

Course Companion

# AP Chemistry

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Every topic handout in one volume

exercises.lol

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# Atomic Structure and Properties

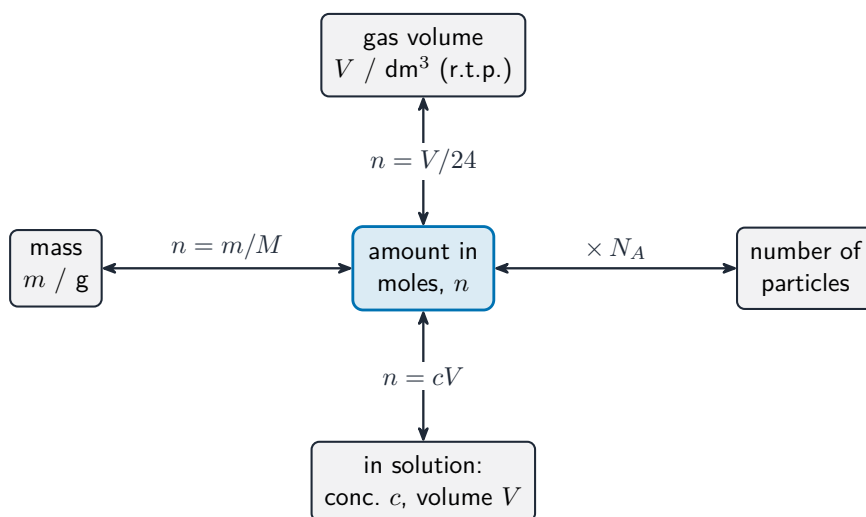
## AP Chemistry

### 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)?

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

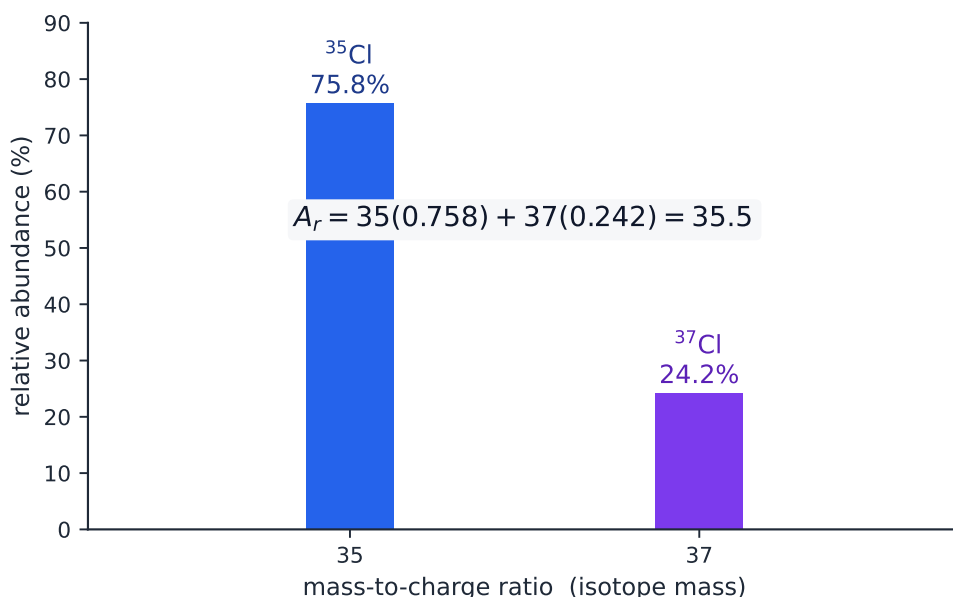
# Mass Spectra of Elements

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 | $\div A_r \rightarrow$ 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  $\text{CH}_2\text{O}$  - if  $M_r = 180$ , it fits  $180/30 = 6$  times: molecular formula  $\text{C}_6\text{H}_{12}\text{O}_6$

*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:

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

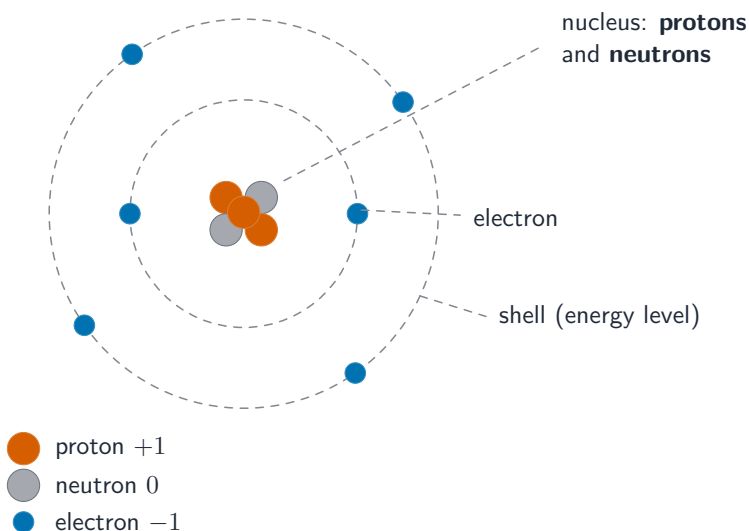
so the empirical formula is  $\text{CH}_2\text{O}$ . If the molar mass were 180 g/mol ( $= 6 \times 30$ ), the molecular formula would be  $\text{C}_6\text{H}_{12}\text{O}_6$  – glucose.

## 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*

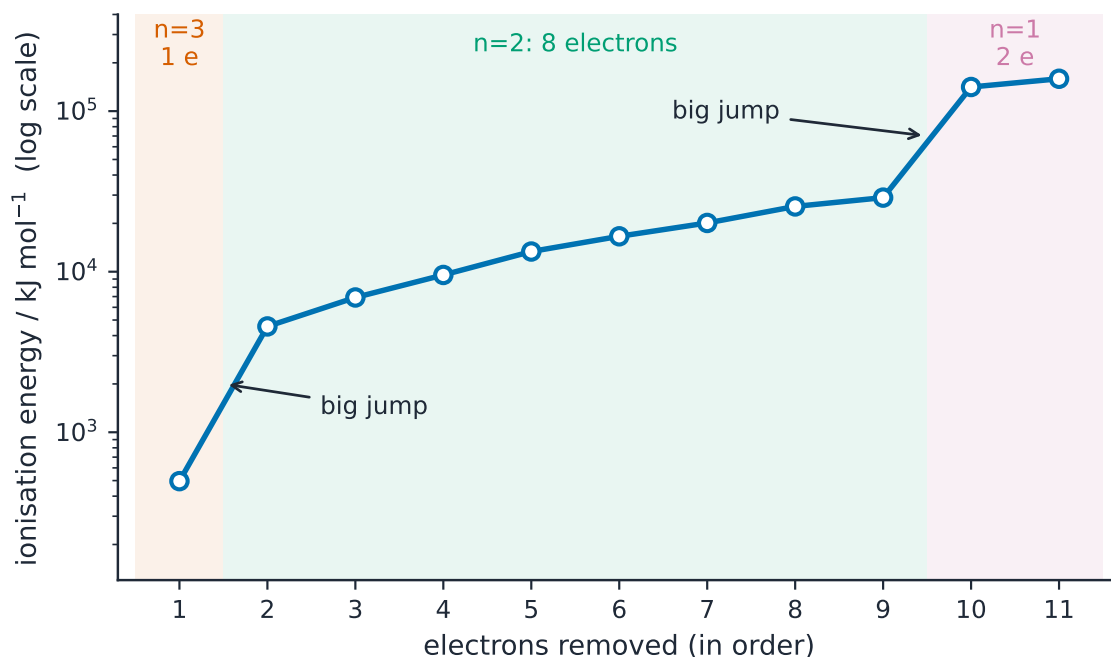
**Worked example.** Write the electron configuration of sulfur ( $Z = 16$ ). Fill subshells in order until 16 electrons are placed:  $1s^2 2s^2 2p^6 3s^2 3p^4$ . The  $3s$  and  $3p$  electrons (six in total) are the valence electrons, so sulfur tends to gain two electrons to complete its octet.

| PERIODIC TABLE OF ELEMENTS |          |          |           |           |           |           |           |           |           |           |           |          |           |           |           |           |          |
|----------------------------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------|----------|
| 1                          | 2        | 3        | 4         | 5         | 6         | 7         | 8         | 9         | 10        | 11        | 12        | 13       | 14        | 15        | 16        | 17        | 18       |
| 1<br>H                     |          |          |           |           |           |           |           |           |           |           |           |          |           |           |           |           | 2<br>He  |
| 3<br>Li                    | 4<br>Be  |          |           |           |           |           |           |           |           |           |           | 5<br>B   | 6<br>C    | 7<br>N    | 8<br>O    | 9<br>F    | 10<br>Ne |
| 11<br>Na                   | 12<br>Mg |          |           |           |           |           |           |           |           |           |           | 13<br>Al | 14<br>Si  | 15<br>P   | 16<br>S   | 17<br>Cl  | 18<br>Ar |
| 19<br>K                    | 20<br>Ca | 21<br>Sc | 22<br>Ti  | 23<br>V   | 24<br>Cr  | 25<br>Mn  | 26<br>Fe  | 27<br>Co  | 28<br>Ni  | 29<br>Cu  | 30<br>Zn  | 31<br>Ga | 32<br>Ge  | 33<br>As  | 34<br>Se  | 35<br>Br  | 36<br>Kr |
| 37<br>Rb                   | 38<br>Sr | 39<br>Y  | 40<br>Zr  | 41<br>Nb  | 42<br>Mo  | 43<br>Tc  | 44<br>Ru  | 45<br>Rh  | 46<br>Pd  | 47<br>Ag  | 48<br>Cd  | 49<br>In | 50<br>Sn  | 51<br>Sb  | 52<br>Te  | 53<br>I   | 54<br>Xe |
| 55<br>Cs                   | 56<br>Ba |          | 72<br>Hf  | 73<br>Ta  | 74<br>W   | 75<br>Re  | 76<br>Os  | 77<br>Ir  | 78<br>Pt  | 79<br>Au  | 80<br>Hg  | 81<br>Tl | 82<br>Pb  | 83<br>Bi  | 84<br>Po  | 85<br>At  | 86<br>Rn |
| 87<br>Fr                   | 88<br>Ra |          | 104<br>Rf | 105<br>Db | 106<br>Sg | 107<br>Bh | 108<br>Hs | 109<br>Mt | 110<br>Ds | 111<br>Rg | 112<br>Cn |          |           |           |           |           |          |
|                            |          |          |           |           |           |           |           |           |           |           |           |          |           |           |           |           |          |
|                            |          | 57<br>La | 58<br>Ce  | 59<br>Pr  | 60<br>Nd  | 61<br>Pm  | 62<br>Sm  | 63<br>Eu  | 64<br>Gd  | 65<br>Tb  | 66<br>Dy  | 67<br>Ho | 68<br>Er  | 69<br>Tm  | 70<br>Yb  | 71<br>Lu  |          |
|                            |          | 89<br>Ac | 90<br>Th  | 91<br>Pa  | 92<br>U   | 93<br>Np  | 94<br>Pu  | 95<br>Am  | 96<br>Cm  | 97<br>Bk  | 98<br>Cf  | 99<br>Es | 100<br>Fm | 101<br>Md | 102<br>No | 103<br>Lr |          |

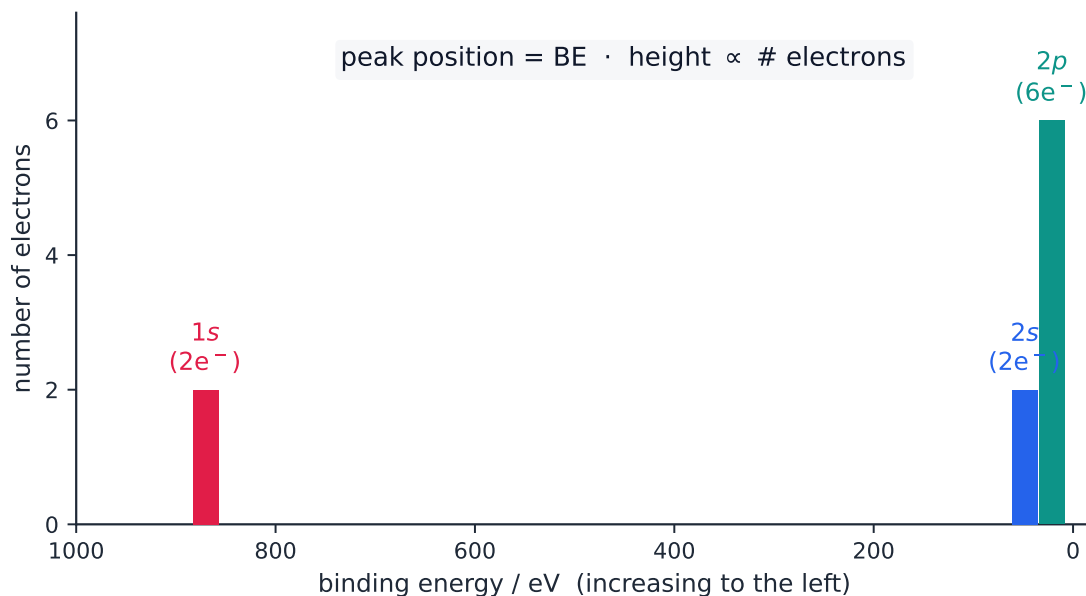
*The periodic table organises elements by atomic structure — electron configuration explains the patterns*

# 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.



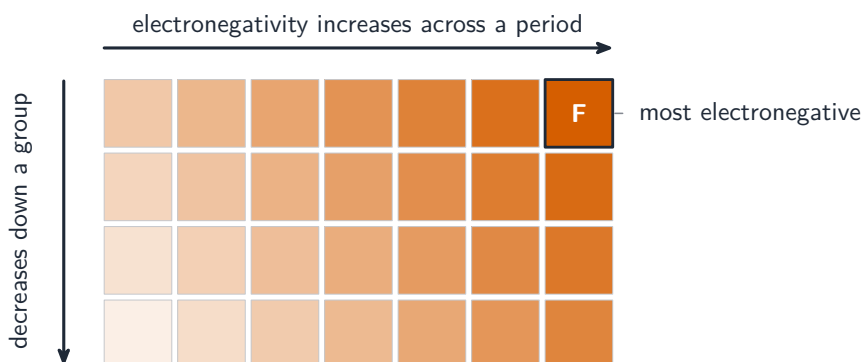
*Successive ionisation energies reveal the shell structure through big jumps*



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

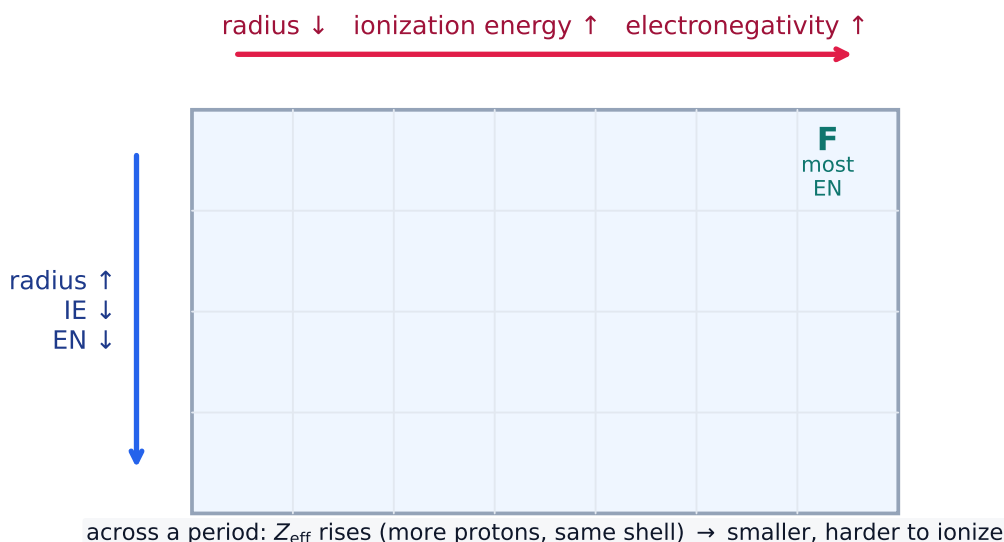
## Periodic Trends

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  $\text{Al}_2\text{O}_3$  so the +6 and −6 cancel.

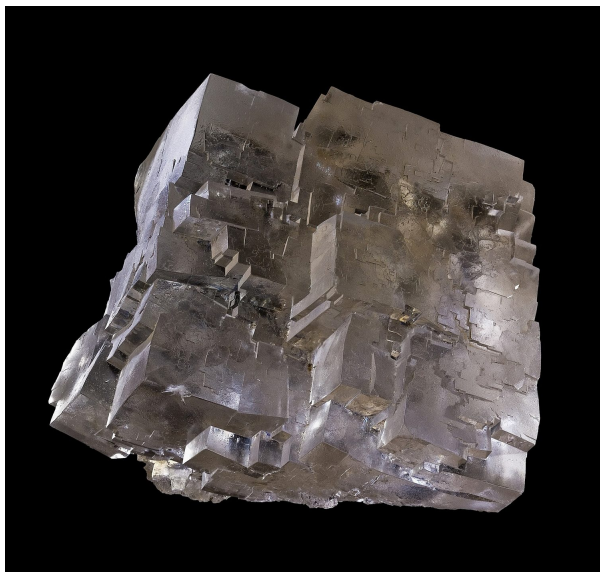
## Exam tips

- 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

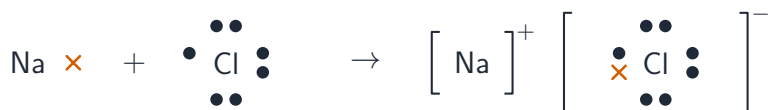
## AP Chemistry

### 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:



sodium gives its outer electron (×) to chlorine

*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.



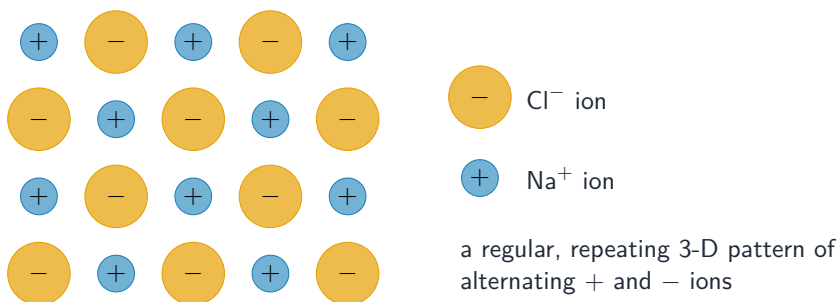
*A diamond crystal: giant covalent networks explain extreme hardness and high melting points*

## 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

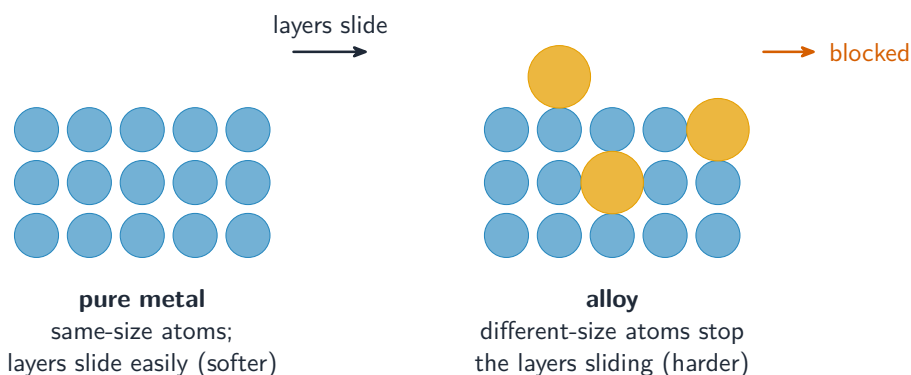
An **ionic solid** is a repeating 3-D **lattice** of alternating cations and anions, held by strong electrostatic attraction. This explains their high melting points, brittleness, and why they conduct only when molten or dissolved (ions freed to move). The **lattice energy** rises with larger ion charges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



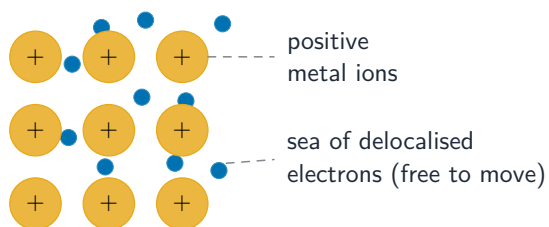
*Ions pack into a giant lattice of alternating positive and negative ions*

# Structure of Metals and Alloys

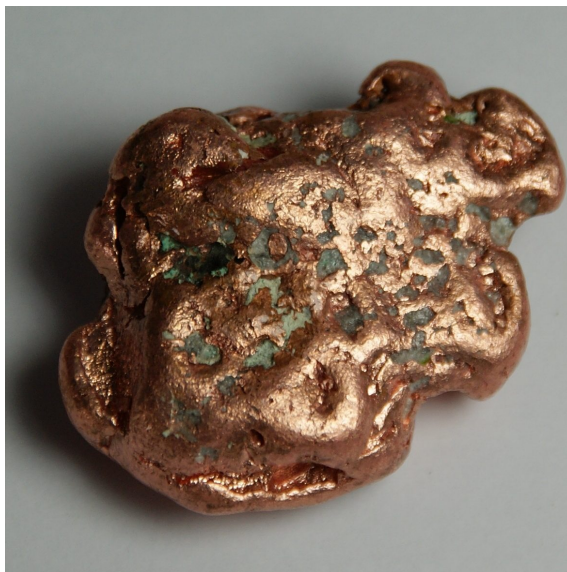
In a metal, cations sit in a lattice bathed in **delocalized** electrons, which explains conductivity, malleability, and luster. An **alloy** mixes metals: a **substitutional** alloy swaps in similar-sized atoms; an **interstitial** alloy (like steel) fits small atoms into the gaps, making it harder.



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



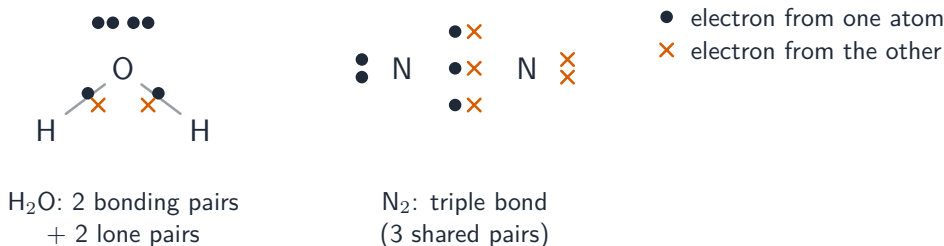
*Metallic bonding: positive ions in a sea of delocalised electrons*



*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,  $\text{CO}_2$ . 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,  $\text{O}=\text{C}=\text{O}$ : each O then has two lone pairs, C has none, and all 16 electrons are placed with every atom at an octet.

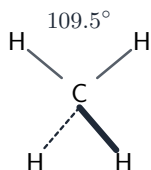
## Resonance and Formal Charge

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.

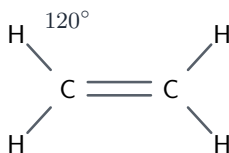
**Worked example.** Assign formal charges in the nitrate ion,  $\text{NO}_3^-$  (one double bond, two single bonds). For N (4 bonds, no lone pairs):  $5 - 0 - 4 = +1$ . For the double-bonded O (2 lone pairs):  $6 - 4 - 2 = 0$ . For each single-bonded O (3 lone pairs):  $6 - 6 - 1 = -1$ . The total is  $+1 + 0 + (-1) + (-1) = -1$ , 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.



$sp^3$ : 4 single bonds  
tetrahedral

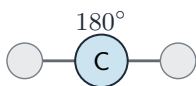


$sp^2$ : 1 double + 2 single  
planar (flat)

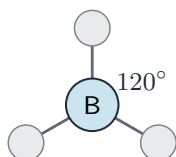


$sp$ : 1 triple bond  
linear

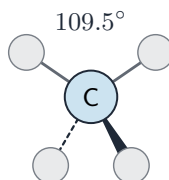
*Hybridisation and shape:  $sp^3$  tetrahedral,  $sp^2$  planar,  $sp$  linear*



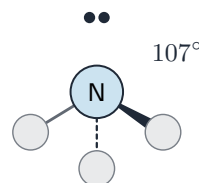
linear  
 $CO_2$



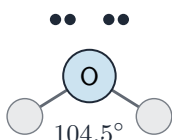
trigonal planar  
 $BF_3$



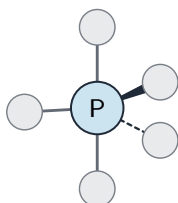
tetrahedral  
 $CH_4$



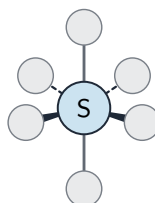
pyramidal  
 $NH_3$



bent  
 $H_2O$



trig. bipyramidal  
 $PF_5$ , 120° & 90°



octahedral  
 $SF_6$ , 90°

*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  $107^\circ$  (a little less than the ideal  $109.5^\circ$ ). 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**  $\sigma$  – orbitals overlapping head-on along the line joining the two atoms. A multiple bond adds a **pi bond**  $\pi$ , 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**.

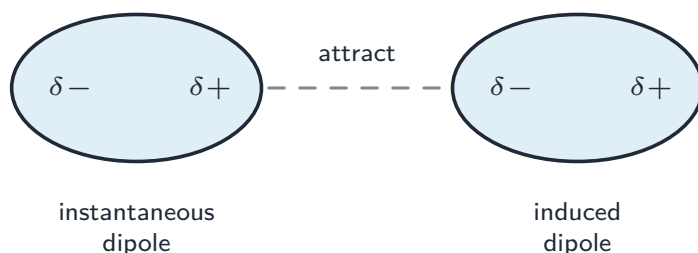
# Properties of Substances and Mixtures

## AP Chemistry

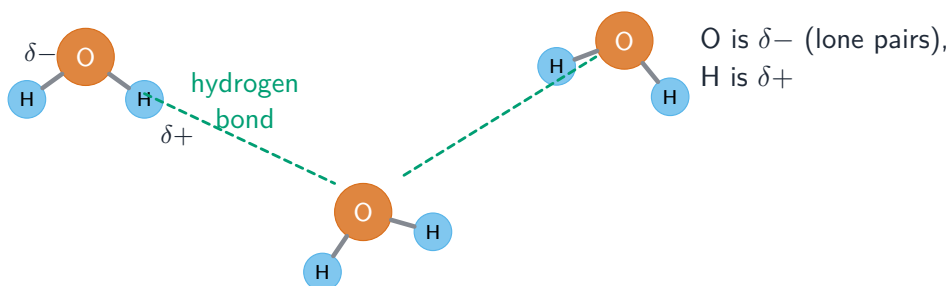
### Intermolecular and Interparticle Forces

#### 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.

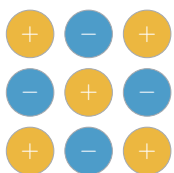
- **Ion–dipole** - : between an **ion** and a polar molecule (the ion pulls on the oppositely-charged end of the dipole). These are the **strongest** of the four here (stronger even than hydrogen bonds), and are exactly what lets water dissolve an ionic solid - each  $\text{Na}^+$  is surrounded by the  $\delta^-$  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  $100^\circ\text{C}$  while methane (16 g/mol, dispersion only) boils at  $-162^\circ\text{C}$ .

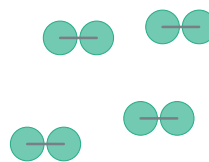
## Properties of Solids

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.

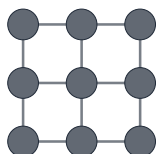
**Metallic** solids conduct electricity and heat and are **malleable** and **ductile**, all because their **free valence electrons** move easily and let the metal ions slide past one another without breaking the bonding. Solids are also either **crystalline** (particles in a regular, repeating 3-D arrangement)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



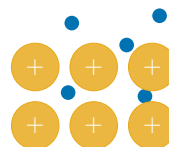
**giant ionic**  
NaCl: high m.p.,  
conducts when molten



**simple molecular**  
I<sub>2</sub>, ice: low m.p.,  
weak forces between



**giant covalent**  
diamond, SiO<sub>2</sub>: very  
high m.p., insulating

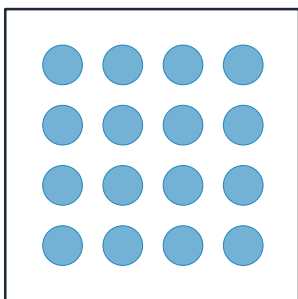


**giant metallic**  
copper: high m.p.,  
conducts (solid + molten)

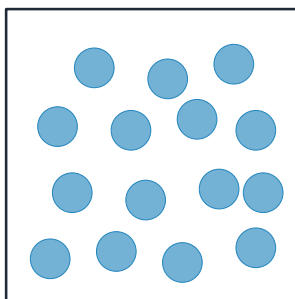
*The four solid structures: giant ionic, simple molecular, giant covalent, and metallic*

## Solids, Liquids, and Gases

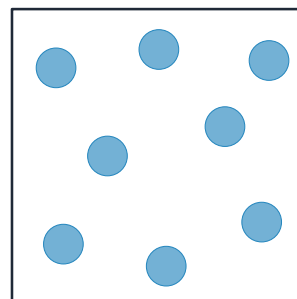
The three states differ in how tightly particles are held. Rising **temperature** raises average kinetic energy; when it overcomes the attractions, the substance melts or boils. Gases are mostly empty space, so they are compressible and fill their container.



**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*



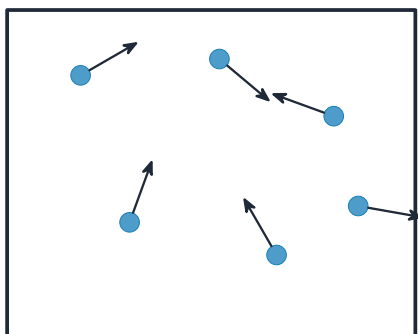
*Steam rising from boiling water: gases expand to fill space and obey the ideal gas law at high  $T$  and low  $P$*

## The Ideal Gas Law

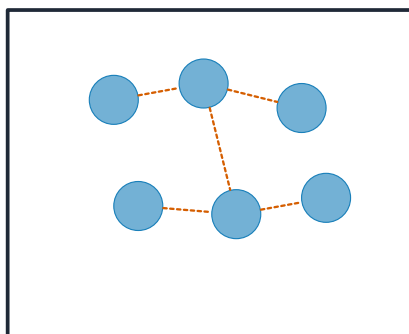
An **ideal gas** obeys

$$PV = nRT,$$

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

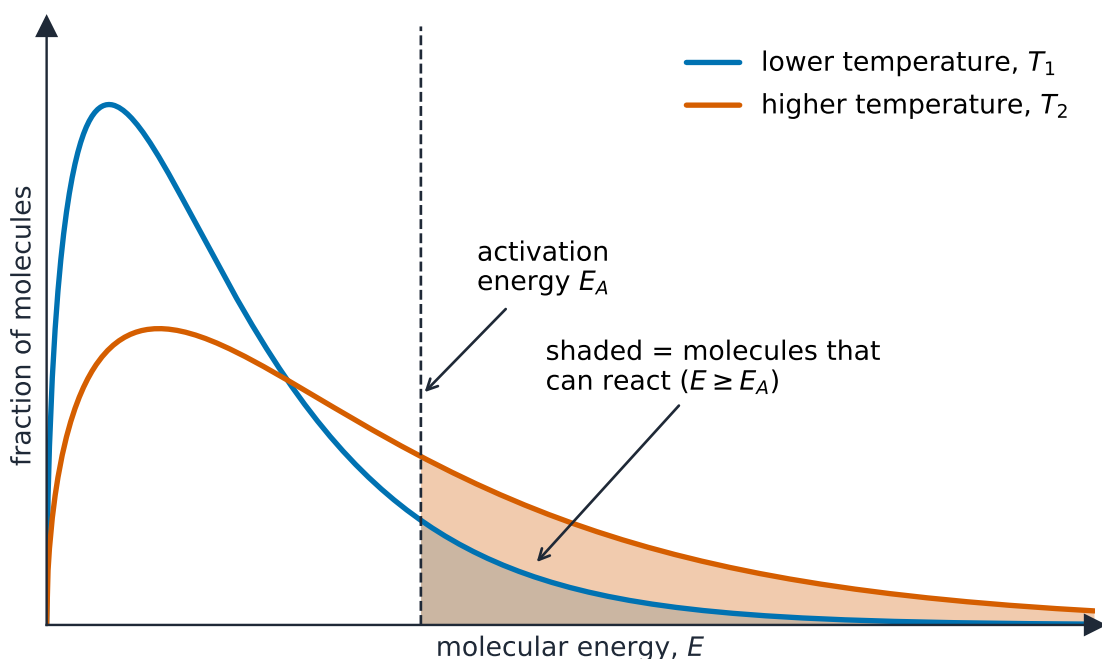
1.5 atm? Using  $R = 0.0821 \text{ L atm}/(\text{mol K})$ ,

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

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:  $M_1V_1 = M_2V_2$ .

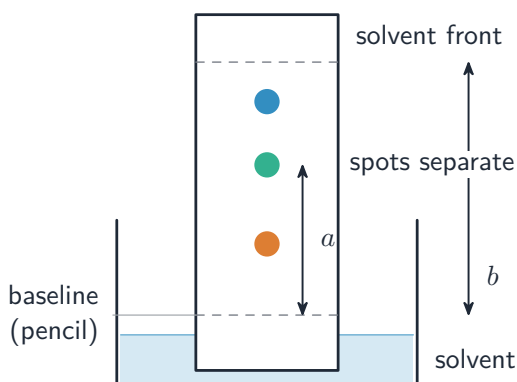
**Worked example.** What volume of water must you add to 50 mL of 6.0 M HCl to make it 2.0 M? The moles of HCl are unchanged, so  $M_1V_1 = M_2V_2$  gives the final volume  $V_2 = \frac{M_1V_1}{M_2} = \frac{6.0 \times 50}{2.0} = 150$  mL. You therefore **add**  $150 - 50 = 100$  mL of water.

## 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  $E = h\nu = \frac{hc}{\lambda}$ . 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,  $\varepsilon$  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  $\varepsilon = 2000 \text{ L}/(\text{mol cm})$ ; in a 1.0 cm cell a sample reads absorbance  $A = 0.40$ . Its concentration is  $c = \frac{A}{\varepsilon b} = \frac{0.40}{2000 \times 1.0} = 2.0 \times 10^{-4} \text{ M}$ . 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  $M = \text{mol/L}$ ; 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

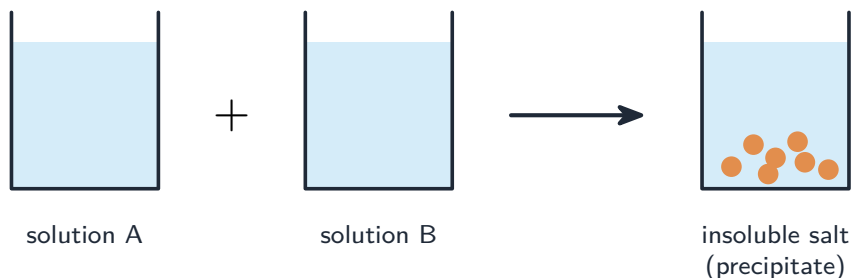


*Magnesium burning: a chemical reaction rearranges atoms and releases energy as light and heat*

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

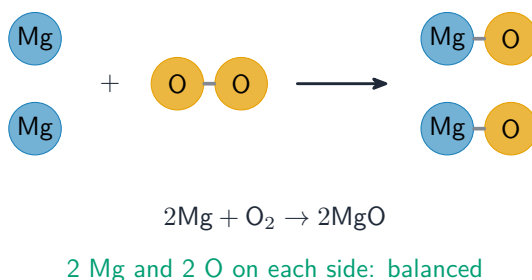
For reactions in water, ionic compounds split into ions. A **net ionic equation** shows only the species that actually change, leaving out the **spectator ions** that appear unchanged on both sides. It captures the real chemistry (e.g.  $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(s)$ ).



*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.



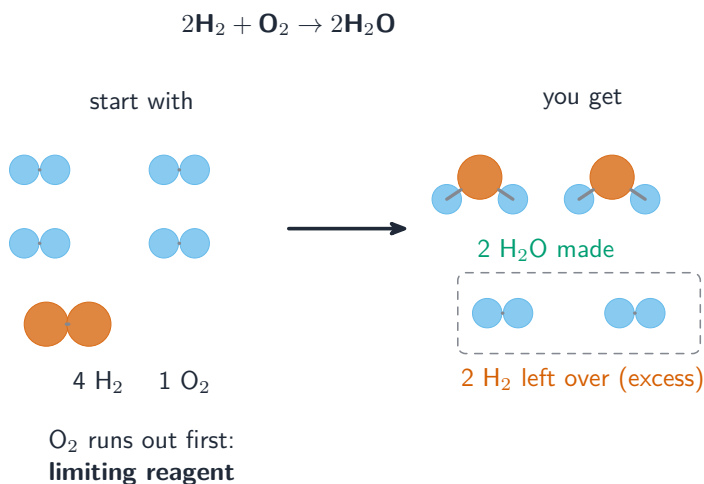
*A balanced equation has the same number of each atom on both sides*

## 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  $\rightarrow$  moles  $\rightarrow$  (mole ratio)  $\rightarrow$  moles  $\rightarrow$  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*

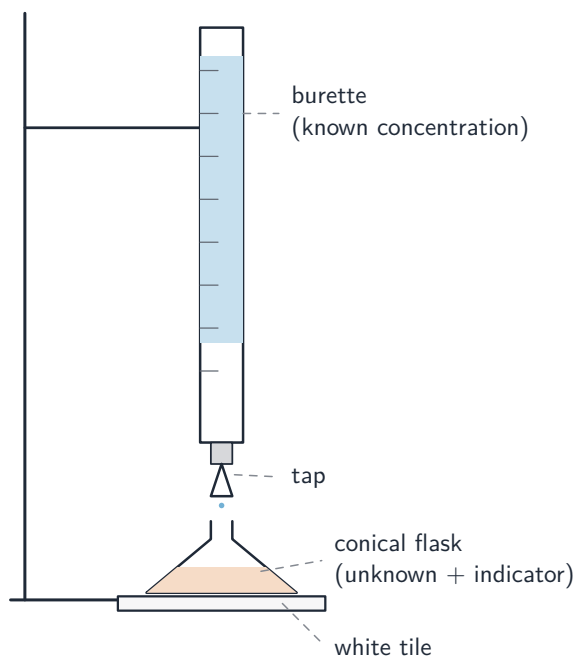
**Worked example.** How much water forms when 4.0 g of hydrogen burns in excess oxygen?  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ . Convert to moles, cross the mole ratio ( $2 : 2 = 1 : 1$  here), convert back:

$$n(\text{H}_2) = \frac{4.0}{2.0} = 2.0 \text{ mol} \Rightarrow n(\text{H}_2\text{O}) = 2.0 \text{ mol} \Rightarrow m = 2.0 \times 18 = 36 \text{ g}.$$

**Worked example (limiting reactant).** 10.0 g of  $\text{N}_2$  reacts with 5.0 g of  $\text{H}_2$  ( $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ ). Which runs out? Moles:  $n(\text{N}_2) = 10.0/28 = 0.36$ ,  $n(\text{H}_2) = 5.0/2 = 2.5$ . The reaction needs 3  $\text{H}_2$  per  $\text{N}_2$ ; you have  $2.5/0.36 = 7.0$ , far more than 3, so  **$\text{N}_2$  is limiting**. It makes  $2 \times 0.36 = 0.72$  mol of ammonia, with hydrogen left over.

# Introduction to Titration

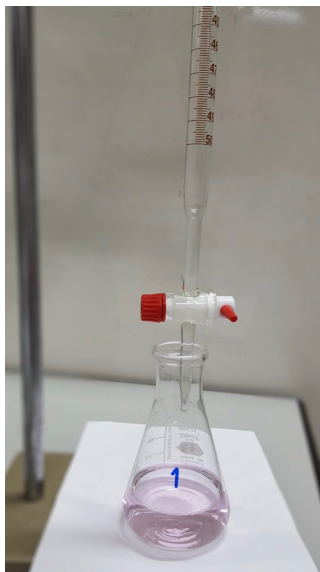
A **titration** finds an unknown concentration by reacting it with a solution of known concentration until they reach the **equivalence point** (stoichiometrically equal). From the known volume and concentration, use the mole ratio to find the unknown. An **indicator** or a pH curve signals the endpoint.



*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:

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



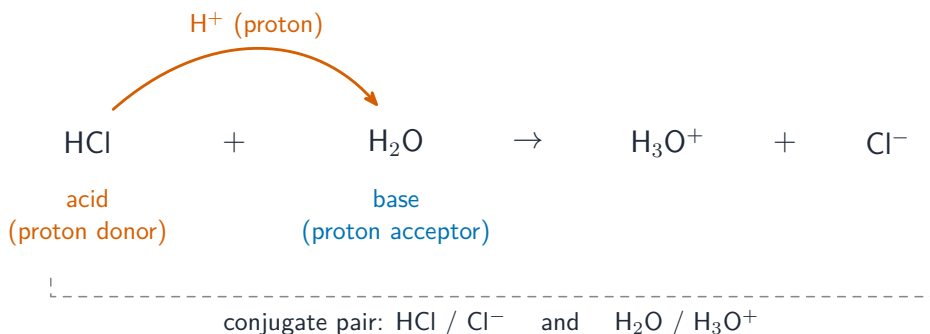
*A titration setup: reacting volumes from a burette find the concentration of an unknown solution*

## 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

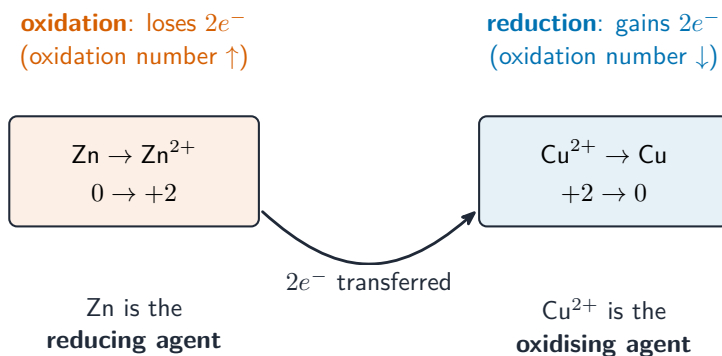
An **acid** donates a proton ( $\text{H}^+$ ); a **base** accepts one (Brønsted–Lowry). They react to form water and a salt:  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ . Strong acids and bases dissociate completely; weak ones only partly.



*Brønsted–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,  $\text{KMnO}_4$ . 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).

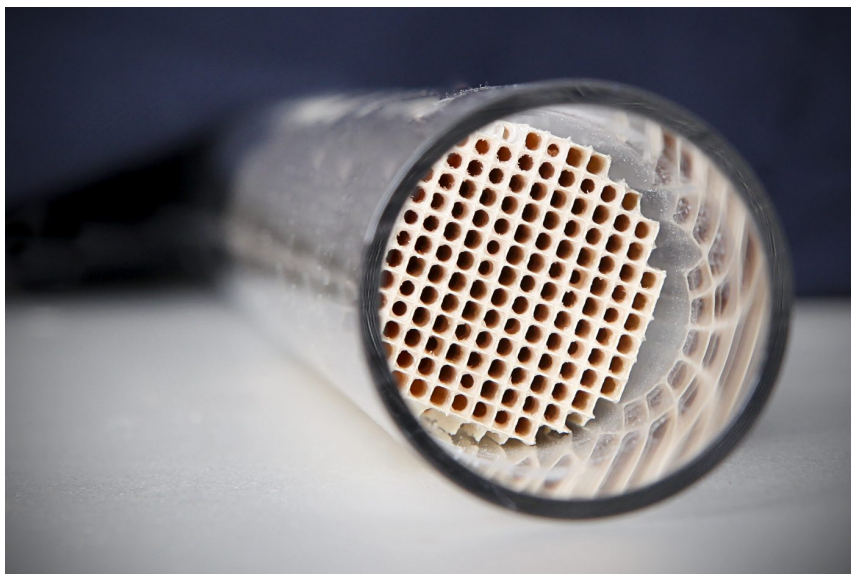
## Exam tips

- 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

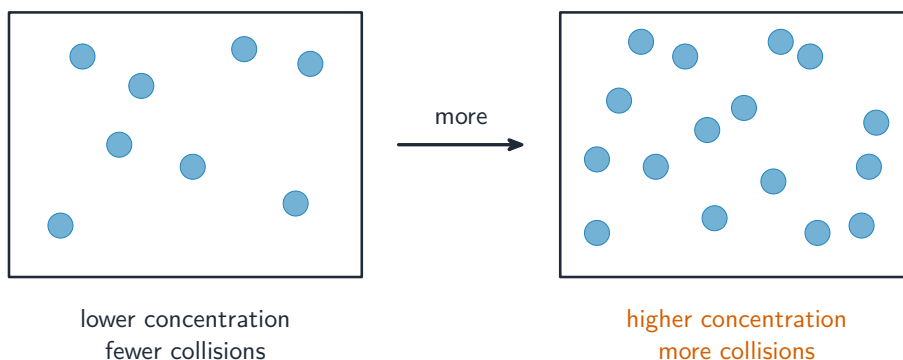
## AP Chemistry

### 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*



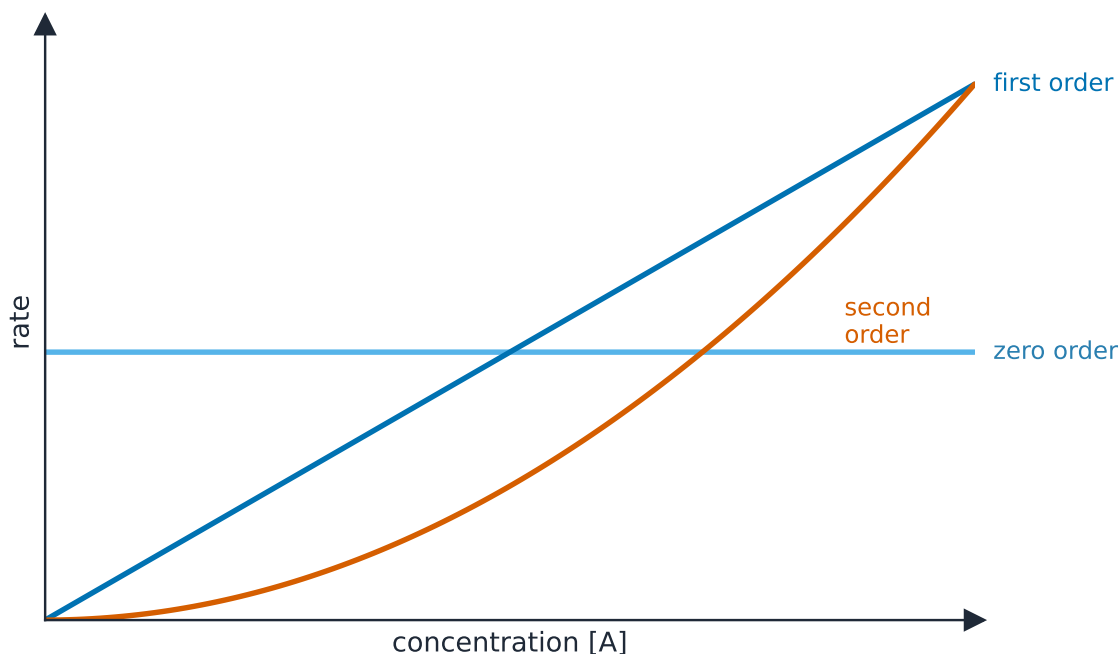
*A gas syringe: measuring gas volume over time gives reaction rate from the slope*

## 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.

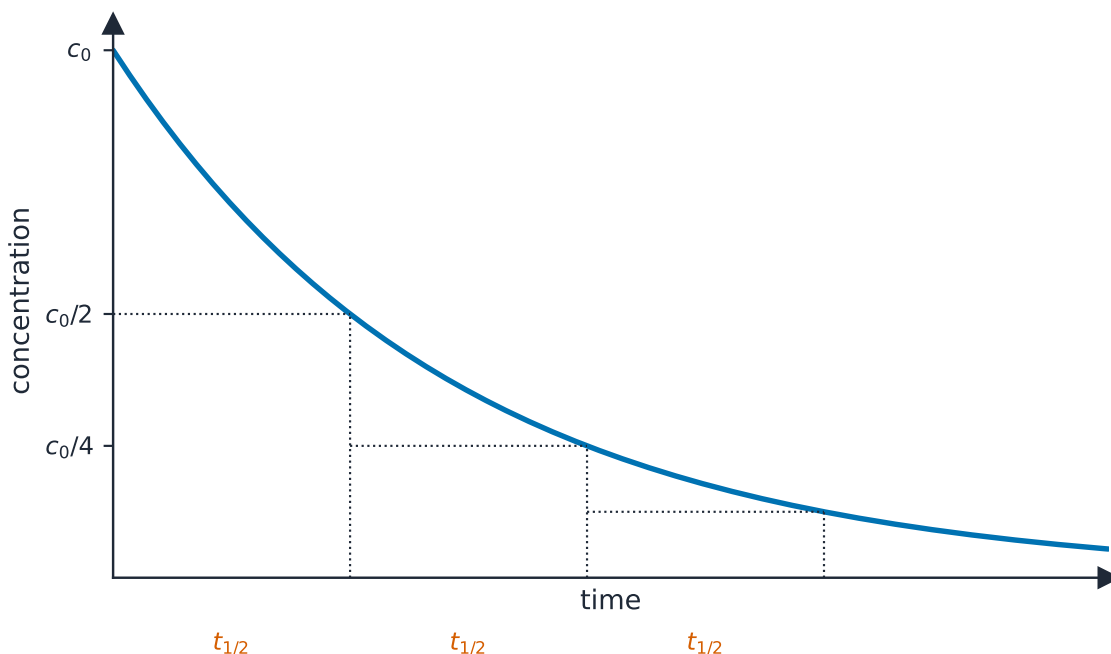


*Rate against concentration for zero-, first-, and second-order reactions*

**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  $\text{rate} = k[\text{A}]^2$ . 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

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

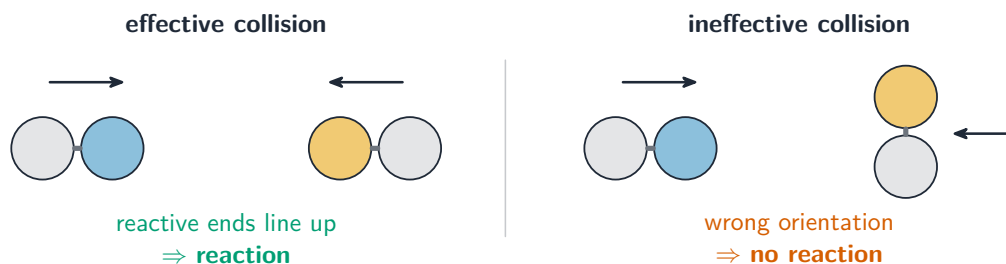
and, being first order, that half-life stays the same no matter how much reactant remains – so after 46 s (2 half-lives) one quarter is left.

# 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

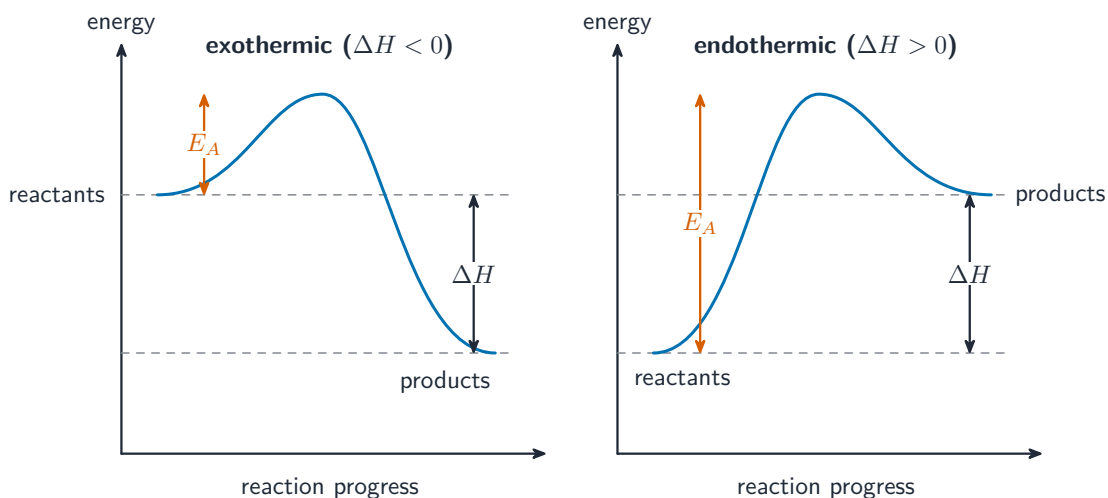
**Collision theory** : molecules must collide with enough energy (the **activation energy**,  $E_a$ ) and the correct **orientation** to react. Higher temperature means more molecules exceed  $E_a$ , so the reaction speeds up sharply.



*A collision only reacts with the right orientation and enough energy*

# Reading an Energy Profile

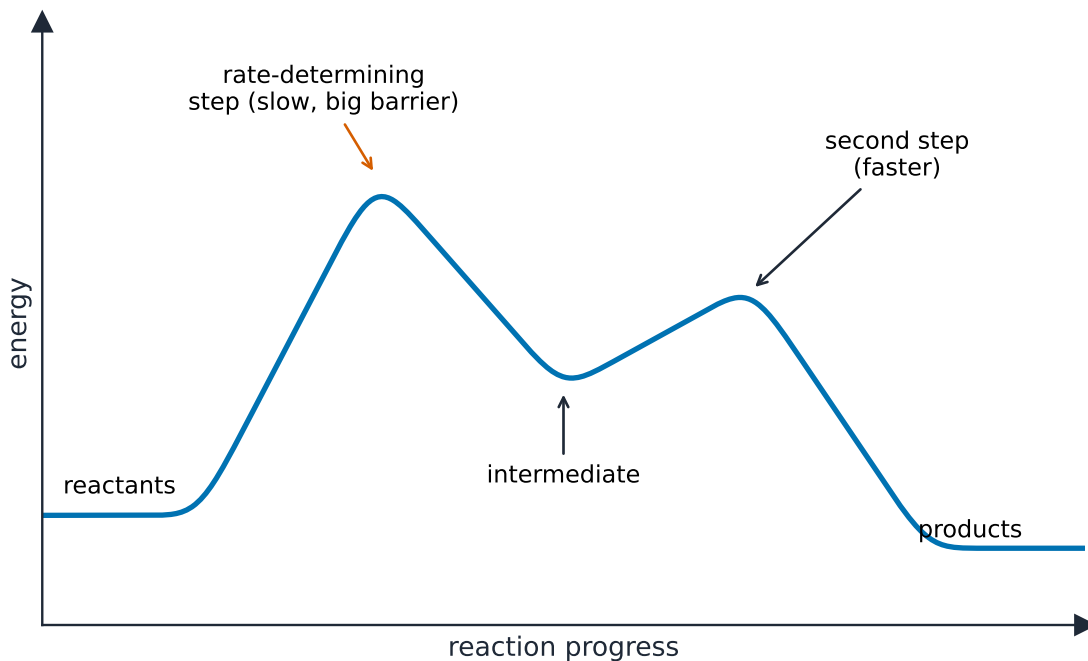
An **energy profile** plots energy along the reaction path. The peak is the **transition state**; the climb from reactants to the peak is  $E_a$ ; the difference between reactant and product energies is the enthalpy change  $\Delta H$  (down for exothermic).



*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  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ . Its molecularity gives the rate law directly:  $\text{rate} = k[\text{NO}_2]^2$ . If experiment shows exactly this, the proposed mechanism is consistent; if experiment gave  $\text{rate} = k[\text{NO}_2]$ , the mechanism would be wrong.

## When the First Step Is Fast

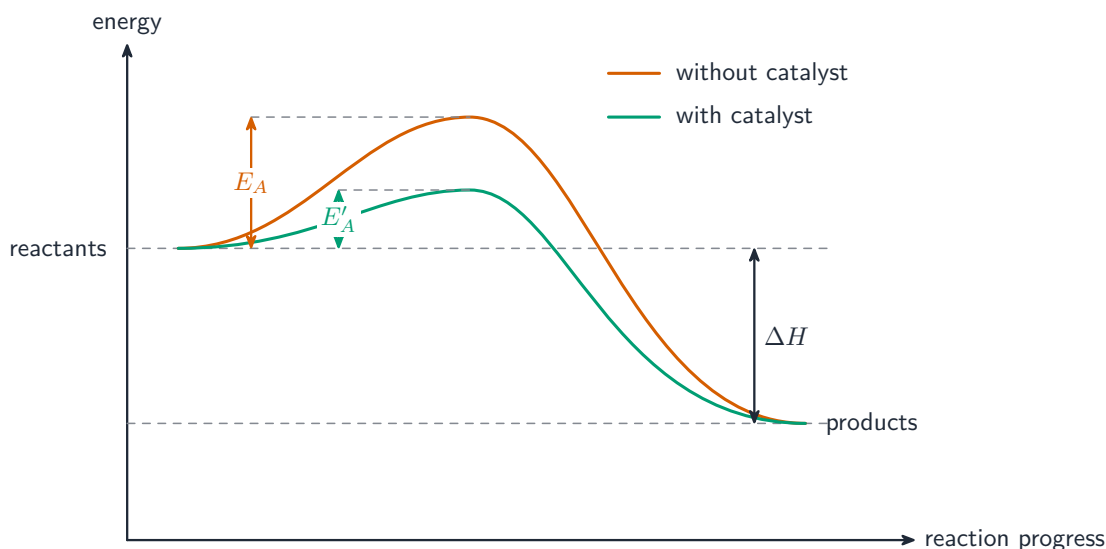
If a fast step precedes the slow one, an intermediate appears in the slow step's rate law. Use the **fast pre-equilibrium** to rewrite that intermediate in terms of reactants, so the final rate law contains only measurable species.

## 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  $\Delta H$  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  $\Delta H$ .
- A **catalyst** lowers the activation energy (a new pathway) but leaves  $\Delta H$  and the equilibrium position unchanged.

# Thermochemistry

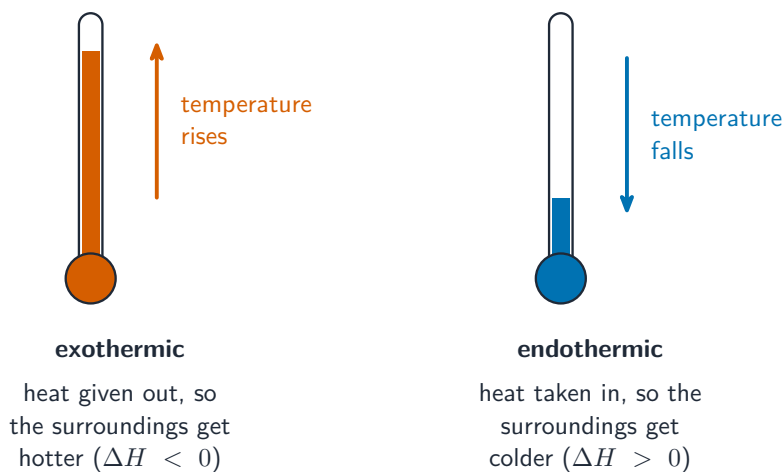
## AP Chemistry

### Endothermic and Exothermic Processes



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

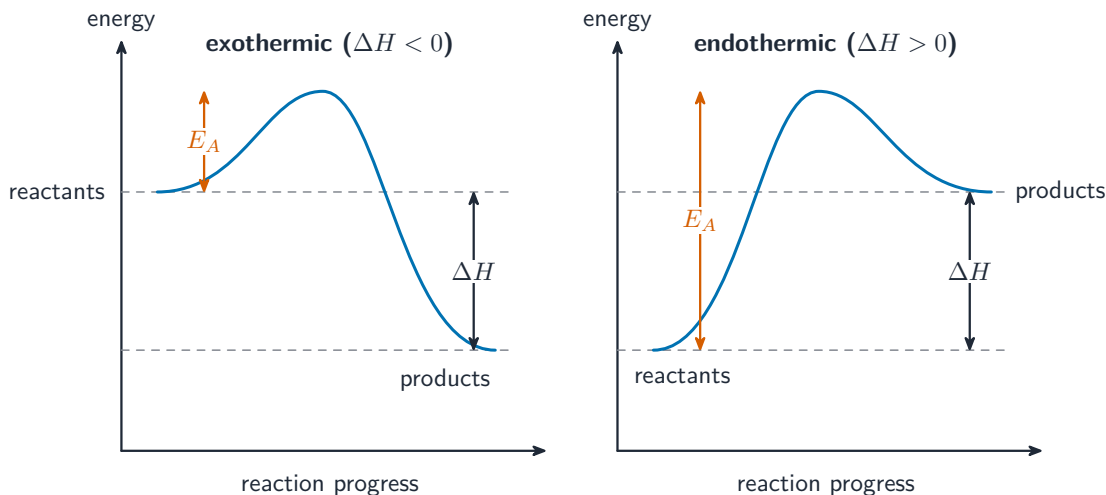
**Thermochemistry** tracks energy in reactions. A process is **exothermic** if it releases energy to the surroundings (feels hot,  $\Delta H < 0$ ) and **endothermic** if it absorbs energy (feels cold,  $\Delta H > 0$ ). Breaking bonds costs energy; forming bonds releases it – the net decides the sign.



*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  $\Delta H$ .



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

## Heat Transfer and Thermal Equilibrium

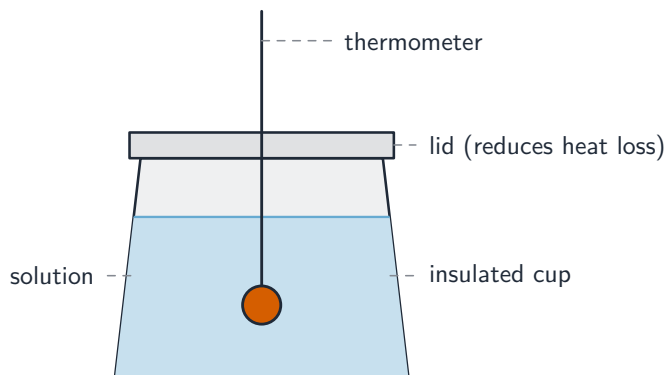
**Heat** flows from hot to cold until objects reach **thermal equilibrium** (equal temperature). Energy is conserved: the heat lost by the hot object equals the heat gained by the cold one.

# 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  $8.0^{\circ}\text{C}$  ( $c = 4.18 \text{ J}/(\text{g}^{\circ}\text{C})$ ). 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 ( $q_{\text{rxn}} = -3.3 \text{ kJ}$ ).

# 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

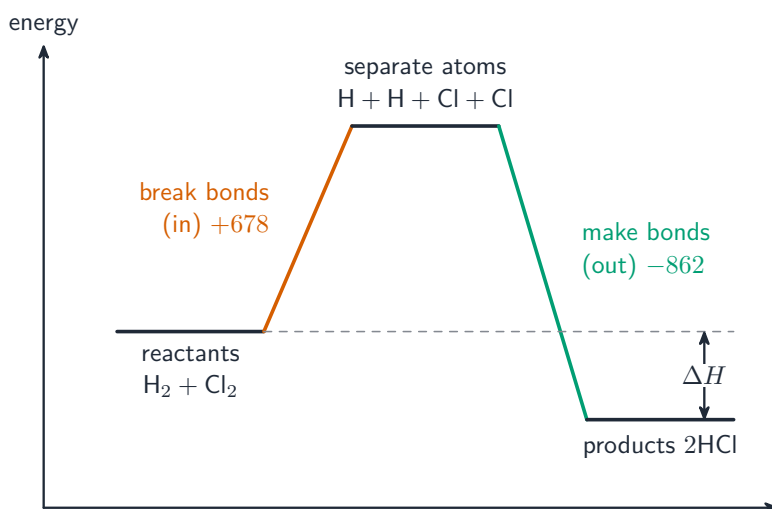
The **enthalpy of reaction**  $\Delta H_{\text{rxn}}$  is the heat released or absorbed at constant pressure. Because enthalpy is a **state function**,  $\Delta H$  depends only on the initial and final states, not the path taken – the key that makes the next three methods work.

## Bond Enthalpies

One way to estimate  $\Delta H$ : 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:  $\Delta H = 678 - 862 = -184 \text{ kJ/mol}$  (exothermic)

*Breaking bonds takes in energy; making bonds releases it*

**Worked example.** Estimate  $\Delta H$  for  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$  using bond enthalpies  $\text{H-H} = 436$ ,  $\text{Cl-Cl} = 242$ ,  $\text{H-Cl} = 431 \text{ kJ/mol}$ . Break both reactant bonds ( $436 + 242 = 678$ ) and form two  $\text{H-Cl}$  bonds ( $2 \times 431 = 862$ ):

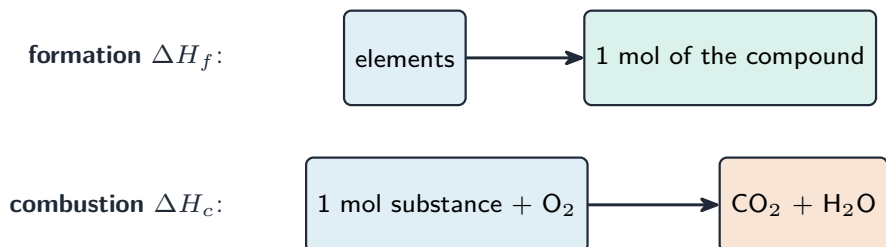
$$\Delta H \approx 678 - 862 = -184 \text{ kJ},$$

exothermic, because the strong  $\text{H-Cl}$  bonds formed release more than the reactant bonds cost.

# Enthalpy of Formation

The **standard enthalpy of formation**  $\Delta H_f^\circ$  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*

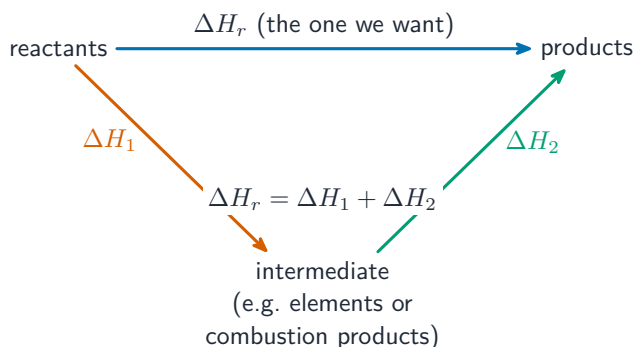
**Worked example.** Find  $\Delta H_{\text{rxn}}^\circ$  for burning methane,  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ , given  $\Delta H_f^\circ$ :  $\text{CH}_4 = -75$ ,  $\text{CO}_2 = -394$ ,  $\text{H}_2\text{O} = -286$  kJ/mol ( $\text{O}_2 = 0$ ). Products minus 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  $\Delta H$  is the sum of the steps'  $\Delta H$  values. Reverse a step and flip the sign; scale a step and scale its  $\Delta H$ . This lets you find a hard-to-measure  $\Delta H$  by combining known reactions – a frequent exam calculation.



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

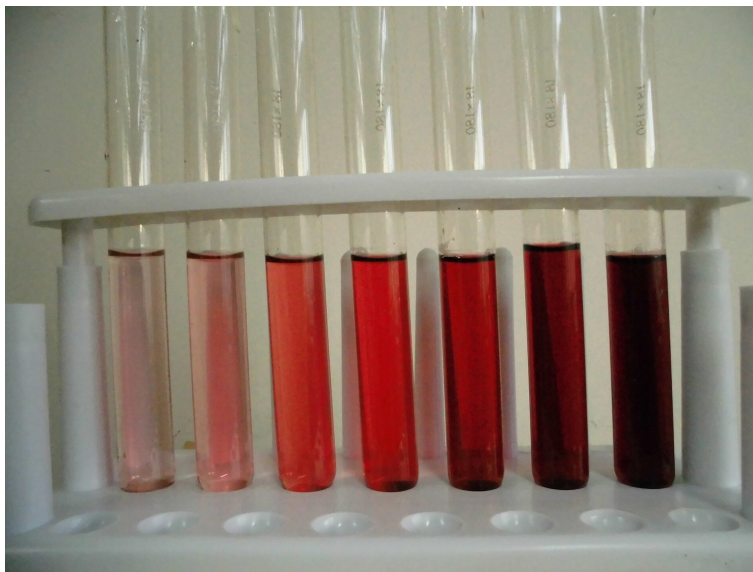
## Exam tips

- An **exothermic** reaction has  $\Delta H < 0$  (feels hot); endothermic has  $\Delta H > 0$  — always give  $\Delta H$  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  $\Delta H$  is the sum of the steps' — reverse a step and flip the sign, scale a step and scale  $\Delta H$ .
- During a **phase change** the temperature stays constant while energy goes into the forces between particles.

# Equilibrium

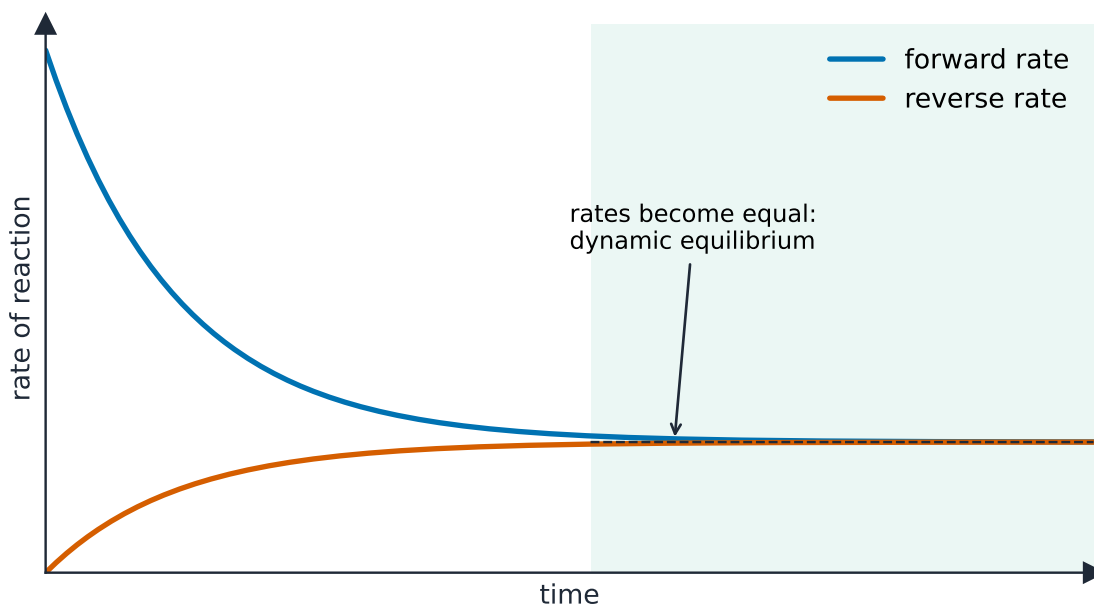
## AP Chemistry

### Introduction to Equilibrium



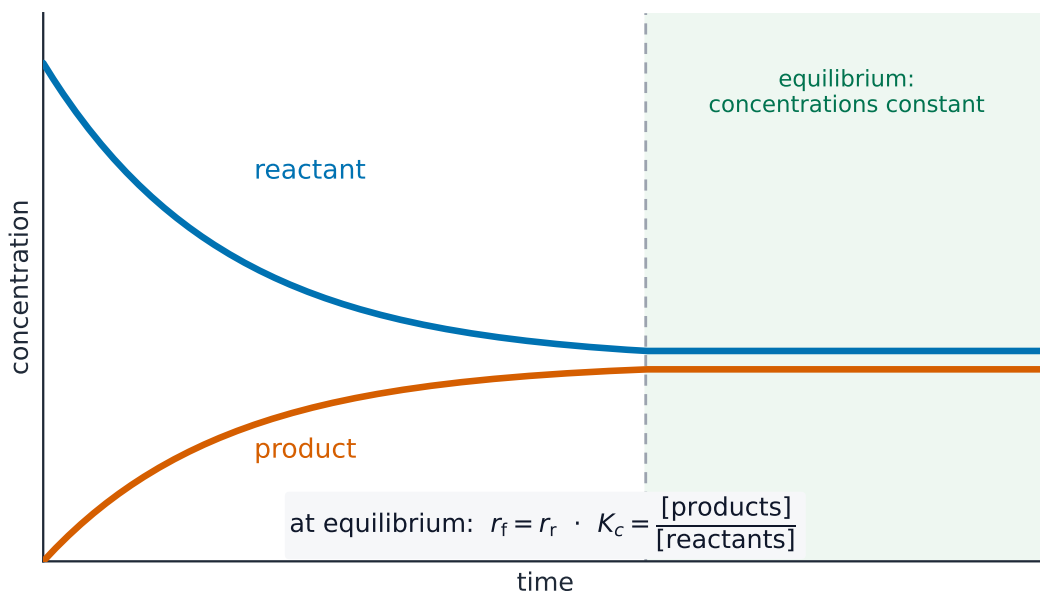
*Cobalt chloride solutions: equilibrium systems shift when conditions change (Le Chatelier)*

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  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ , the equilibrium concentrations are  $[\text{N}_2\text{O}_4] = 0.20 \text{ M}$  and  $[\text{NO}_2] = 0.10 \text{ M}$ . Then

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.10)^2}{0.20} = 0.050.$$

The  $\text{NO}_2$  coefficient of 2 becomes the power;  $\text{N}_2\text{O}_4$  (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  $n$ th 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  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$  with  $K_c = 50$ , start with 0.100 M each of  $\text{H}_2$  and  $\text{I}_2$ . The ICE table gives equilibrium  $[\text{H}_2] = [\text{I}_2] = 0.100 - x$  and  $[\text{HI}] = 2x$ . 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  $[\text{HI}] = 2x = 0.156$  M. Taking the square root of both sides works here because the expression is a perfect square.

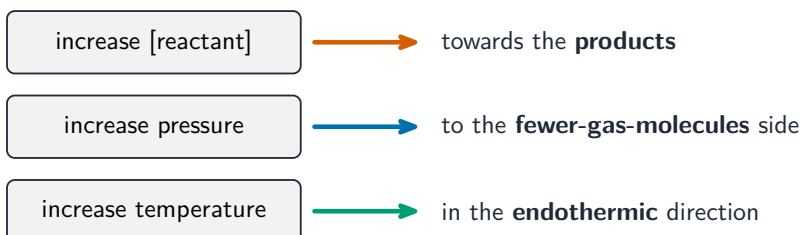
## Representations of Equilibrium

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.

the equilibrium shifts to *oppose* the change you make



a **catalyst** speeds both directions equally, so it gives *no shift*

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



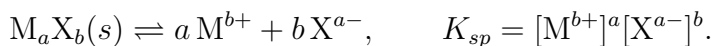
*An ammonia plant: industrial equilibria like Haber's process are driven by pressure, temperature and catalysts*

# 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:



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  $[Ag^+] = [Cl^-] = s$ , so  $K_{sp} = s^2$  and

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

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

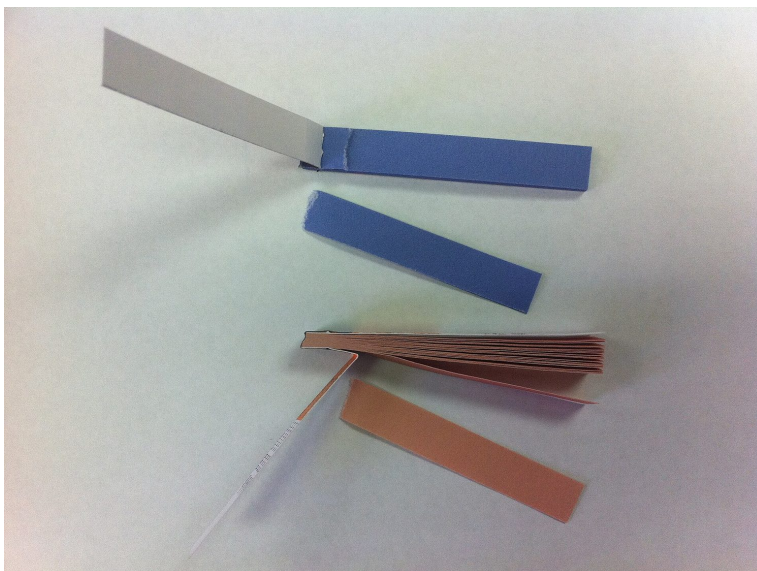
## Exam tips

- 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  $\rightarrow$  shift forward; raise pressure  $\rightarrow$  shift toward fewer gas moles; raise temperature  $\rightarrow$  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

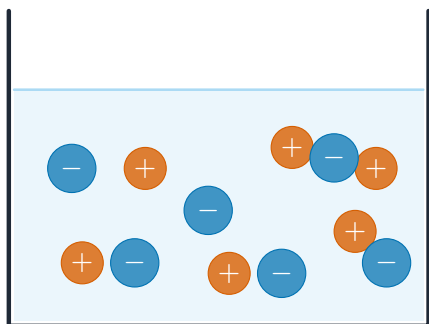
## AP Chemistry

### Introduction to Acids and Bases



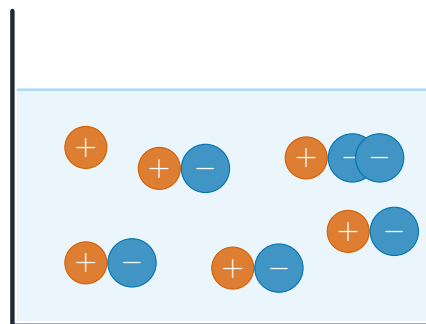
*Litmus paper: acid–base indicators change colour with  $H^+$  concentration (pH)*

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

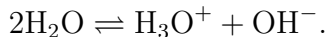
*A strong acid is fully dissociated; a weak acid is only partly dissociated*



*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** :



One water molecule passes a proton to another, making a **hydronium ion** ( $\text{H}_3\text{O}^+$ , the ion we loosely write as  $\text{H}^+$ ) and a hydroxide ion. This equilibrium has its own constant, the **ion-product constant of water** :

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

at 25 °C. Defining  $\text{pOH} = -\log[\text{OH}^-]$  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  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  and  $\text{pH} = \text{pOH} = 7.0$ . This is what **neutral** means. Acidic means  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$  (pH below 7); basic is the reverse.

**Worked example.** A solution has  $[\text{H}_3\text{O}^+] = 2.0 \times 10^{-3}$  M. Find  $[\text{OH}^-]$ . Because  $K_w$  always holds in water,

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12} \text{ M}.$$

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.

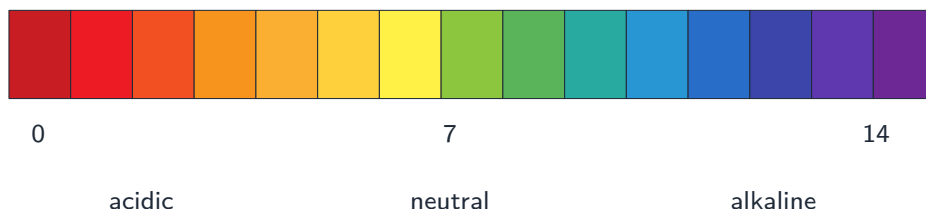


*pH strips: water autoionizes so pure water is pH 7; acids and bases shift  $\text{H}^+$  and  $\text{OH}^-$*

## pH and pOH of Strong Acids and Bases

The **pH** scale measures acidity:  $\text{pH} = -\log[\text{H}^+]$ , with  $\text{pH} + \text{pOH} = 14$  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.

$$\text{pH} = -\log[\text{H}^+]$$



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  $[\text{H}^+] = 0.010 \text{ M}$  and

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

For a strong **base** like 0.010 M NaOH,  $\text{pOH} = 2.0$ , so  $\text{pH} = 14 - 2.0 = 12.0$ .

# 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  $\text{p}K_a + \text{p}K_b = 14$  – a stronger acid always has a weaker conjugate base. Because dissociation is small, find  $[\text{H}^+]$  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  $x = [\text{H}^+]$  at equilibrium; the ICE table gives  $K_a = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$  (small- $x$  approximation), so

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

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

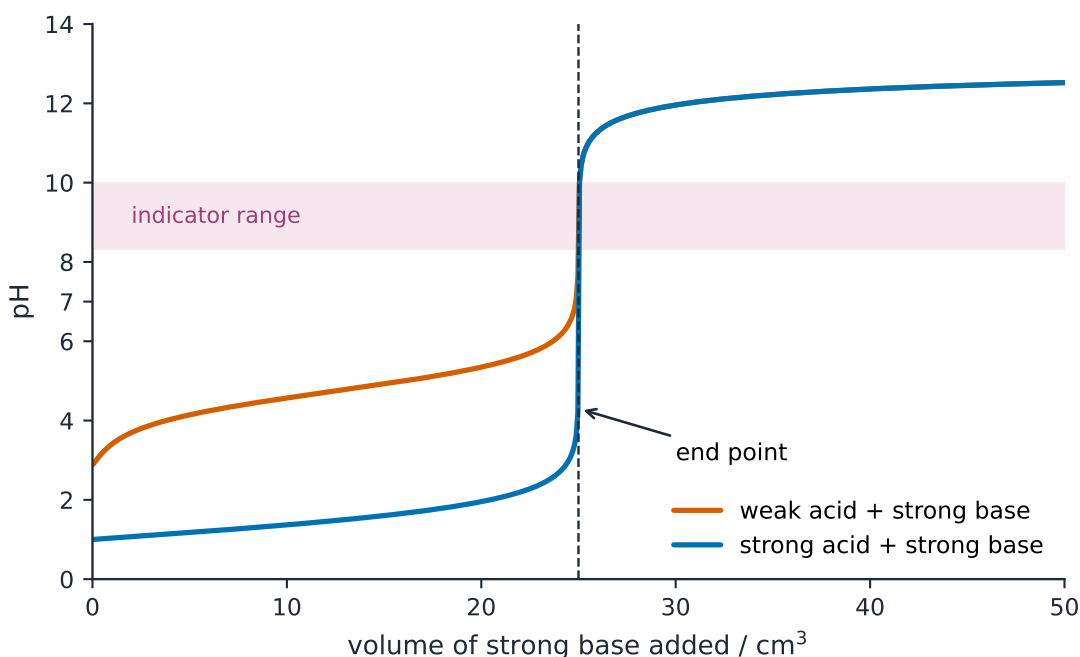
# Acid-Base Reactions and Buffers

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  $\text{pH} = \text{p}K_a$  (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

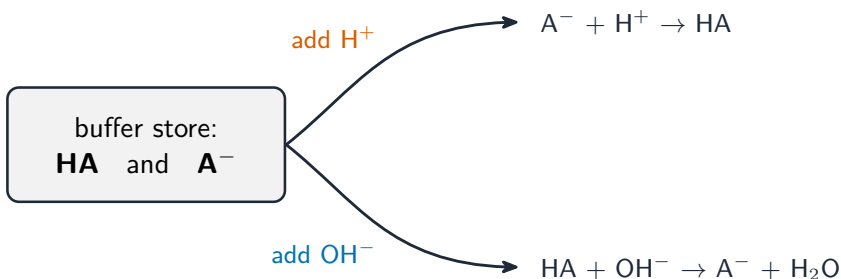
Strength has structural roots. An acid is stronger when its **conjugate base is more stable** – for example, more electronegative atoms or resonance spreading the negative charge stabilize it. For oxoacids, more oxygen atoms on the central atom means a stronger acid.

## pH and pK<sub>a</sub>

$pK_a = -\log K_a$ : 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.



either way, the pH barely changes

*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:

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

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

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

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

A little more conjugate base than acid pushes the pH just above  $\text{p}K_a$ , 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  $\text{H}^+$  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  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ ; since  $K_w$  rises with temperature, neutral pH drifts below 7 above 25 °C. Use  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  (25 °C) to convert between  $[\text{OH}^-]$  and  $[\text{H}_3\text{O}^+]$ .
- $\text{pH} = -\log[\text{H}^+]$  is **logarithmic** — each unit is a ten-fold change in  $[\text{H}^+]$ .
- A **strong** acid/base dissociates completely (so  $[\text{H}^+] = \text{concentration}$ ); 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  $\text{pH} = \text{p}K_a$ .
- A smaller  $\text{p}K_a$  means a stronger acid.

# Thermodynamics and Electrochemistry

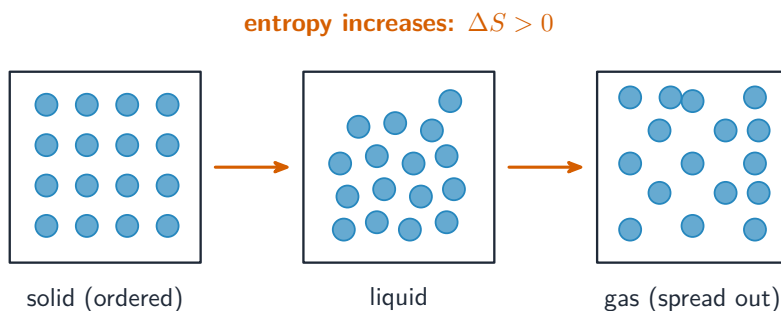
## AP Chemistry

### 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  $\rightarrow$  liquid  $\rightarrow$  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  $S^\circ$ . 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.

|                 | $\Delta S$ positive                         | $\Delta S$ negative                        |
|-----------------|---------------------------------------------|--------------------------------------------|
| $\Delta H$ neg. | feasible at<br><b>all</b> temperatures      | feasible only at<br><b>low</b> temperature |
| $\Delta H$ pos. | feasible only at<br><b>high</b> temperature | <b>never</b> feasible                      |

$$\Delta G = \Delta H - T\Delta S; \quad \text{feasible when } \Delta G \leq 0$$

*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

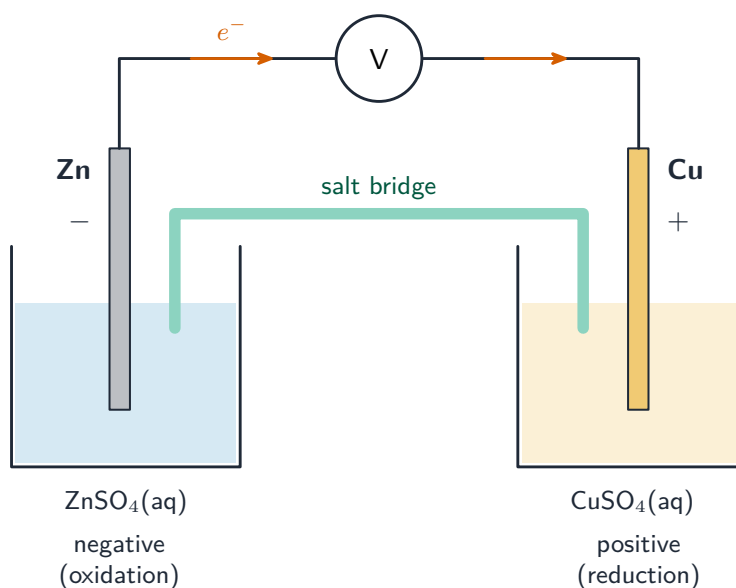
Whether a salt dissolves depends on the free-energy change of dissolving. Dissolving often increases entropy (ordered solid  $\rightarrow$  dispersed ions) but may cost enthalpy; the sign of  $\Delta G$  (and thus  $K_{sp}$ ) follows from  $\Delta H - T\Delta S$ .

# 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**



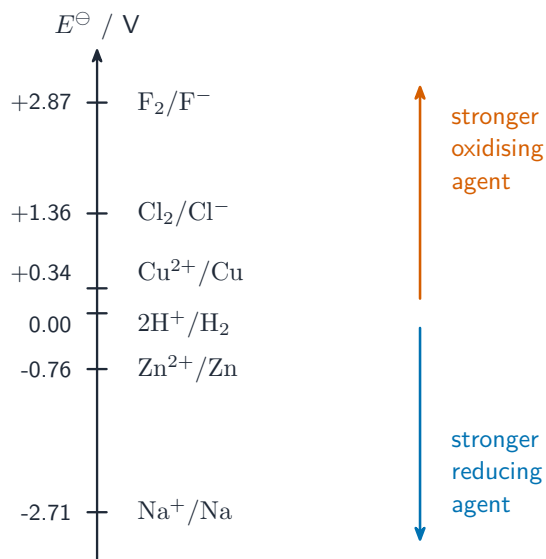
*Commercial batteries: galvanic cells convert chemical free energy into electrical work*

## Cell Potential and Free Energy

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

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

where  $n$  is moles of electrons and  $F$  the Faraday constant. A **positive**  $E_{\text{cell}}^{\circ}$  means a favorable (galvanic) reaction.



*The electrochemical series of standard electrode potentials*

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

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

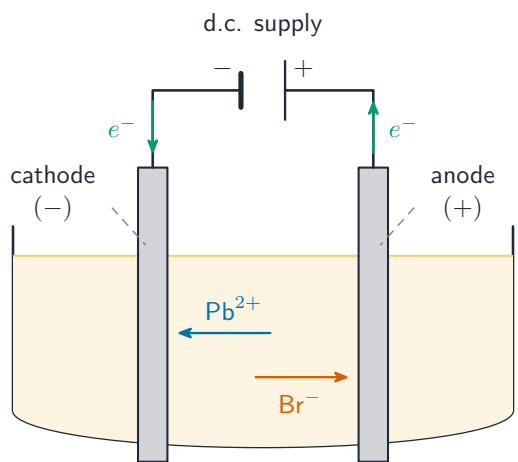
It is positive, so the reaction is spontaneous and the cell (a Daniell cell) acts as a battery.

## 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  $E_{\text{cell}}$  falls, reaching zero at equilibrium (a dead battery). Changing a concentration shifts  $E_{\text{cell}}$  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  $\times$  time to charge, charge to moles of electrons ( $F = 96,485 \text{ C/mol}$ ), then use the half-reaction's electron ratio to get moles (and mass) of product.



molten lead(II) bromide,  $\text{PbBr}_2$

cathode:  $\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$  (silvery lead)

anode:  $2\text{Br}^- \rightarrow \text{Br}_2 + 2e^-$  (red-brown bromine)

*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 ( $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ ). How much copper is deposited? The charge is  $Q = It = 2.0 \times 1800 = 3600 \text{ C}$ , giving  $3600/96485 = 0.0373 \text{ mol}$  of electrons. Since each Cu needs 2 electrons, 0.0187 mol of Cu forms, a mass of  $0.0187 \times 63.5 = 1.2 \text{ g}$ .

## 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**  $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$  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).