgCl(s)$).



Mixing two solutions can form an insoluble precipitate

Three Ways to Represent a Reaction

The same reaction can be shown as a **symbolic** equation, a **particulate** drawing (atoms and molecules), and a **macroscopic** observation (what you see). Moving between these levels – connecting the equation to the particles to the beaker – is a core skill.



$2Mg + O_2 \rightarrow 2MgO$

2 Mg and 2 O on each side: balanced

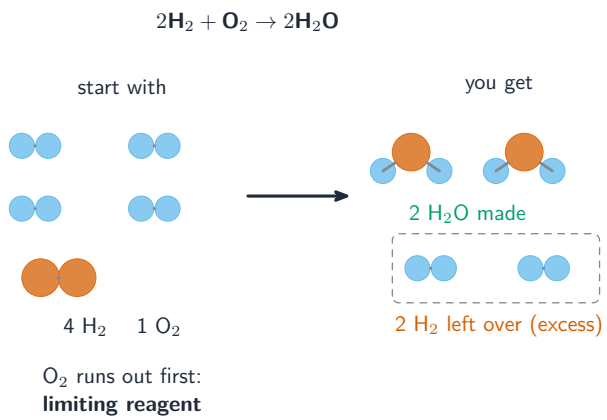
A balanced equation has the same number of each atom on both sides

Physical Changes versus Chemical Changes

A **physical change** alters form but not identity (melting, dissolving); a **chemical change** makes new substances by breaking and forming bonds. Dissolving salt is physical; the salt is unchanged and recoverable.

Stoichiometry

Stoichiometry uses the balanced equation's mole ratios to relate amounts of reactants and products. The path is always grams → moles → (mole ratio) → moles → grams. The **limiting reactant** runs out first and sets the maximum product (the **theoretical yield**); the **percent yield** compares actual to theoretical.



The limiting reactant runs out first and decides how much product forms

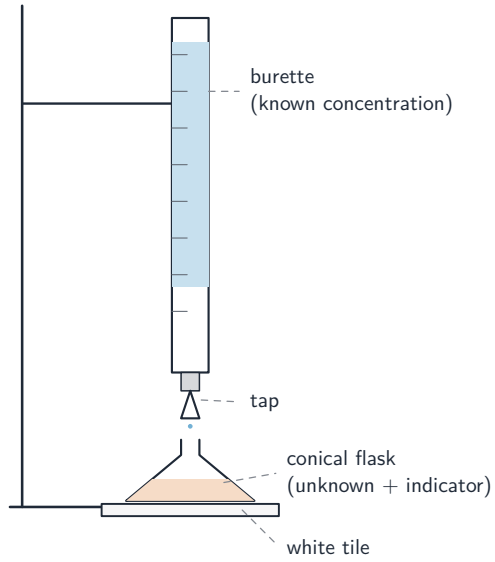
Worked example. How much water forms when 4.0 g of hydrogen burns in excess oxygen? $2H_2 + O_2 \rightarrow 2H_2O$. Convert to moles, cross the mole ratio ($2 : 2 = 1 : 1$ here), convert back:

$$n(H_2) = \frac{4.0}{2.0} = 2.0 \text{ mol} \;\Rightarrow\; n(H_2O) = 2.0 \text{ mol} \;\Rightarrow\; m = 2.0 \times 18 = 36 \text{ g}.$$

Worked example (limiting reactant). 10.0 g of N_2 reacts with 5.0 g of H_2 ($N_2 + 3H_2 \rightarrow 2NH_3$). Which runs out? Moles: $n(N_2) = 10.0/28 = 0.36$, $n(H_2) = 5.0/2 = 2.5$. The reaction needs 3 H_2 per N_2; you have $2.5/0.36 = 7.0$, far more than 3, so **N_2 is limiting**. It makes $2 \times 0.36 = 0.72$ mol of ammonia, with hydrogen left over.

Introduction to Titration

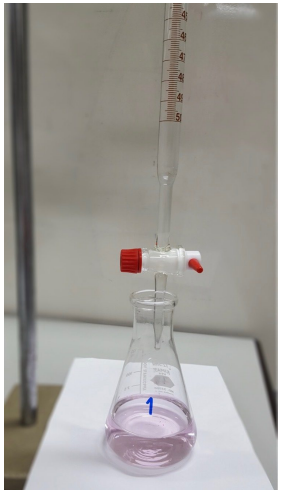
A **titration** finds an unknown concentration by reacting it with a solution of known concentration until they reach the **equivalence point** (stoichiometrically equal). From the known volume and concentration, use the mole ratio to find the unknown. An **indicator** or a pH curve signals the endpoint.



Titration apparatus: a burette delivers a known solution into a conical flask

Worked example. 25.0 mL of hydrochloric acid is exactly neutralized by 30.0 mL of 0.100 M NaOH. Find the acid's concentration. The reaction is $1 : 1$, so the moles match:

$$n(\text{NaOH}) = 0.0300 \times 0.100 = 3.00 \times 10^{-3} \text{ mol} = n(\text{HCl}), \qquad [\text{HCl}] = \frac{3.00 \times 10^{-3}}{0.0250} = 0.120 \text{ M}.$$



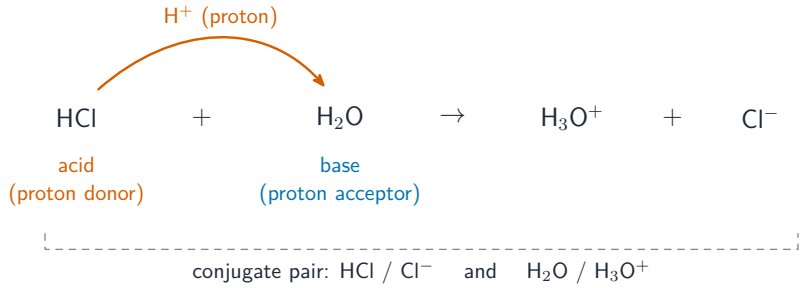
A titration setup: reacting volumes from a burette find the concentration of an unknown solution

Types of Chemical Reactions

Common patterns include **synthesis** (combining), **decomposition** (breaking apart), **combustion** (with oxygen, releasing energy), **precipitation** (forming an insoluble solid), **acid–base** (proton transfer), and **redox** (electron transfer). Recognizing the type helps predict the products.

Acid-Base Reactions

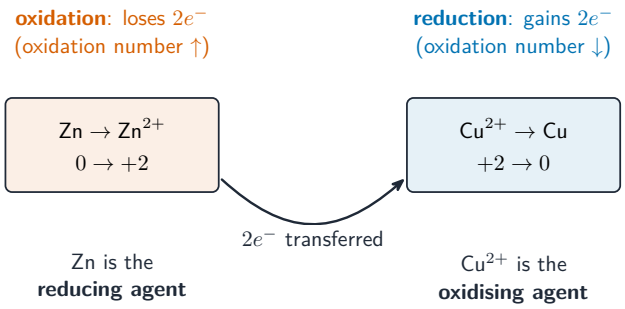
An **acid** donates a proton (H^+); a **base** accepts one (Brønsted–Lowry). They react to form water and a salt: $H^+ + OH^- \rightarrow H_2O$. Strong acids and bases dissociate completely; weak ones only partly.



Bronsted-Lowry: an acid donates a proton to a base, forming two conjugate pairs

Oxidation-Reduction (Redox) Reactions

In a **redox** reaction, electrons transfer between species. **Oxidation** is loss of electrons (oxidation number rises); **reduction** is gain (oxidation number falls). Track changes with **oxidation numbers**, and remember every oxidation is paired with a reduction – the electrons lost equal the electrons gained.



Redox is electron transfer: the reducing agent is oxidised, the oxidising agent reduced

Worked example. Find the oxidation number of manganese in permanganate, $KMnO_4$. Potassium is $+1$ and each oxygen is -2 (four of them, -8). The whole formula is neutral, so $(+1) + \text{Mn} + (-8) = 0$, giving $\text{Mn} = +7$ – its maximum, which is why permanganate is a powerful oxidizing agent (it can only gain electrons).

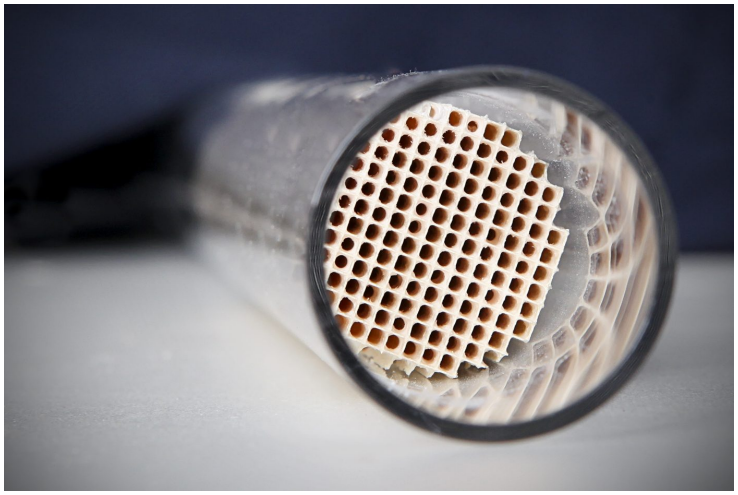
Exam tips

- Balance every equation and work in **moles** — convert grams→moles, cross the mole ratio, then convert back.
- Find the **limiting reactant** by comparing mole ratios; it sets the maximum product (theoretical yield).
- In redox, remember **OIL RIG**: oxidation is loss of electrons, reduction is gain; every oxidation is paired with a reduction.
- For titrations use the balanced ratio to link the known and unknown at the **equivalence point**.
- A **net ionic equation** shows only the species that change; leave out spectator ions.

Kinetics

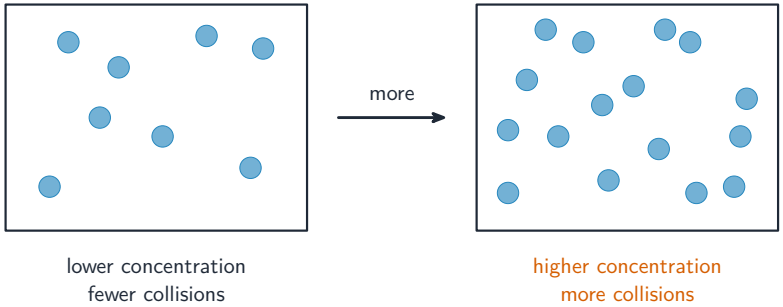
AP Chemistry

How Fast a Reaction Goes



A catalytic converter: catalysts speed rates by lowering activation energy without being consumed

Kinetics studies **reaction rate** – how fast reactants become products. Rate is the change in concentration per unit time, and it typically **decreases** as reactants are used up. Rate rises with higher concentration, higher temperature, greater surface area, and a catalyst.



More particles in the same volume collide more often, so the rate rises

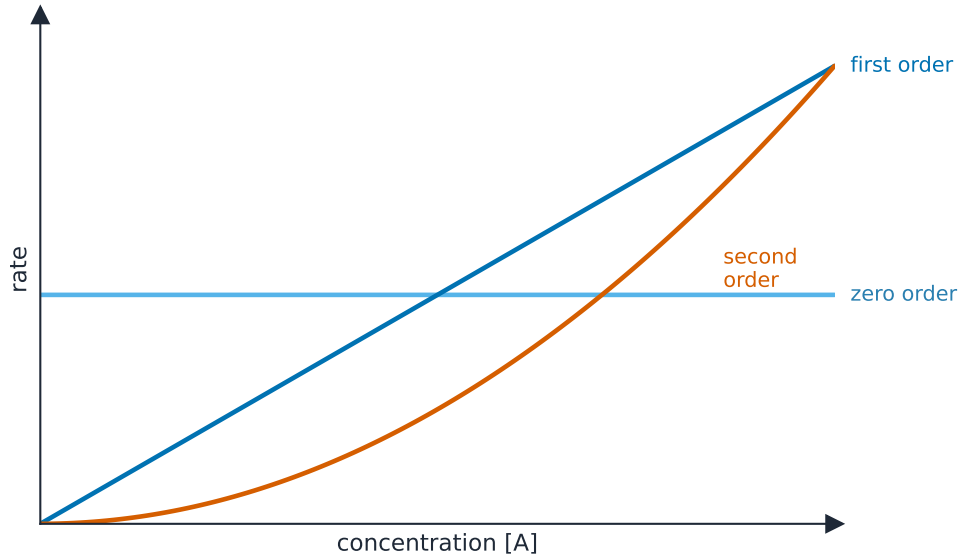
A gas syringe: measuring gas volume over time gives reaction rate from the slope

Writing the Rate Law

The **rate law** relates rate to reactant concentrations:

$$\text{rate} = k[\text{A}]^m[\text{B}]^n,$$

where k is the **rate constant** and m, n are the **orders**. Orders are found **experimentally** (not from the balanced coefficients) by seeing how the rate changes when you change one concentration at a time.

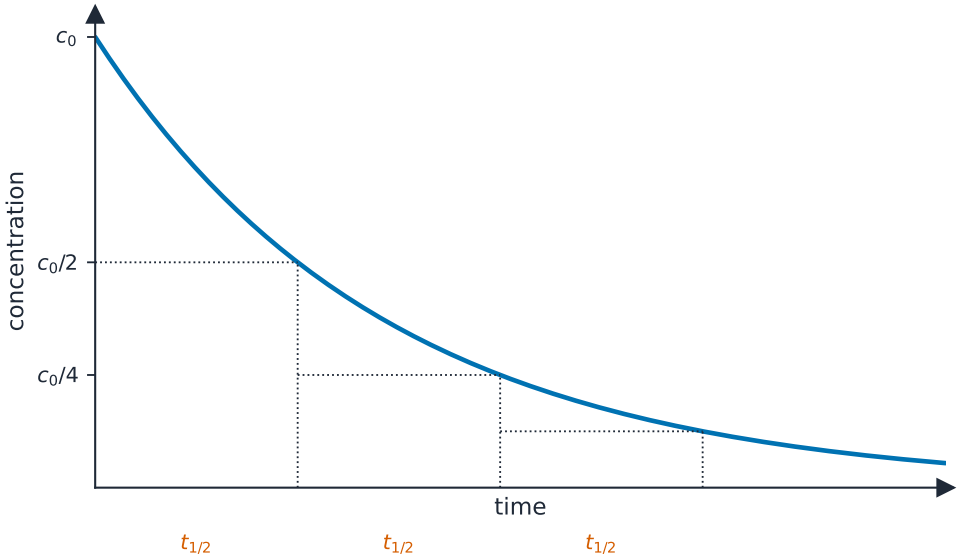


Rate against concentration for zero-, first-, and second-order reactions

Worked example. In experiments, doubling [A] makes the rate **four times** larger, while doubling [B] leaves the rate unchanged. So the reaction is **second order** in A ($2^2 = 4$) and **zero order** in B, giving rate $= k[\text{A}]^2$. The overall order is $2 + 0 = 2$. Never read the orders off the balanced coefficients – only experiment gives them.

Concentration Over Time

The **integrated rate laws** describe how concentration falls with time and give straight-line tests:



A first-order reaction has a constant half-life

- **Zero order:** [A] vs t is linear.
- **First order:** ln[A] vs t is linear; constant **half-life** .
- **Second order:** $\frac{1}{[A]}$ vs t is linear.

Whichever plot is straight tells you the order and gives k from its slope.

Worked example. A first-order reaction has rate constant $k = 0.030\ \text{s}^{-1}$. Its half-life is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.030} = 23\ \text{s},$$

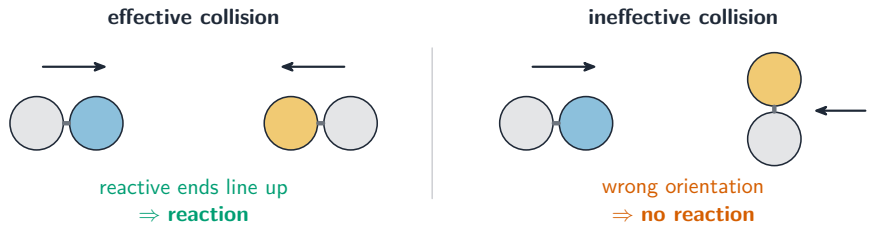
and, being first order, that half-life stays the same no matter how much reactant remains – so after 46 s (2 half-lives) one quarter is left.

The Steps a Reaction Really Takes

A **reaction mechanism** is the sequence of **elementary steps** that actually occur. Their **molecularity** (how many particles collide in a step) sets that step's rate law directly. Species made in one step and used up in a later one are **intermediates** .

Why Collisions Do or Do Not React

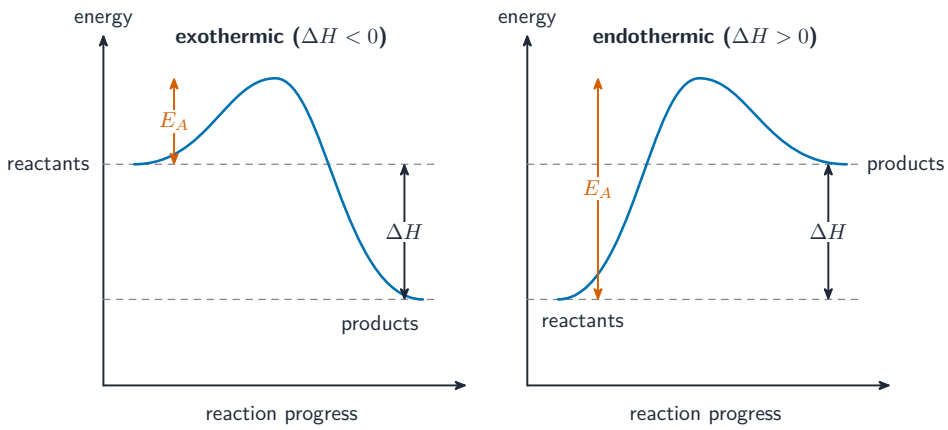
Collision theory : molecules must collide with enough energy (the **activation energy** , E_a) and the correct **orientation** to react. Higher temperature means more molecules exceed E_a, so the reaction speeds up sharply.



A collision only reacts with the right orientation and enough energy

Reading an Energy Profile

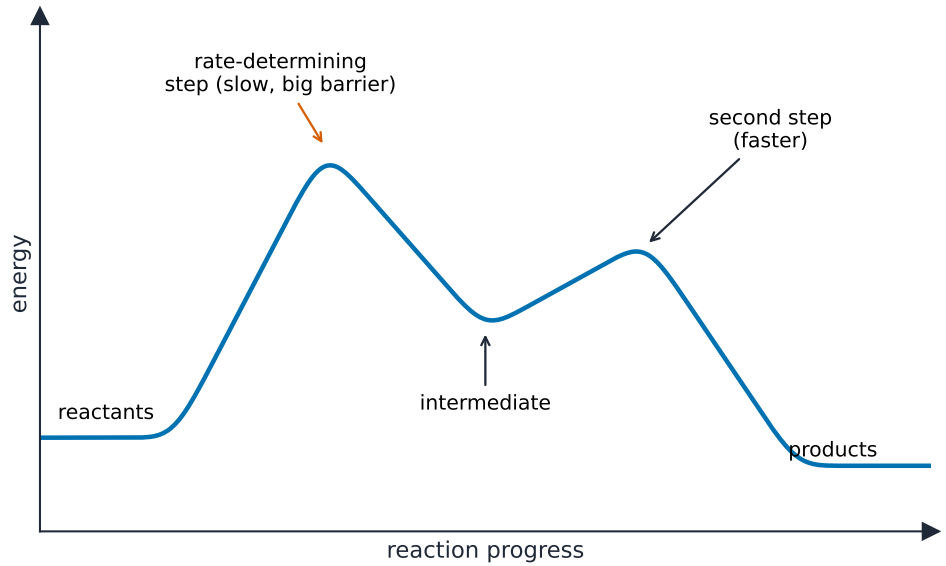
An **energy profile** plots energy along the reaction path. The peak is the **transition state**; the climb from reactants to the peak is E_a; the difference between reactant and product energies is the enthalpy change ΔH (down for exothermic).



Exothermic reactions end lower than the reactants; endothermic end higher

The Sequence of Steps

In a multi-step mechanism, the steps must **add up** to the overall balanced equation (intermediates cancel). Each step has its own energy hill; the tallest hill is the slowest step.



The slow step with the higher barrier is rate-determining

Finding the Rate Law From a Mechanism

The **rate-determining step** is the slowest step; its molecularity gives the overall rate law. A valid mechanism must (1) add to the overall reaction and (2) predict the experimentally observed rate law.

Worked example. Suppose the slow (rate-determining) step is the bimolecular collision $NO_2 + NO_2 \rightarrow NO_3 + NO$. Its molecularity gives the rate law directly: rate $= k[NO_2]^2$. If experiment shows exactly this, the proposed mechanism is consistent; if experiment gave rate $= k[NO_2]$, the mechanism would be wrong.

When the First Step Is Fast

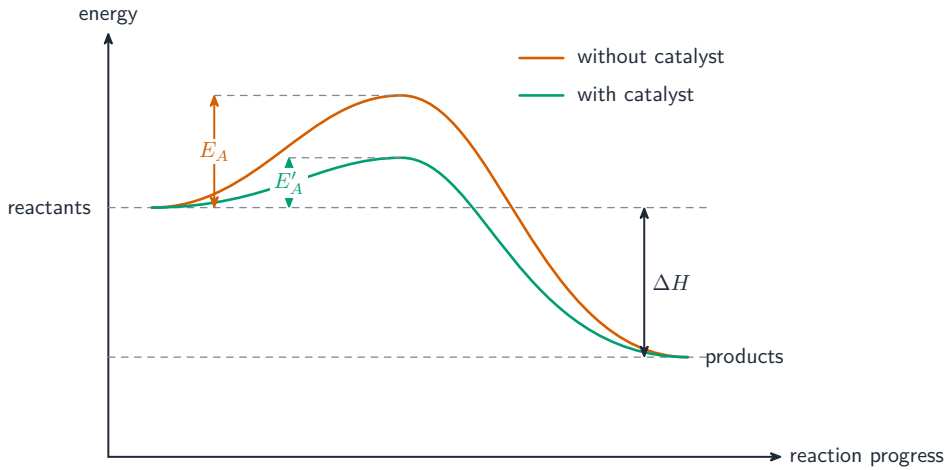
If a fast step precedes the slow one, an intermediate appears in the slow step's rate law. Use the **fast pre-equilibrium** to rewrite that intermediate in terms of reactants, so the final rate law contains only measurable species.

Energy Profiles for Many Steps

A multi-step reaction's profile shows several peaks (one per step) with valleys (intermediates) between them. The **highest** peak is the rate-determining transition state – it controls the overall rate.

How Catalysts Speed Things Up

A **catalyst** speeds a reaction by providing a new pathway with a **lower activation energy**, without being consumed. It does not change ΔH or the equilibrium position – only how fast equilibrium is reached. On an energy profile, a catalyst lowers the peak(s).



A catalyst gives a route with lower activation energy; the enthalpy change is unchanged

Exam tips

- Rate rises with **concentration, temperature, surface area, and a catalyst** — explain each with **collision theory** (more, or more energetic, successful collisions).
- Temperature works mainly by getting **more particles above the activation energy**, not just more collisions.
- **Reaction orders come from experiment**, not the balanced coefficients — see how the rate changes when one concentration is varied.
- On an **energy profile** the hill height is the activation energy and the reactant–product gap is ΔH.
- A **catalyst** lowers the activation energy (a new pathway) but leaves ΔH and the equilibrium position unchanged.

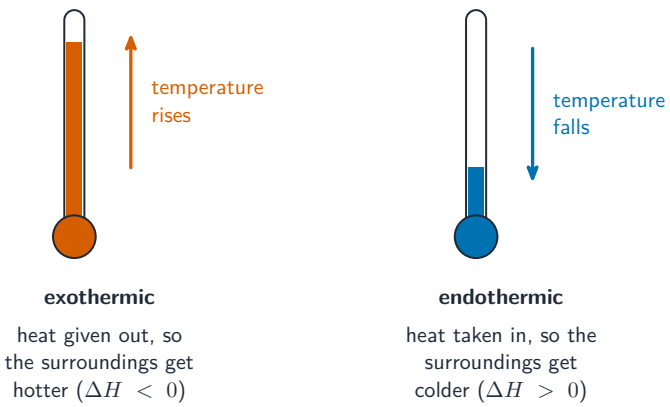
Thermochemistry

AP Chemistry

Endothermic and Exothermic Processes

An instant cold pack: endothermic processes absorb heat from the surroundings

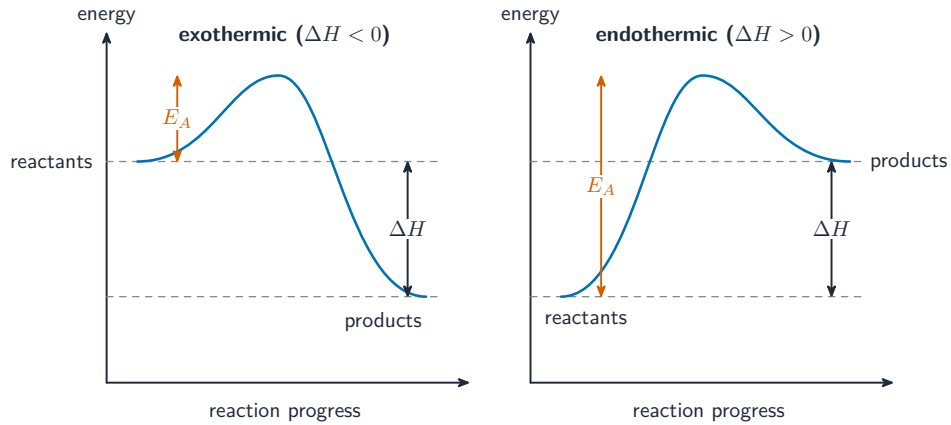
Thermochemistry tracks energy in reactions. A process is **exothermic** if it releases energy to the surroundings (feels hot, $\Delta H < 0$) and **endothermic** if it absorbs energy (feels cold, $\Delta H > 0$). Breaking bonds costs energy; forming bonds releases it – the net decides the sign.



An exothermic reaction warms the surroundings; an endothermic one cools them

Energy Diagrams

An energy diagram plots energy from reactants to products. Reactants above products means exothermic; below means endothermic. The vertical gap between them is the enthalpy change ΔH.



Energy diagrams: exothermic products sit below the reactants, endothermic above

Heat Transfer and Thermal Equilibrium

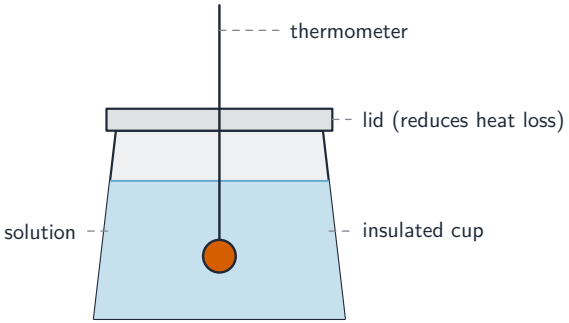
Heat flows from hot to cold until objects reach **thermal equilibrium** (equal temperature). Energy is conserved: the heat lost by the hot object equals the heat gained by the cold one.

Heat Capacity and Calorimetry

The heat to change a substance's temperature is

$$q = mc\,\Delta T,$$

where c is the **specific heat** (energy per gram per degree). **Calorimetry** measures a reaction's heat by tracking the temperature change of surrounding water: the heat the water gains equals the heat the reaction releases.



Calorimetry: measure the temperature change of a known mass of solution

Worked example. A reaction in a coffee-cup calorimeter warms 100 g of water by 8.0 °C ($c = 4.18$ J/(g °C)). The heat absorbed by the water is

$$q = mc\,\Delta T = 100 \times 4.18 \times 8.0 = 3.3 \times 10^3 \text{ J}.$$

By energy conservation the reaction **released** this 3.3 kJ, so it is exothermic ($q_{\text{rxn}} = -3.3$ kJ).

Energy of Phase Changes

During a **phase change** (melting, boiling) the temperature stays **constant** while heat goes into breaking intermolecular forces, not raising kinetic energy. The energy needed is $q = n\,\Delta H_{\text{fus}}$ (melting) or $q = n\,\Delta H_{\text{vap}}$ (boiling) – the flat steps on a heating curve.

Steam from boiling water: phase changes absorb or release energy at constant temperature

Introduction to Enthalpy of Reaction

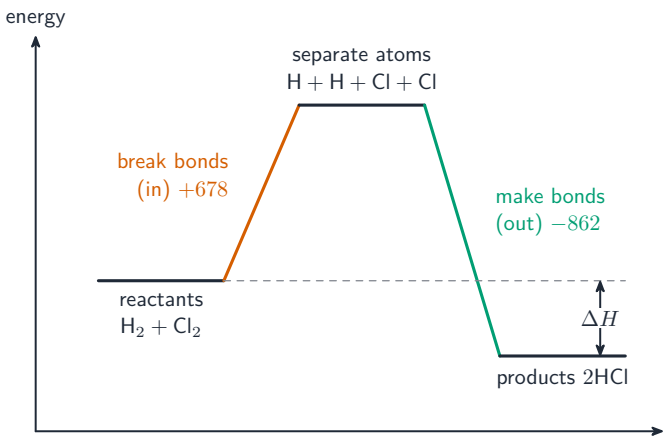
The **enthalpy of reaction** ΔH_{rxn} is the heat released or absorbed at constant pressure. Because enthalpy is a **state function**, ΔH depends only on the initial and final states, not the path taken – the key that makes the next three methods work.

Bond Enthalpies

One way to estimate ΔH: sum the energy to **break** all reactant bonds, then subtract the energy **released** forming product bonds:

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

This is an approximation, since bond enthalpies are averages.



net: $\Delta H = 678 - 862 = -184$ kJ/mol (exothermic)

Breaking bonds takes in energy; making bonds releases it

Worked example. Estimate ΔH for $H_2 + Cl_2 \rightarrow 2HCl$ using bond enthalpies H–H = 436, Cl–Cl = 242, H–Cl = 431 kJ/mol. Break both reactant bonds (436+242 = 678) and form two H–Cl bonds ($2 \times 431 = 862$):

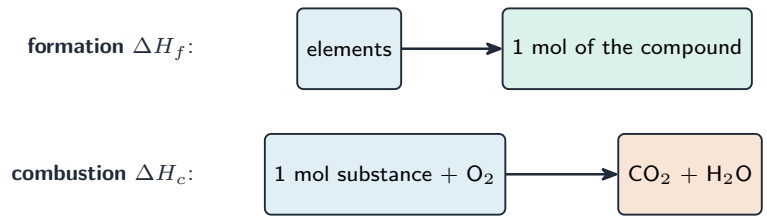
$$\Delta H \approx 678 - 862 = -184 \text{ kJ},$$

exothermic, because the strong H–Cl bonds formed release more than the reactant bonds cost.

Enthalpy of Formation

The **standard enthalpy of formation** ΔH_f° is the enthalpy to make one mole of a compound from its elements (zero for an element in its standard state). Then

$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}).$$



Formation makes a compound from its elements; combustion burns it in oxygen

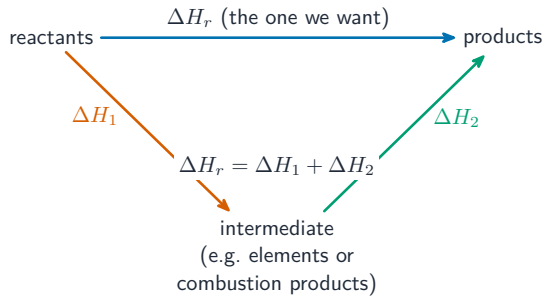
Worked example. Find $\Delta H_{\text{rxn}}^\circ$ for burning methane, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, given ΔH_f°: $CH_4 = -75$, $CO_2 = -394$, $H_2O = -286$ kJ/mol ($O_2 = 0$). Products minus reactants:

$$\Delta H_{\text{rxn}}^\circ = [-394 + 2(-286)] - [-75 + 0] = -966 + 75 = -891 \text{ kJ},$$

a large release, as expected for a combustion.

Hess's Law

Hess's law : if a reaction is the sum of several steps, its ΔH is the sum of the steps' ΔH values. Reverse a step and flip the sign; scale a step and scale its ΔH. This lets you find a hard-to-measure ΔH by combining known reactions – a frequent exam calculation.



Hess's law: the direct and indirect routes give the same total enthalpy change

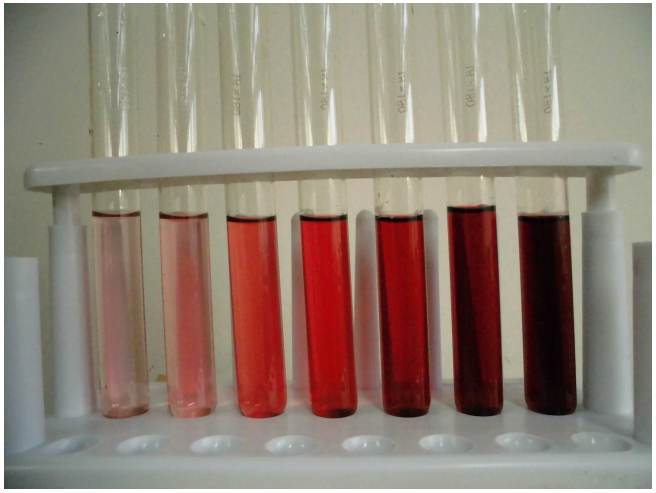
Exam tips

- An **exothermic** reaction has $\Delta H < 0$ (feels hot); endothermic has $\Delta H > 0$ — always give ΔH a sign and units.
- In calorimetry use $q = mc\Delta T$ with the mass of the **water/solution**; the reaction releases what the water gains.
- Bond enthalpies: $\Delta H \approx \sum(\text{bonds broken}) - \sum(\text{bonds made})$ — breaking is endothermic, making is exothermic (the classic sign trap).
- **Hess's law**: the total ΔH is the sum of the steps' — reverse a step and flip the sign, scale a step and scale ΔH.
- During a **phase change** the temperature stays constant while energy goes into the forces between particles.

Equilibrium

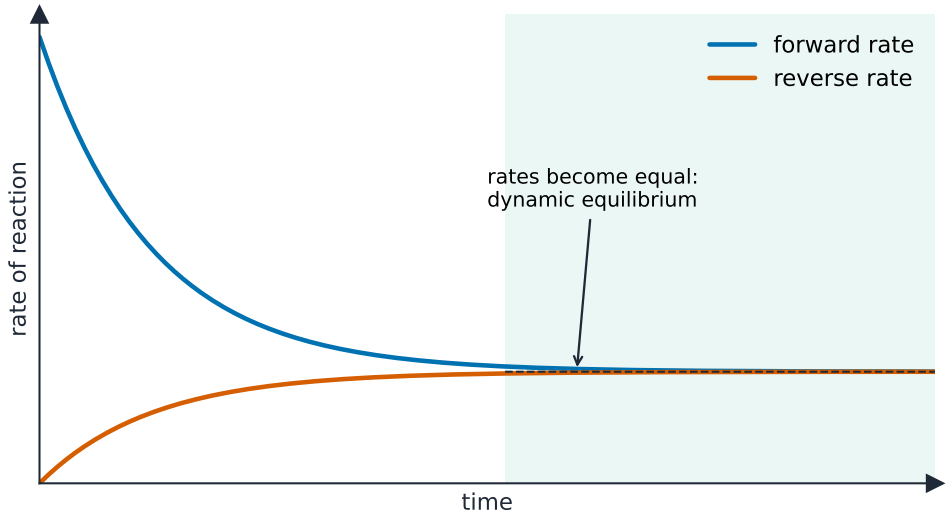
AP Chemistry

Introduction to Equilibrium



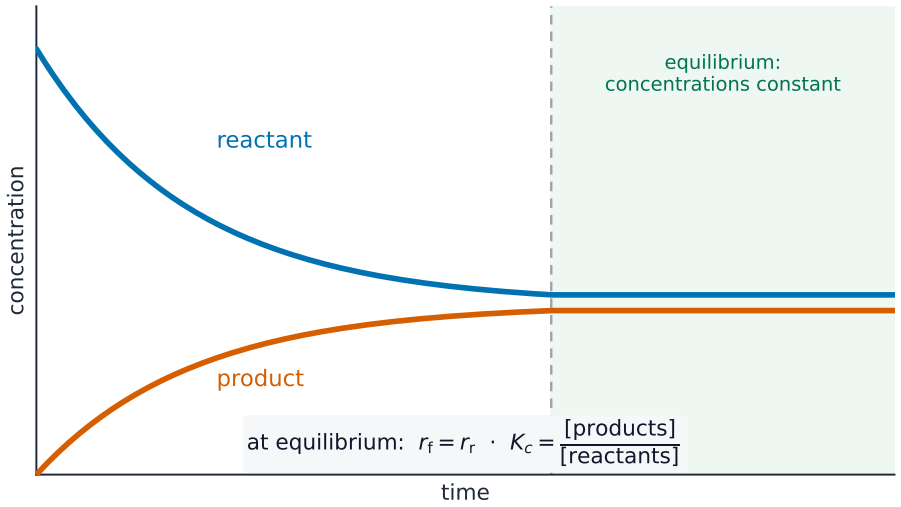
Cobalt chloride solutions: equilibrium systems shift when conditions change (Le Chatelier)

A **reversible reaction** runs both ways. **Chemical equilibrium** is reached when the forward and reverse rates become **equal**, so concentrations stop changing. Equilibrium is **dynamic** – both reactions continue, but at matching rates, so nothing appears to change.



Dynamic equilibrium: the forward and reverse rates become equal

The rates graph above explains *why* concentrations settle; this next graph shows *what* the concentrations do – reactants fall and products rise until, once the rates match, both hold constant (they need not be equal).



Reactant and product concentrations change, then hold constant once equilibrium is reached

Direction of Reversible Reactions

At equilibrium the amounts of reactants and products are fixed but usually **not** equal. Whether the mixture favors products or reactants depends on the reaction; you compare the current state to the equilibrium condition to predict which way it shifts.

The Reaction Quotient and Equilibrium Constant

The **reaction quotient** Q has the same form as the equilibrium expression but uses **current** concentrations:

$$Q = \frac{[\text{products}]}{[\text{reactants}]} \text{ (each raised to its coefficient).}$$

At equilibrium Q equals the **equilibrium constant** K. Comparing them predicts direction: $Q < K$ shifts **forward** (toward products); $Q > K$ shifts **reverse**; $Q = K$ means already at equilibrium.

Calculating the Equilibrium Constant

Write K from the balanced equation (pure solids and liquids are left out). From equilibrium concentrations (or partial pressures for K_p), plug in and compute. K_c uses molarities; K_p uses pressures.

Worked example. For $N_2O_4 \rightleftharpoons 2NO_2$, the equilibrium concentrations are $[N_2O_4] = 0.20$ M and $[NO_2] = 0.10$ M. Then

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.10)^2}{0.20} = 0.050.$$

The NO_2 coefficient of 2 becomes the power; N_2O_4 (coefficient 1) is just to the first power.

Magnitude of the Equilibrium Constant

- $K \gg 1$: products strongly favored (reaction nearly complete).
- $K \ll 1$: reactants favored (little reaction).
- $K \approx 1$: significant amounts of both.

The size of K tells you where the equilibrium "sits."

Properties of the Equilibrium Constant

K changes in predictable ways: reversing a reaction **inverts** K $(1/K)$; multiplying coefficients by n raises K to the nth power; adding reactions **multiplies** their K values. Only **temperature** changes the value of K itself.

Calculating Equilibrium Concentrations

Use an **ICE table** (Initial, Change, Equilibrium): fill in starting amounts, express the change with x using the mole ratios, then substitute into the K expression and solve for x. When K is small, the approximation "x is negligible" often simplifies the algebra.

Worked example. For $H_2 + I_2 \rightleftharpoons 2HI$ with $K_c = 50$, start with 0.100 M each of H_2 and I_2. The ICE table gives equilibrium $[H_2] = [I_2] = 0.100 - x$ and $[HI] = 2x$. Substitute:

$$K_c = \frac{(2x)^2}{(0.100 - x)^2} = 50 \;\Rightarrow\; \frac{2x}{0.100 - x} = \sqrt{50} = 7.07 \;\Rightarrow\; x = 0.078,$$

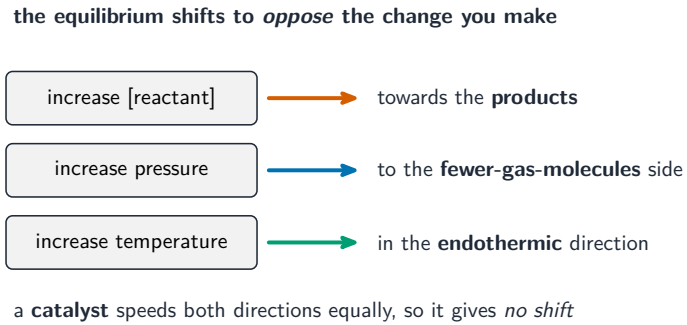
so $[HI] = 2x = 0.156$ M. Taking the square root of both sides works here because the expression is a perfect square.

Representations of Equilibrium

A particulate picture at equilibrium shows a fixed mix of reactant and product particles. Graphs of concentration vs time level off (never reaching zero) once equilibrium is reached – both curves flatten at the same moment.

Introduction to Le Chatelier's Principle

Le Chatelier's principle : if you disturb a system at equilibrium, it shifts to **partly counteract** the change. Adding a reactant shifts forward; removing product shifts forward; increasing pressure (by reducing volume) shifts toward the side with fewer gas moles; raising temperature shifts in the endothermic direction.



Le Chatelier's principle: the equilibrium shifts to oppose the change made

An ammonia plant: industrial equilibria like Haber's process are driven by pressure, temperature and catalysts

The Reaction Quotient and Le Chatelier's Principle

You can justify every Le Chatelier shift with Q versus K: a disturbance changes Q, and the system reacts to bring Q back to K. This quantitative view backs up the qualitative rule and is the fuller answer on the exam.

Introduction to Solubility Equilibria

For a slightly soluble salt, the **solubility product** K_{sp} is the equilibrium constant for its dissolving:

$$\mathrm{M}_a\mathrm{X}_b(s) \rightleftharpoons a\,\mathrm{M}^{b+} + b\,\mathrm{X}^{a-}, \qquad K_{sp} = [\mathrm{M}^{b+}]^a[\mathrm{X}^{a-}]^b.$$

A smaller K_{sp} means less soluble. The **common-ion effect** – adding an ion already in the salt – pushes the equilibrium back and **lowers** solubility.

Worked example. Silver chloride has $K_{sp} = 1.8 \times 10^{-10}$. If its molar solubility is s, then $[\mathrm{Ag}^+] = [\mathrm{Cl}^-] = s$, so $K_{sp} = s^2$ and

$$s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}\ \mathrm{M}.$$

Adding NaCl (a common ion) would raise $[\mathrm{Cl}^-]$, forcing s down – far less AgCl would dissolve.

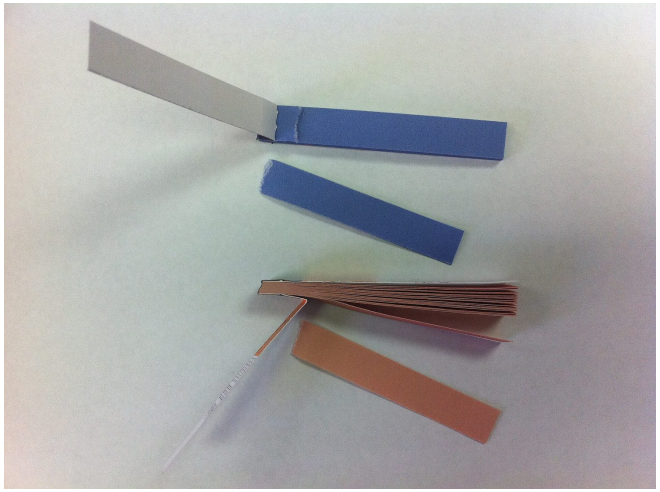
Exam tips

- At equilibrium the forward and reverse **rates** are equal, but the **amounts** are usually not.
- Leave pure solids and liquids out of the K expression; a large K favours products, a small K favours reactants.
- Apply **Le Chatelier**: add reactant → shift forward; raise pressure → shift toward fewer gas moles; raise temperature → shift in the **endothermic** direction.
- A **catalyst does not shift** the position of equilibrium — it only speeds the approach.
- Use an **ICE table** for equilibrium concentrations, and the small-x approximation when K is small.

Acids and Bases

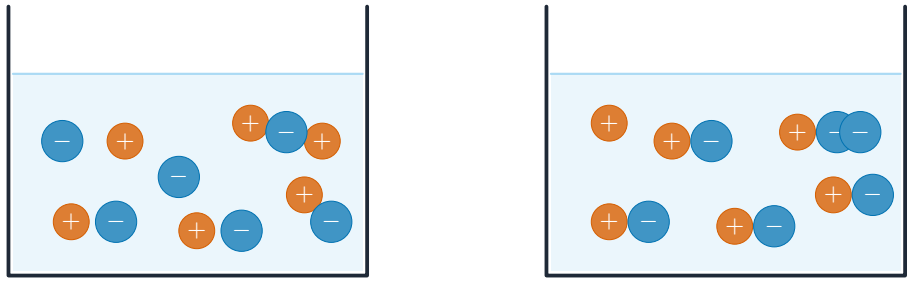
AP Chemistry

Introduction to Acids and Bases



Litmus paper: acid–base indicators change colour with H^+ concentration (pH)

By the **Brønsted–Lowry** definition, an **acid** is a proton (H^+) **donor** and a **base** is a proton **acceptor**. When an acid donates a proton it becomes its **conjugate base**; a base gaining a proton becomes its **conjugate acid**. Water is **amphoteric** – it can act as either.



strong acid
fully dissociated: many ions

weak acid
mostly molecules: few ions

A strong acid is fully dissociated; a weak acid is only partly dissociated

pH test strips: acid–base strength and concentration set the pH you measure

The Autoionization of Water

Even pure water conducts a tiny current, because water molecules react with each other in a reaction called **autoionization**:

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

One water molecule passes a proton to another, making a **hydronium ion** (H_3O^+, the ion we loosely write as H^+) and a hydroxide ion. This equilibrium has its own constant, the **ion-product constant of water**:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

at 25 °C. Defining $\text{pOH} = -\log[OH^-]$ and taking $-\log$ of the K_w expression gives the rule the rest of this topic leans on:

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.0$$

(again at 25 °C). Know one of pH or pOH and you get the other by subtracting from 14.

In pure water the two ions form in equal numbers, so $[H_3O^+] = [OH^-]$ and $\text{pH} = \text{pOH} = 7.0$. This is what **neutral** means. Acidic means $[H_3O^+] > [OH^-]$ (pH below 7); basic is the reverse.

Worked example. A solution has $[H_3O^+] = 2.0 \times 10^{-3}$ M. Find $[OH^-]$. Because K_w always holds in water,

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12} \text{ M}.$$

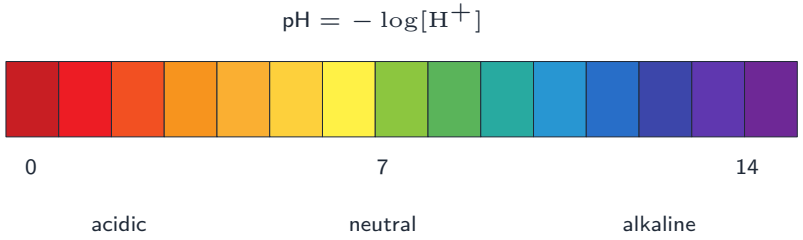
The hydroxide concentration is far smaller than the hydronium, confirming the solution is acidic.

K_w is **temperature dependent**: autoionization is endothermic, so heating water shifts it forward and raises K_w. At 50 °C, $K_w > 1.0 \times 10^{-14}$, so neutral water has $\text{pH} = \text{pOH} < 7.0$. It is still neutral, because the ion concentrations are still equal – neutral means equal ions, not a pH of exactly 7.

pH strips: water autoionizes so pure water is pH 7; acids and bases shift H+ and OH-

pH and pOH of Strong Acids and Bases

The **pH** pH scale measures acidity: $\mathrm{pH} = -\log[\mathrm{H}^+]$, with $\mathrm{pH} + \mathrm{pOH} = 14$ at 25 °C. A **strong acid** or **strong base** dissociates **completely**, so its ion concentration equals its concentration – read pH directly. Lower pH means more acidic.



The pH scale: pH is the negative log of the hydrogen-ion concentration

Worked example. Find the pH of 0.010 M HCl. Because HCl is a strong acid it is fully dissociated, so $[\mathrm{H}^+] = 0.010$ M and

$$\mathrm{pH} = -\log(0.010) = 2.0.$$

For a strong **base** like 0.010 M NaOH, pOH = 2.0, so pH = 14 − 2.0 = 12.0.

Weak Acid and Base Equilibria

A **weak acid** only **partly** dissociates, described by an equilibrium constant K_a (larger K_a = stronger weak acid); a weak base has K_b. For any conjugate acid–base pair the two are linked through water, $K_a \times K_b = K_w$, so $\mathrm{p}K_a + \mathrm{p}K_b = 14$ – a stronger acid always has a weaker conjugate base. Because dissociation is small, find $[\mathrm{H}^+]$ with an ICE table and the K_a expression, often using the small-x approximation.

Worked example. Find the pH of 0.10 M acetic acid, $K_a = 1.8 \times 10^{-5}$. Let $x = [\mathrm{H}^+]$ at equilibrium; the ICE table gives $K_a = \dfrac{x^2}{0.10 - x} \approx \dfrac{x^2}{0.10}$ (small-x approximation), so

$$x = \sqrt{K_a \times 0.10} = \sqrt{1.8 \times 10^{-6}} = 1.3 \times 10^{-3}\ \mathrm{M} \ \Rightarrow\ \mathrm{pH} = -\log(1.3 \times 10^{-3}) = 2.9.$$

The weak acid is far less acidic than a strong acid of the same concentration (which would be pH 1.0).

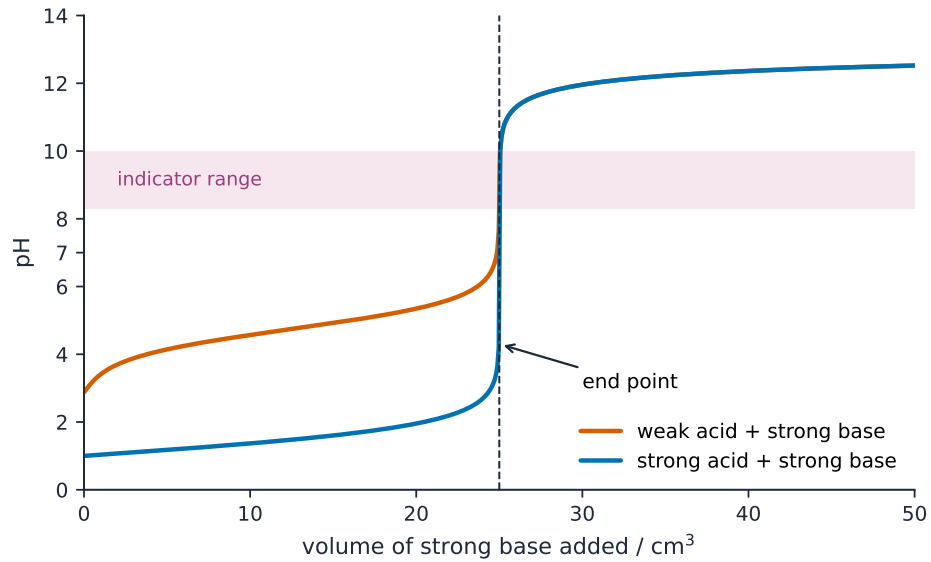
Acid-Base Reactions and Buffers

A **buffer** resists pH change. It contains a weak acid **and** its conjugate base (or a weak base and its conjugate acid) in comparable amounts. Added acid is neutralized by the conjugate base, and added base by the weak acid, so pH barely moves.

Acid-Base Titrations

A **titration curve** plots pH as base (or acid) is added. Key points: the **equivalence point** (moles of acid = moles of base – a steep jump), and the **half-equivalence point**, where $\mathrm{pH} = \mathrm{p}K_a$ (half the weak acid is converted, so a buffer is at its center).

An **acid-base indicator** is itself a weak acid whose protonated and deprotonated forms have **different colours**, so its colour responds to pH. You pick an indicator whose colour change happens near the titration's equivalence-point pH, so the colour flips just as the reaction completes.



A titration curve has a steep jump near the equivalence point

Molecular Structure of Acids and Bases

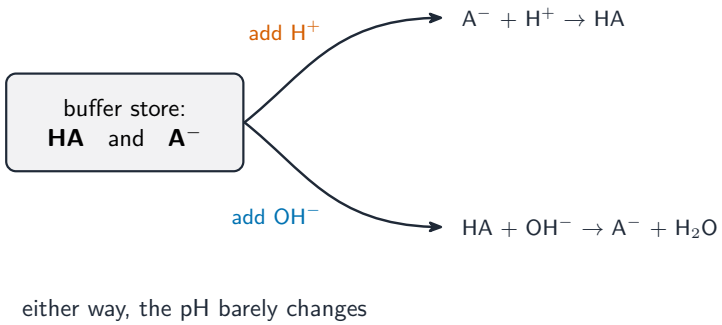
Strength has structural roots. An acid is stronger when its **conjugate base is more stable** – for example, more electronegative atoms or resonance spreading the negative charge stabilize it. For oxoacids, more oxygen atoms on the central atom means a stronger acid.

pH and pKa

$pK_a = -\log K_a$: a **smaller** pK_a means a **stronger** acid. Comparing pH to pK_a tells you the dominant form: below pK_a the acid form dominates; above it, the conjugate base form dominates.

Properties of Buffers

A buffer works best when the weak acid and conjugate base concentrations are **similar** (pH near pK_a). Choose a buffer whose pK_a is close to the target pH. Diluting a buffer barely changes its pH, because the acid-to-base **ratio** stays the same.



A buffer resists pH change by mopping up added acid or base

The Henderson-Hasselbalch Equation

For a buffer, the pH follows from the acid-to-base ratio:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}.$$

When the concentrations are equal, the log is zero and $\mathrm{pH} = \mathrm{p}K_a$. Use it to design a buffer or find its pH quickly.

Worked example. A buffer holds 0.20 M acetic acid ($\mathrm{p}K_a = 4.74$) and 0.30 M acetate. Its pH is

$$\mathrm{pH} = 4.74 + \log\frac{0.30}{0.20} = 4.74 + \log(1.5) = 4.74 + 0.18 = 4.92.$$

A little more conjugate base than acid pushes the pH just above $\mathrm{p}K_a$, as the equation predicts.

Buffer Capacity

Buffer capacity is how much acid or base a buffer can absorb before its pH changes sharply. It is greatest when the components are **concentrated** and in roughly **equal** amounts. Once one component is used up, the buffer fails.

pH and Solubility

The solubility of a salt with a basic anion **rises** in acidic solution: the added H^+ reacts with the anion, removing it from the solubility equilibrium and pulling more solid to dissolve (Le Chatelier applied to K_{sp}). So pH can control whether an ionic solid dissolves.

Exam tips

- **Neutral means equal ions, not pH 7.** In pure water $[H_3O^+] = [OH^-]$; since K_w rises with temperature, neutral pH drifts below 7 above 25 °C. Use $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (25 °C) to convert between $[OH^-]$ and $[H_3O^+]$.
- $\mathrm{pH} = -\log[H^+]$ is **logarithmic** — each unit is a ten-fold change in $[H^+]$.
- A **strong** acid/base dissociates completely (so $[H^+]$ = concentration); a **weak** one only partly, needing K_a.
- A **buffer** contains a weak acid **and** its conjugate base together; it resists pH change by mopping up added acid or base.
- On a titration curve the **equivalence point** is the steep jump; the **half-equivalence point** has $\mathrm{pH} = \mathrm{p}K_a$.
- A smaller $\mathrm{p}K_a$ means a stronger acid.

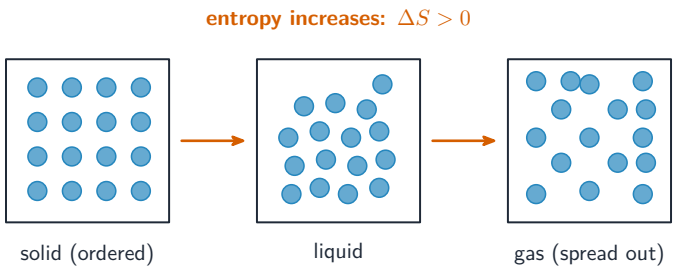
Thermodynamics and Electrochemistry

AP Chemistry

Introduction to Entropy

Household batteries: electrochemical cells convert chemical free energy into electrical work

Entropy S measures the dispersal of energy and matter – loosely, the number of ways to arrange a system. Entropy **increases** when a substance goes solid → liquid → gas, when a solid dissolves, when gas moles increase, or when temperature rises. More disorder means higher entropy.



Entropy rises from solid to liquid to gas

Absolute Entropy and Entropy Change

Every substance has a positive absolute entropy S°. For a reaction,

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants}).$$

Predict its **sign** from the change in gas moles: making more gas raises entropy ($\Delta S > 0$).

Gibbs Free Energy and Thermodynamic Favorability

Gibbs free energy combines enthalpy and entropy:

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

A process is **thermodynamically favorable** when $\Delta G < 0$. So exothermic ($\Delta H < 0$) and entropy-increasing ($\Delta S > 0$) reactions are always favorable; when the two oppose, **temperature** decides.

	ΔS **positive**	ΔS **negative**
ΔH **neg.**	feasible at **all** temperatures	feasible only at **low** temperature
ΔH **pos.**	feasible only at **high** temperature	**never** feasible

$\Delta G = \Delta H - T\Delta S$; **feasible when** $\Delta G \leq 0$

Whether a reaction is favorable, from the signs of the enthalpy and entropy change

Worked example. A reaction has $\Delta H = +40$ kJ/mol and $\Delta S = +120$ J/(mol K). It is endothermic (unfavorable enthalpy) but entropy-increasing, so it becomes favorable only when hot enough. Setting $\Delta G = \Delta H - T\Delta S < 0$ and matching units ($\Delta S = 0.120$ kJ):

$$T > \frac{\Delta H}{\Delta S} = \frac{40}{0.120} = 333 \text{ K } (60\,^\circ\text{C}).$$

Thermodynamic and Kinetic Control

$\Delta G < 0$ says a reaction *can* happen, not that it *will* happen fast. A reaction can be thermodynamically favorable yet **kinetically** slow because of a high activation energy (diamond $\rightarrow$ graphite). Thermodynamics gives the direction; kinetics gives the speed.

Free Energy and Equilibrium

Free energy links to the equilibrium constant:

$$\Delta G^\circ = -RT \ln K.$$

So $\Delta G^\circ < 0$ gives $K > 1$ (products favored), and $\Delta G^\circ > 0$ gives $K < 1$. At equilibrium $\Delta G = 0$.

A battery converts free energy of a spontaneous redox reaction into electrical work

Free Energy of Dissolution

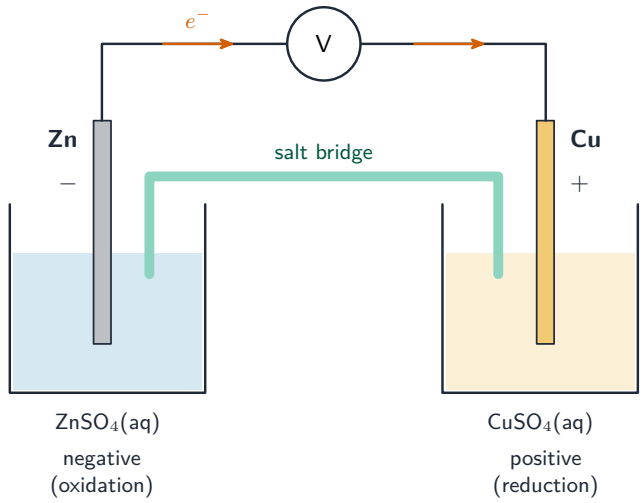
Whether a salt dissolves depends on the free-energy change of dissolving. Dissolving often increases entropy (ordered solid $\rightarrow$ dispersed ions) but may cost enthalpy; the sign of ΔG (and thus K_{sp}) follows from $\Delta H - T\Delta S$.

Coupled Reactions

An unfavorable reaction ($\Delta G > 0$) can be driven by **coupling** it to a favorable one ($\Delta G < 0$) that shares a common intermediate, as long as the **sum** has $\Delta G < 0$. This is how cells use ATP to power otherwise unfavorable processes.

Galvanic and Electrolytic Cells

Redox reactions can move electrons through a wire:



A galvanic cell with a salt bridge and voltmeter

- A **galvanic (voltaic) cell** uses a **favorable** reaction ($\Delta G < 0$) to produce electricity – a battery.
- An **electrolytic cell** uses electricity to **force** an unfavorable reaction ($\Delta G > 0$).

In both, **oxidation** happens at the **anode** and **reduction** at the **cathode**.

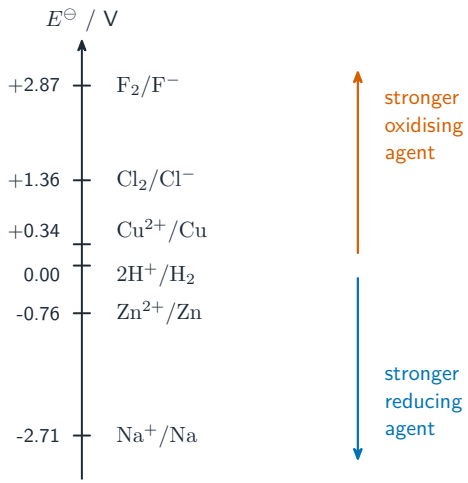
Commercial batteries: galvanic cells convert chemical free energy into electrical work

Cell Potential and Free Energy

The **cell potential** E°_{cell} measures the driving force in volts, found from standard reduction potentials ($E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$). It links to free energy by

$$\Delta G^\circ = -nFE^\circ_{\text{cell}},$$

where n is moles of electrons and F the Faraday constant. A **positive** E°_{cell} means a favorable (galvanic) reaction.



The electrochemical series of standard electrode potentials

Worked example. A cell pairs a copper cathode ($Cu^{2+} + 2e^- \to Cu$, $E^\circ = +0.34$ V) with a zinc anode ($Zn^{2+} + 2e^- \to Zn$, $E^\circ = -0.76$ V). The cell potential is

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (-0.76) = 1.10 \text{ V}.$$

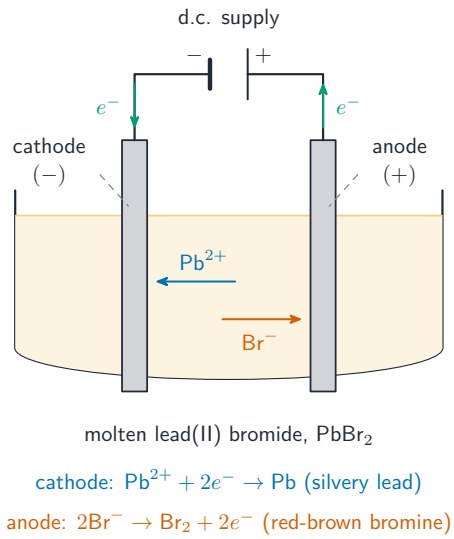
It is positive, so the reaction is spontaneous and the cell (a Daniell cell) acts as a battery.

Cell Potential Under Nonstandard Conditions

Away from standard conditions, the potential shifts with concentration – the **Nernst equation** (qualitatively): as reactants are consumed, Q rises and E_{cell} falls, reaching zero at equilibrium (a dead battery). Changing a concentration shifts E_{cell} the way Le Chatelier predicts.

Electrolysis and Faraday's Law

In **electrolysis**, the charge passed determines how much substance is deposited or produced – **Faraday's law**. Convert current × time to charge, charge to moles of electrons ($F = 96{,}485$ C/mol), then use the half-reaction's electron ratio to get moles (and mass) of product.



Electrolysis: ions move to the electrodes and are discharged

Worked example. A current of 2.0 A flows for 30 minutes through copper(II) sulfate ($Cu^{2+} + 2e^- \rightarrow Cu$). How much copper is deposited? The charge is $Q = It = 2.0 \times 1800 = 3600$ C, giving $3600/96485 = 0.0373$ mol of electrons. Since each Cu needs 2 electrons, 0.0187 mol of Cu forms, a mass of $0.0187 \times 63.5 = 1.2$ g.

Exam tips

- A process is **thermodynamically favourable** when $\Delta G < 0$; combine enthalpy and entropy with $\Delta G = \Delta H - T\Delta S$ (match units — kJ vs J).
- Entropy **increases** solid→liquid→gas and when more gas moles are produced.
- Favourable does **not** mean fast — a high activation energy can make a $\Delta G < 0$ reaction extremely slow (kinetic control).
- In electrochemistry a **positive** $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ means a spontaneous (galvanic) cell; oxidation is at the **anode**, reduction at the **cathode**.
- In electrolysis the charge passed ($Q = It$) fixes the amount deposited (Faraday's law).