Course Companion

AP Chemistry

Every topic handout in one volume

全部专题讲义合集

exercises.lol

Contents 目录

1. **Atomic Structure and Properties** 2
2. **Compound Structure and Properties** 15
3. **Properties of Substances and Mixtures** 26
4. **Chemical Reactions** 41
5. **Kinetics** 52
6. **Thermochemistry** 65
7. **Equilibrium** 76
8. **Acids and Bases** 88
9. **Thermodynamics and Electrochemistry** 102

Atomic Structure and Properties

AP Chemistry

Moles and Molar Mass

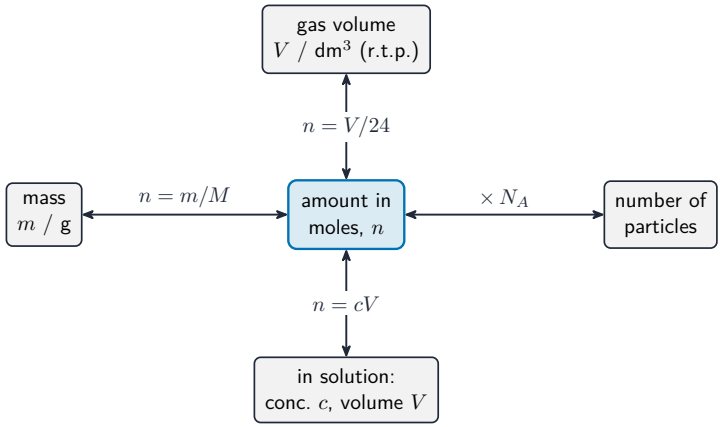
A one-carat diamond weighs only 0.200 g, yet it holds about 1.00×10^{22} carbon atoms. If you counted one atom per second, you would need more than 300 trillion years. Chemists never count atoms one by one. They weigh a sample and convert the mass to a number of particles. This unit shows how, and then looks inside the atom to explain why each element behaves as it does.

Because atoms are far too small to count, chemists count in **moles** 摩尔. One mole contains **Avogadro's number** 阿伏伽德罗常数 of particles, approximately 6.022×10^{23}. The **molar mass** 摩尔质量 (grams per mole; use atomic masses from the periodic table and add them for a compound) 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 numbers match on purpose. One water molecule has a mass of 18.0 **atomic mass units** 原子质量单位 (amu), and one mole of water has a mass of 18.0 g. The same number works at both scales because Avogadro's number is the number of amu in one gram.



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)?

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

Worked example (counting atoms inside a molecule). How many hydrogen atoms are in 5.00 g of glucose, $C_6H_{12}O_6$ ($M = 180.2$ g/mol)? Use dimensional analysis and let the units cancel:

$$5.00 \text{ g} \times \frac{1 \text{ mol glucose}}{180.2 \text{ g}} \times \frac{12 \text{ mol H}}{1 \text{ mol glucose}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol H}} = 2.01 \times 10^{23} \text{ H atoms}.$$

The middle factor comes from the formula: every glucose molecule carries 12 H atoms. Forgetting it gives the number of molecules, not atoms.

Mass Spectra of Elements

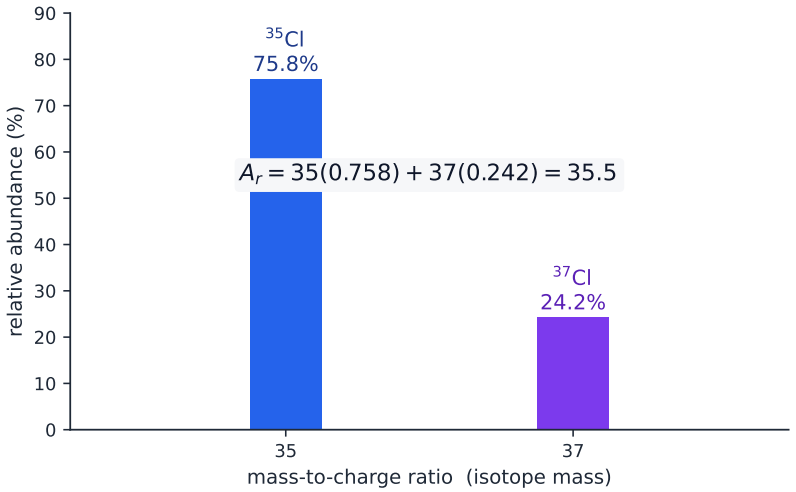
A **mass spectrometer** 质谱仪 separates ions by mass-to-charge ratio, giving a **mass spectrum** 质谱. For singly charged atomic ions, its peaks identify each **isotope** 同位素 (same element, different neutron count), with signals showing their **relative abundance** 相对丰度. The element's average **atomic mass** 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

exercises.lol exercises.com.cn



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.

Worked example (working backwards). Boron has two isotopes, boron-10 and boron-11, and an average atomic mass of 10.81. Let x be the fraction of boron-10. Then

$$10x + 11(1 - x) = 10.81 \quad \Rightarrow \quad x = 0.19.$$

So natural boron is about 19% boron-10 and 81% boron-11. A mass spectrum of boron would show a peak at 11 roughly four times as tall as the peak at 10.

Elemental Composition of Pure Substances

The **percent composition** 百分组成 of a compound is each element's mass fraction. From it you find the **empirical formula** 实验式 (simplest whole-number ratio of atoms) by converting each element's mass to moles and dividing by the smallest. The **molecular formula** 分子式 is a whole-number multiple of the empirical formula, found from the molar mass.

The **law of definite proportions** 定比定律 says that every pure sample of a compound has the same mass ratio of its elements. Water from a river and water from

a lab both contain 11.2% hydrogen by mass. Some substances are made of separate molecules, such as H_2O. Others, such as NaCl, are huge networks of ions; their formula only gives the ratio, called the **formula unit** 化学式单位.

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.

Worked example (a ratio that is not whole). An iron oxide is 69.9% Fe and 30.1% O by mass. In 100 g:

$$\mathrm{Fe}:\frac{69.9}{55.85}=1.252\ \text{mol},\qquad \mathrm{O}:\frac{30.1}{16.00}=1.881\ \text{mol}.$$

Dividing by 1.252 gives $1 : 1.50$. Do not round 1.50 to 2. Multiply both by 2 to get $2 : 3$, so the formula is Fe_2O_3.

Worked example (combustion analysis). A 0.500 g sample of a compound containing only C, H and O burns completely in oxygen to give 0.733 g of CO_2 and 0.300 g of H_2O. All the carbon ends up in the CO_2 and all the hydrogen in the water:

$$\mathrm{C}:\ \frac{0.733}{44.01}=0.01666\ \text{mol}\ (0.200\ \text{g}),\qquad \mathrm{H}:\ 2\times\frac{0.300}{18.02}=0.0333\ \text{mol}\ (0.0336\ \text{g}).$$

Oxygen came partly from the air, so find the sample's oxygen by difference: $0.500 - 0.200 - 0.0336 = 0.266$ g, which is 0.01665 mol. The ratio C : H : O is $1 : 2 : 1$, so the empirical formula is CH_2O.

exercises.lol exercises.com.cn

Composition of Mixtures

Unlike a pure compound, a **mixture** 混合物 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.

Elemental analysis also measures **purity** 纯度. Compare the measured mass percent of an element with the value for the pure compound.

Worked example (purity of table salt). Pure NaCl is $35.45/58.44 = 60.7\%$ chlorine by mass. A salt sample mixed with sand (which has no chlorine) contains 48.5% Cl. The fraction of the sample that is NaCl is

$$\frac{48.5}{60.7}=0.799,$$

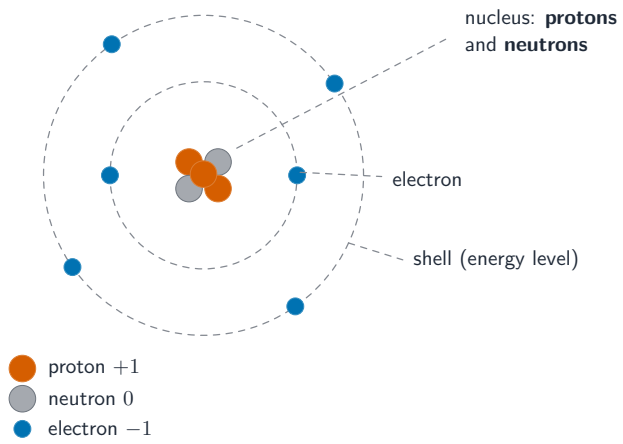
so the sample is about 80% NaCl. Now suppose the impurity is another chloride instead of sand. KCl is only 47.6% Cl, so it would *lower* the chlorine percent. LiCl is 83.6% Cl, so it would *raise* it above 60.7%. A result above the pure value is a clue that the impurity is richer in that element than the compound.

Atomic Structure and Electron Configuration

An atom is a tiny **nucleus** 原子核 (protons and neutrons) surrounded by electrons in **shells** and **subshells** (s, p, d, f). The **electron configuration** 电子排布 lists how electrons fill these, lowest energy first (e.g. $1s^2\,2s^2\,2p^6$). For main-group atoms, the outer-shell electrons are the **valence electrons** 价电子 that take part in bonding. Transition-metal bonding can also involve electrons in an inner d subshell. **Coulomb's law** 库仑定律 explains their energies:

$$F \propto \frac{q_1 q_2}{r^2}.$$

The attraction grows with the charges and falls quickly with distance. Electrons closer to the nucleus, with less **shielding** 屏蔽 from it, are held more tightly. Inner electrons are called **core electrons** 内层电子. They sit close to the nucleus and also shield the outer electrons from part of its charge. The charge an outer electron actually feels is the **effective nuclear charge** 有效核电荷, roughly the number of protons minus the number of core electrons.



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

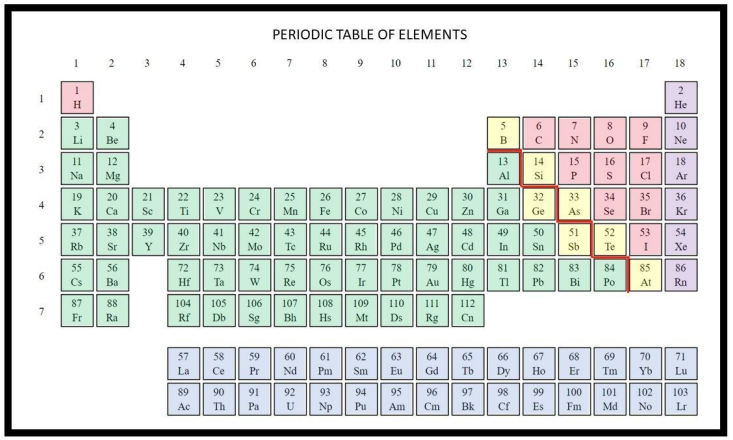


Flame tests: each metal ion gives its own colour because heat excites its electrons and, as they drop back down, they emit light of specific wavelengths

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.

exercises.lol exercises.com.cn

Worked example (ions). For ions, add or remove electrons from the configuration. S^{2-} gains two: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$, the same as argon. Na^+ loses its $3s$ electron: $1s^2\,2s^2\,2p^6$, the same as neon. Removing a second electron from Na^+ means taking a core $2p$ electron, which is far closer to the nucleus and feels about 9 units of charge instead of about 1. That is why sodium forms +1 ions in ordinary compounds rather than +2 ions.



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

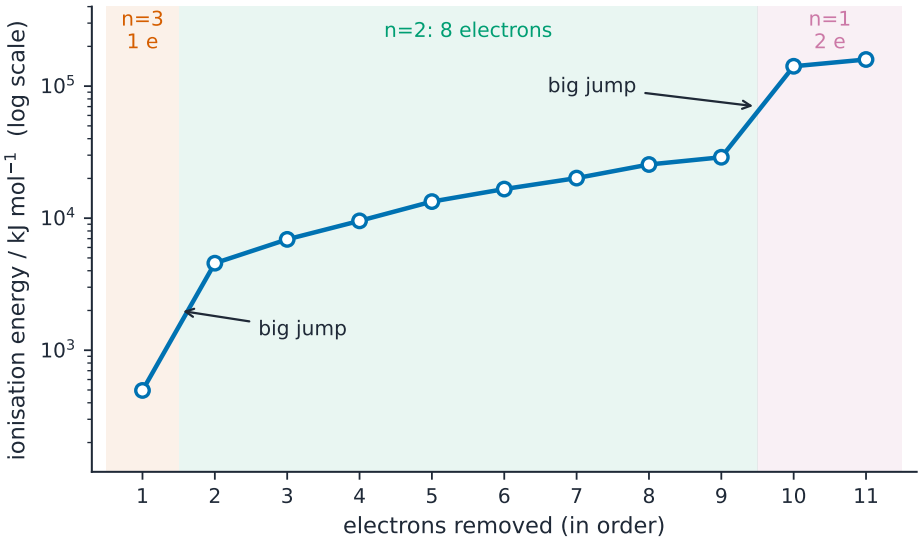
Photoelectron Spectroscopy

Photoelectron spectroscopy 光电子能谱 (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.

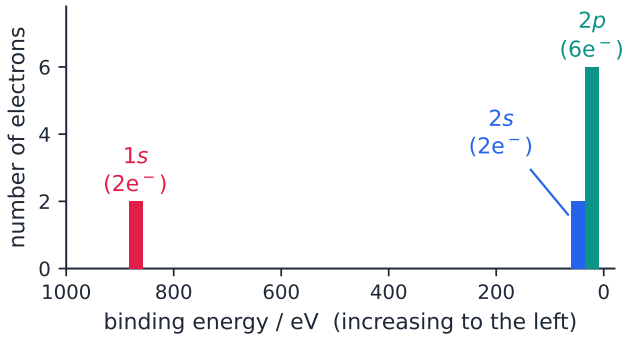
Two more rules help you read a spectrum. First, on a spectrum with binding energy decreasing from left to right, peaks at the far left (largest binding energy) belong to the $1s$ electrons, the closest to the nucleus. Second, the same core subshell generally has higher binding energy across a period, because more protons pull on it. The $1s$ peak of sodium (11 protons) lies further left than the $1s$ peak of neon (10 protons).

Worked example (identify the element). A photoelectron spectrum has three peaks. From left to right their relative heights are 2, 2 and 3. The peaks are $1s$, $2s$ and $2p$, so the configuration is $1s^2\,2s^2\,2p^3$. That is 7 electrons: nitrogen. If instead there were four peaks with heights 2, 2, 6 and 1, the configuration would be $1s^2\,2s^2\,2p^6\,3s^1$: sodium.

Worked example (from energy to light). The first ionization energy of sodium is 496 kJ/mol. One atom needs $\dfrac{496\,000}{6.022\times10^{23}} = 8.24\times10^{-19}$ J. The longest wavelength that can remove the electron is $\lambda = \dfrac{hc}{E} = \dfrac{(6.626\times10^{-34})(3.00\times10^{8})}{8.24\times10^{-19}} = 2.41\times10^{-7}$ m, in the ultraviolet. Always change molar energies to energy per atom before using $E = hc/\lambda$.



Successive ionisation energies reveal the shell structure through big jumps



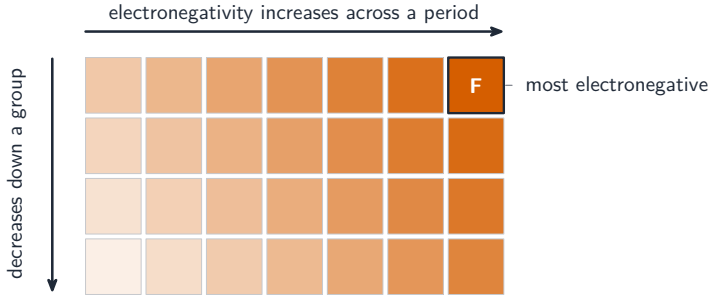
The photoelectron spectrum of neon: one peak per subshell, height set by electron count

exercises.lol exercises.com.cn

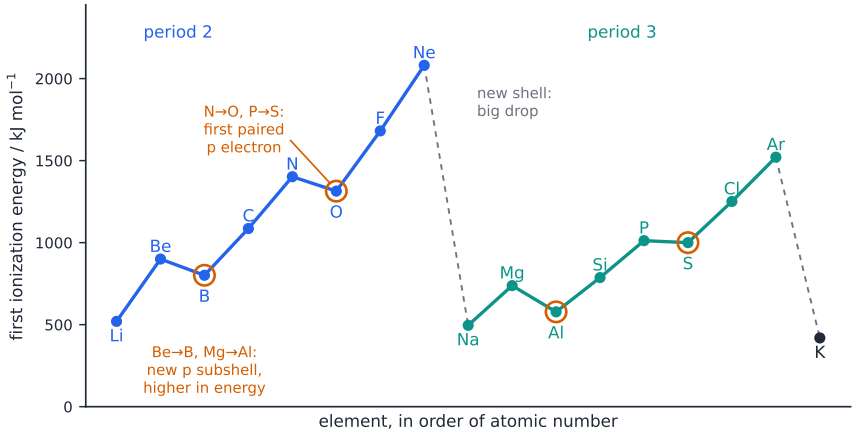
Periodic Trends

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

- **Atomic radius** 原子半径 decreases across a period (stronger pull) and increases down a group (more shells).
- **Ionization energy** 电离能 (energy to remove an electron) increases across, decreases down – opposite to radius.
- **Electronegativity** 电负性 (pull on shared electrons) increases across and up, toward fluorine.
- **Electron affinity** 电子亲和能 (energy released when an atom gains an electron) generally becomes more favourable across a period, for the same reason: a higher effective nuclear charge pulls the incoming electron in.



Electronegativity rises across a period and falls down a group



Ionization energy rises across each period, drops at each new shell, and dips slightly at boron/aluminium and oxygen/sulfur

The trend has two small dips, and both can be explained. Boron's first ionization energy is lower than beryllium's because boron's outer electron is in a $2p$ subshell, slightly higher in energy than $2s$ and partly shielded by it. Oxygen's is lower than nitrogen's because oxygen's fourth $2p$ electron must share an orbital with another electron, and the two repel each other.

Ionic radius 离子半径 follows a similar logic. A cation is smaller than its atom: it has lost its outer shell, or at least some outer electrons, while the nuclear charge stays the same. An anion is larger: the extra electrons repel each other. For **isoelectronic** 等电子 ions (same number of electrons), the one with more protons is smaller:

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

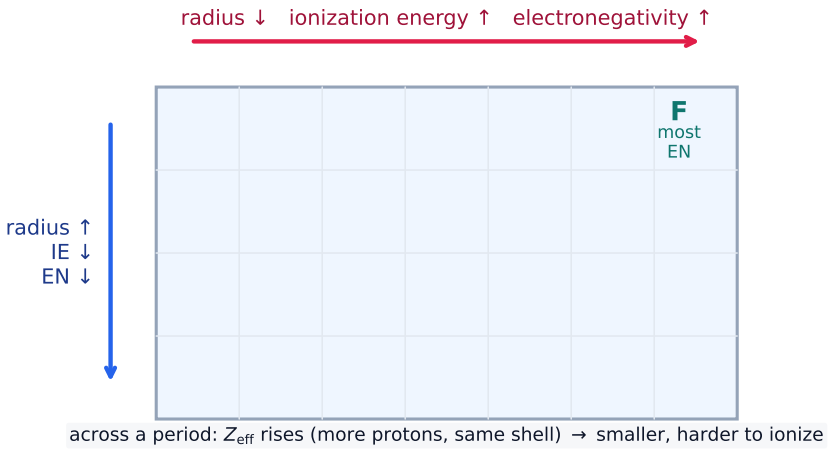
All four have 10 electrons, but the nuclear charge rises from 8 to 12.

Exam skill (explaining with Coulomb's law). "Explain using atomic structure" questions earn full credit with three linked steps: name the difference in structure (protons, shells, or shielding), say how it changes the distance or the charge, then use **Coulomb's law** ($F \propto q_1 q_2 / r^2$) to say how the attraction changes.

- *Why is Al^{3+} smaller than Al?* Al loses its three $n = 3$ electrons, so the ion's outermost electrons are in $n = 2$, closer to the nucleus. Thirteen protons now attract only ten electrons, so the pull on each is stronger and the ion is smaller.
- *Why is Ag larger than Cu?* Silver's valence electron is in $n = 5$, copper's in $n = 4$, so it is further from the nucleus on average. Silver has more protons, but the extra inner electrons shield them, so the attraction on the valence electron is weaker and the atom is larger.

> **Worked example (predicting from trends).** The atomic radius of chlorine is 99 pm and of iodine is 133 pm. Bromine lies between them in group 17, so a good estimate is the average, about 116 pm. The measured value is 114 pm. Periodicity lets you estimate a property you have no data for.

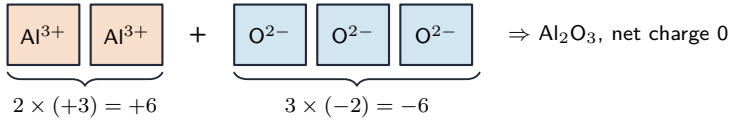
exercises.lol exercises.com.cn



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** 阳离子; nonmetals gain electrons to form **anions** 阴离子. Oppositely charged ions attract into an **ionic compound** 离子化合物, 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.



An ionic formula balances charge: two aluminium ions (+6) and three oxide ions (-6) make Al2O3

Elements in the same group form **analogous compounds** (compounds with the same pattern of formula). Magnesium forms $MgCl_2$, so calcium and strontium form $CaCl_2$ and $SrCl_2$; sodium forms Na_2O, so potassium forms K_2O. Reactivity also follows the table. Group 1 metals react more violently with water going down the group, because the outer electron is further from the nucleus and easier to lose: lithium fizzes, sodium races around, and potassium bursts into flame. Halogens become less reactive going down, because a larger atom pulls an extra electron in less strongly.

Common mistakes.

- Taking the simple average of the isotope masses. Weight each mass by its **abundance**: chlorine is 35.5, not 36.
- Rounding a mole ratio such as $1 : 1.33$ to $1 : 1$. A decimal near .33, .5 or .67 means you multiply: $1 : 1.33 \times 3 = 3 : 4$.
- Reading the tallest PES peak as the most tightly held electrons. Peak **height** gives the number of electrons; peak **position** (binding energy) gives how tightly they are held, and the core $1s$ peak is furthest out.
- Explaining a smaller radius across a period by "more shells". Across a period the shell count stays the same; the **nuclear charge** rises while shielding hardly changes, so the electrons are pulled closer.
- Removing a transition metal's $3d$ electrons before its $4s$ electrons when it forms an ion. The $4s$ electrons are lost **first**: Fe^{2+} is $[Ar]\,3d^6$, not $[Ar]\,4s^2\,3d^4$.
- Saying ionization energy falls down a group because the nucleus has less charge. The nuclear charge **rises**, but the outer electron is further away and more shielded, so it is held less tightly.

Practice

Answer each before reading the answers below.

1. What is the mass of 0.250 mol of $CaCO_3$ ($M = 100.09$ g/mol)?
2. A compound is 40.0% C, 6.7% H and 53.3% O by mass, and its molar mass is about 180 g/mol. Find its empirical and molecular formulas.
3. An element has two isotopes: mass 69 (60.1%) and mass 71 (39.9%). Calculate its average atomic mass and identify the element.
4. Write the ground-state electron configurations of Fe and Fe^{3+}.
5. In the photoelectron spectrum of sodium, which peak is the tallest, and which has the greatest binding energy? Explain both.
6. Use Coulomb's law to explain why the first ionization energy of Mg is greater than that of Na.

Answers

1. $0.250 \times 100.09 = 25.0$ g.
2. Per 100 g: C 3.33 mol, H 6.65 mol, O 3.33 mol, a ratio of $1 : 2 : 1$, so the empirical formula is CH_2O (30 g/mol). $180 \div 30 = 6$, so the molecular formula is $C_6H_{12}O_6$.
3. $69(0.601) + 71(0.399) = 69.8$ amu: gallium.
4. Fe: $[Ar]\,4s^2 3d^6$. Fe^{3+}: $[Ar]\,3d^5$, because the $4s$ electrons are removed first.
5. The $2p$ peak is tallest, because it holds 6 electrons (the peak height is proportional to the number of electrons). The $1s$ peak has the greatest binding energy, because those electrons are closest to the nucleus and least shielded.

exercises.lol exercises.com.cn

6. Both lose a $3s$ electron from the same shell with similar shielding, but Mg has 12 protons and Na has 11. The greater nuclear charge attracts the electron more strongly, so more energy is needed to remove it.

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

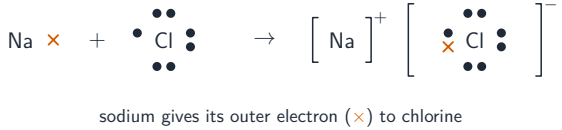
Hit a salt crystal with a hammer and it shatters. Hit a copper coin and it only bends. Drag a diamond across glass and the glass is scratched. All three are solids at room temperature, yet they behave completely differently, because their particles are held together in different ways. This unit links those properties to the bonds inside, and then to the shapes of molecules.



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

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

- **Ionic bond** 离子键: electrostatic attraction holds oppositely charged ions together. Electron transfer from a metal to a nonmetal can form these ions.
- **Covalent bond** 共价键: nonmetals **share** electrons (small difference). A big-but-not-huge difference gives a **polar covalent** 极性共价 bond.
- **Metallic bond** 金属键: metal atoms share a "sea" of mobile electrons.



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

Bond type is really a **continuum**, not three separate boxes. The atom with the higher electronegativity pulls the shared electrons toward itself and gets a **partial negative charge** ($\delta-$); the other atom is $\delta+$. The larger the electronegativity difference, the larger the bond dipole and the more **ionic character** the bond has. C–H bonds are treated as nonpolar, because carbon (2.5) and hydrogen (2.1) are so close.

> **Worked example (rank bond polarity).** Use electronegativities H 2.1, C 2.5, N 3.0, O 3.5, F 4.0. The differences are H–F 1.9, H–O 1.4, H–N 0.9 and H–C 0.4. So the polarity order is H–F > H–O > H–N > H–C, and in each bond the $\delta-$ end is the non-hydrogen atom. Electronegativity alone does not decide ionic versus covalent, though: as a rule, a metal with a nonmetal is ionic and two nonmetals are covalent.



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

Bond	Bond order	Length / pm	Bond energy / kJ mol^{-1}
C–C	1	154	347
C=C	2	134	614
C≡C	3	120	839

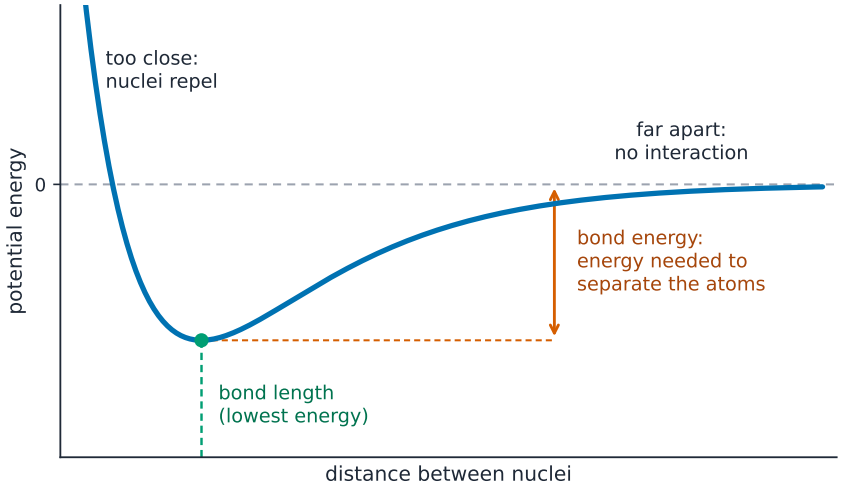
Atom size matters too. H–F (92 pm) is much shorter than H–I (161 pm), because

exercises.lol exercises.com.cn

iodine's outer electrons are in a shell much further from its nucleus. At very short distances the curve rises steeply, because the two nuclei repel each other.

For ions, **Coulomb's law** sets the strength: the attraction grows with the ion charges and is larger for smaller ions, which can come closer together.

> **Worked example (rank lattice strength).** Rank MgO, NaF, NaCl and KCl from strongest to weakest attraction. MgO has charges of 2+ and 2−, four times the product of the others, so it is strongest. Among the 1+/1− salts, compare size: F^- is smaller than Cl^-, and Na^+ is smaller than K^+. So the order is MgO > NaF > NaCl > KCl. Their melting points follow the same order: 2852, 993, 801 and 770 °C.



Potential energy is lowest at the bond length; the well depth is the bond energy

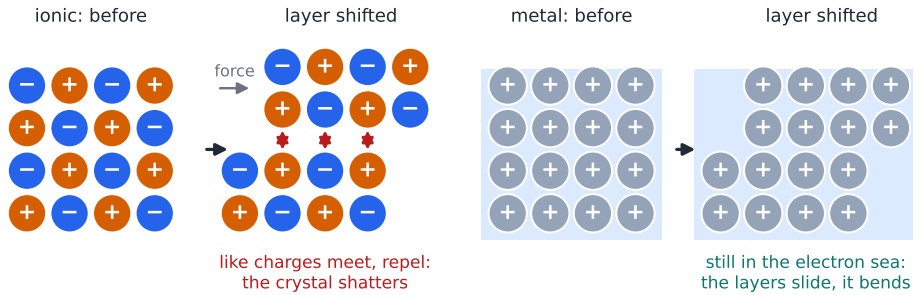
Exam skill (sketching a curve). Asked to draw the curve for an Al–Cl bond of length 220 pm and energy 425 kJ/mol, put the minimum at $x = 220$ pm and $y = -425$ kJ/mol. Then draw a steep rise to the left of it (the nuclei repel), and a slow rise to the right that levels off at zero (separate atoms). For a shorter, stronger bond, the minimum moves *left and down*; for a longer, weaker one, *right and up*.

Structure of Ionic Solids

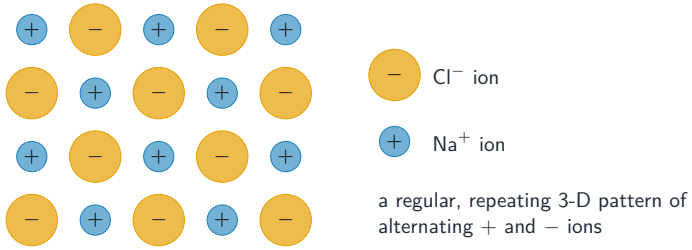
An **ionic solid** 离子固体 is a repeating 3-D **lattice** 晶格 of alternating cations and anions, held by strong electrostatic attraction. This explains their high melting points, brittleness, and why they conduct only when molten or dissolved (ions freed to move). The **lattice energy** rises with larger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

exercises.lol exercises.com.cn

The ions arrange themselves so that each one is surrounded by ions of the **opposite** charge: attraction is as large as possible and repulsion as small as possible. In a particle drawing, show cations and anions alternating, and draw the smaller ion smaller (for example, Na^+ smaller than Cl^-).



A force that shifts an ionic layer by one ion lines up like charges, which repel; in a metal the shifted ions are still surrounded by the electron sea

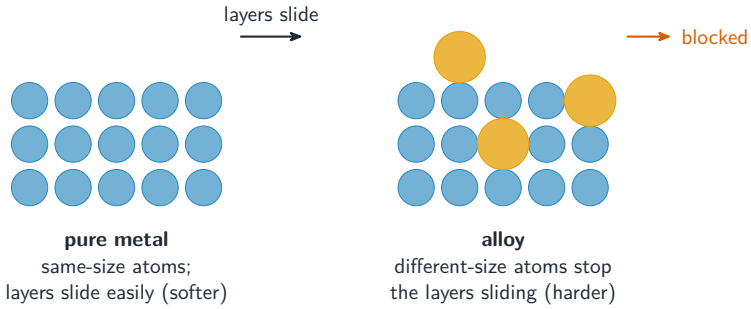


Ions pack into a giant lattice of alternating positive and negative ions

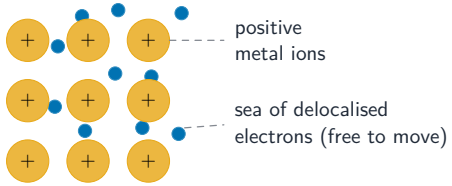
Structure of Metals and Alloys

In a metal, cations sit in a lattice bathed in **delocalized** 离域 electrons, which explains conductivity, malleability, and luster. An **alloy** 合金 combines a metal with one or more other elements: a **substitutional** alloy swaps in similar-sized atoms; an **interstitial** alloy (like steel) fits small atoms into the gaps, making it harder.

Brass is a substitutional alloy: zinc atoms, close in size to copper atoms, replace some of the copper in the lattice. Brass is harder than pure copper but still easy to shape. **Steel** is interstitial: small carbon atoms sit in the gaps between much larger iron atoms. They lock the layers in place, so steel is harder and stronger, but less malleable and less ductile than pure iron. Both alloys still conduct electricity, because the delocalized electrons remain.



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



Metallic bonding: positive ions in a sea of delocalised electrons

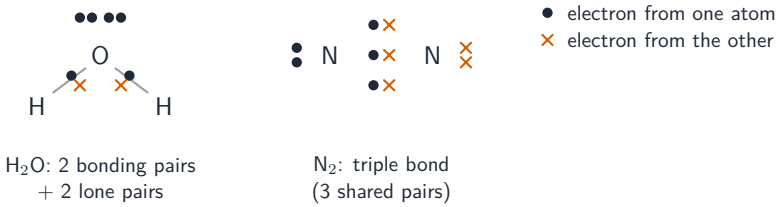


Native copper: metallic bonding gives a shiny, malleable solid with delocalised electrons

exercises.lol exercises.com.cn

Lewis Diagrams

A **Lewis diagram** 路易斯结构 shows valence electrons as bonding pairs and **lone pairs** 孤对电子, giving most atoms an **octet** 八隅体 (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.

Worked example (a triple bond). Draw hydrogen cyanide, HCN. Valence electrons: $1+4+5 = 10$. Put C in the centre (H can form only one bond, so it is never central): H–C–N uses 4 electrons. Putting the remaining 6 on N as three lone pairs leaves C with only 4 electrons. Move two of N's lone pairs into bonds: H–C≡N, with one lone pair on N. Now C has 8, N has 8 and H has 2.

Some molecules break the octet rule:

- **Fewer than eight**: boron in BF_3 has only 6 electrons around it.
- **More than eight (expanded octet)**: atoms in period 3 and below, such as P, S, Cl and Xe, can hold 10 or 12, as in PCl_5 and SF_6.
- **Odd numbers of electrons**: NO has 11 valence electrons, so one atom must be left with an unpaired electron. The Lewis model cannot describe such molecules well; this is one of its limits.

Resonance and Formal Charge

When two or more valid Lewis diagrams differ only in electron placement, one delocalized electron distribution is represented by these contributors – **resonance** 共振. The molecule does not switch between them. **Formal charge** 形式电荷 (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

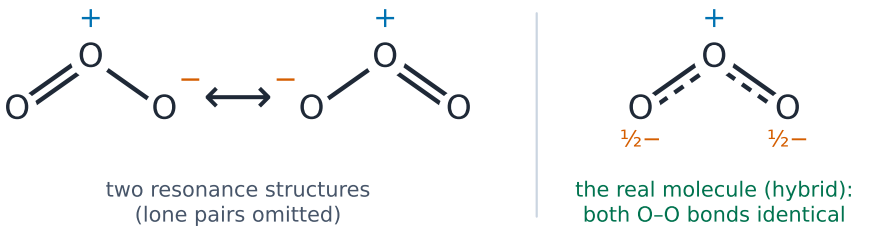
most electronegative atom.

> **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.

Each N–O bond in nitrate is "one and a third" bonds: shorter and stronger than a single bond, longer and weaker than a double bond. Resonance changes predictions about bond length that a single Lewis diagram would get wrong.

> **Worked example (unequal bond lengths).** In the hydrogen carbonate ion, HCO_3^-, carbon bonds to three oxygens, but one of them also carries the H. The negative charge is shared, by resonance, between the two oxygens *without* H, so each of those C–O bonds is "one and a half" bonds. The C–OH bond is a single bond in the two main resonance contributors. So two C–O bonds are equal and shorter, and the C–OH bond is longer.

> **Worked example (choosing with formal charge).** Two Lewis diagrams can be drawn for CO_2 with octets everywhere: O=C=O, and O≡C–O. In O=C=O every formal charge is 0. In O≡C–O the triple-bonded O is $6-2-3=+1$, C is $4-0-4=0$, and the single-bonded O is $6-6-1=-1$. The first structure has all formal charges at zero, so it is the better model, and it matches the measured fact that both C–O bonds in CO_2 are the same length.



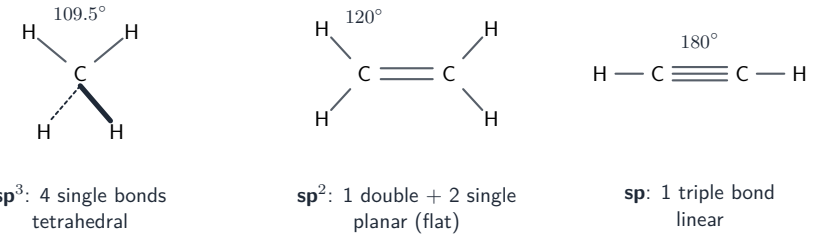
Ozone has two resonance structures; the real molecule is their hybrid

VSEPR and Bond Hybridization

VSEPR 价层电子对互斥 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** 杂化 (*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.

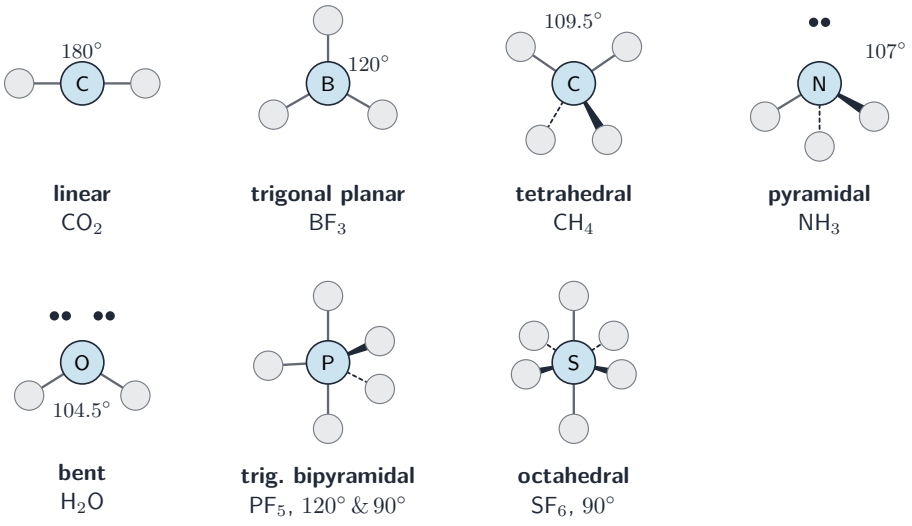
Electron domains	Lone pairs	Molecular shape	Example	Ideal angles
2	0	linear	CO_2	180°
3	0 / 1	trigonal planar / bent	BF_3 / SO_2	120°
4	0 / 1 / 2	tetrahedral / trigonal pyramidal / bent	CH_4 / NH_3 / H_2O	109.5° (less with lone pairs)
5	0 / 1 / 2 / 3	trigonal bipyramidal / seesaw / T-shaped / linear	PCl_5 / SF_4 / ClF_3 / XeF_2	90°, 120°, 180°
6	0 / 1 / 2	octahedral / square pyramidal / square planar	SF_6 / BrF_5 / XeF_4	90°, 180°

The hybridization of the central atom matches the number of domains: 2 domains *sp* (180°), 3 domains sp^2 (120°), 4 domains sp^3 (109.5°). AP does not ask about hybrids for 5 or 6 domains; for those you only need the shape.



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

exercises.lol exercises.com.cn



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.

Worked example (an expanded octet). Predict the shape of XeF_4 and whether it is polar. Valence electrons: $8 + 4(7) = 36$. Four Xe–F bonds use 8, and three lone pairs on each F use 24, so 4 electrons (2 lone pairs) remain on Xe. Xenon has 6 domains: octahedral electron geometry. The two lone pairs sit opposite each other, at 180°, as far apart as possible. The four F atoms form a **square planar** shape. The four Xe–F dipoles point in opposite pairs and cancel, so XeF_4 is **nonpolar**, even though every bond is polar. By contrast, SF_4 (5 domains, 1 lone pair) is seesaw-shaped and polar.

Bonds form when atomic orbitals **overlap**. Every single bond is one **sigma bond** σ 键 – orbitals overlapping head-on along the line joining the two atoms. A multiple bond adds a **pi bond** π 键, 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 restricts rotation about the bond. A C=C double bond can give **cis** and **trans** forms – **geometric isomers** 几何异构体 – when each double-bonded

exercises.lol exercises.com.cn

carbon has two different attached groups. Ethene does not meet this condition.

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.

Common mistakes.

- Naming the molecular shape from the **electron** geometry. Ammonia has four electron domains (tetrahedral electron geometry), but its **molecular** shape, which counts atoms only, is trigonal pyramidal; water is bent.
- Saying a molecule with polar bonds must be polar. In CO_2 and CCl_4 the bond dipoles **cancel** by symmetry, so the molecule is non-polar.
- Saying resonance structures flip back and forth. The real ion is one **delocalized** structure; in NO_3^- all three N–O bonds are the same length.
- Saying a double bond is twice as strong as a single bond. The extra **pi** bond is weaker than a sigma bond, so a double bond is stronger but less than twice as strong.
- Reading a deeper well on a potential-energy curve as a longer bond. A deeper well means a **stronger** bond; the minimum's position gives the bond length, and stronger bonds between the same atoms are usually **shorter**.
- Explaining the high melting point of MgO by "more bonds". MgO has larger ion **charges** (2+ and 2−) and small ions, so the Coulombic attraction, and the lattice energy, is much larger.
- Forgetting the ion's charge when counting valence electrons. For NO_3^- add **one** electron; for a cation subtract them.

Practice

Answer each before reading the answers below.

1. Describe the Lewis structure of CO_2. Predict its shape and whether the molecule is polar.
2. ClF_3 has three bonding pairs and two lone pairs on Cl. Predict its shape and explain why it has a dipole moment.
3. Estimate the C–O–H bond angle in ethanol and explain your estimate.
4. Which has the greater lattice energy, MgO or NaF? Justify your answer.
5. For ozone drawn with one O = O double bond and one O–O single bond, calculate the formal charge on each atom. What do the two resonance structures tell you about the real bond lengths?
6. State the hybridization of each carbon in ethene, C_2H_4, and count the sigma and pi bonds.
7. Explain why steel (carbon atoms in iron) is harder than pure iron.

Answers

1. O = C = O with two lone pairs on each O; two electron domains around C, so it is linear. The two bond dipoles are equal and opposite, so the molecule is nonpolar.
2. Five electron domains with the two lone pairs in equatorial positions give a T shape. The bond dipoles do not cancel in a T shape, so the molecule is polar (a trigonal planar shape would be nonpolar).
3. About 109°: O has four electron domains (two bonds and two lone pairs), so a near-tetrahedral angle is a reasonable estimate. The exact angle depends on the attached groups; ethanol need not have the same angle as water.
4. MgO. Its ions carry charges of 2+ and 2− compared with 1+ and 1−, and the ions are of similar size, so by Coulomb's law the attraction is much greater.
5. Central O: $6 - 2 - 3 = +1$; double-bonded O: $6 - 4 - 2 = 0$; single-bonded O: $6 - 6 - 1 = -1$. The two resonance structures mean both bonds are really the same length, between a single and a double bond.
6. Each carbon is sp^2. There are 5 sigma bonds (four C–H and one C–C) and 1 pi bond.
7. The small carbon atoms fill gaps between iron atoms (an interstitial alloy) and make it harder for layers of iron atoms to slide past 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**.

exercises.lol exercises.com.cn

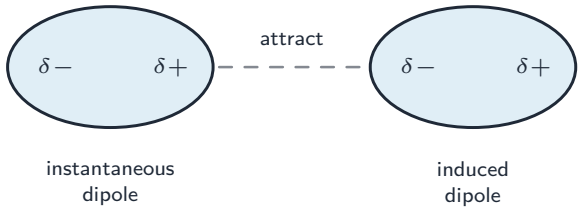
Properties of Substances and Mixtures

AP Chemistry

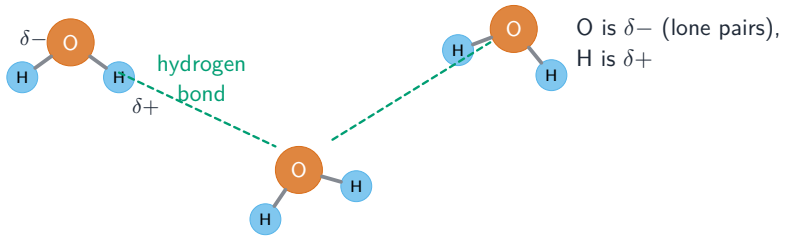
Intermolecular and Interparticle Forces

A gecko can run up a glass window and hang from the ceiling by one toe, with no glue and no suction. Its toes are covered in millions of tiny hairs that get extremely close to the surface, close enough for weak attractions between molecules to add up to a strong grip. Those same weak attractions decide whether a substance is a gas or a liquid at room temperature, why oil and water do not mix, and how a chromatography strip separates inks. This unit is about them. **Intermolecular forces** 分子间作用力 (IMFs) are attractions **between** molecules – much weaker than bonds, but they set melting/boiling points. The main types are listed below; their relative strengths depend on the particles and conditions:

- **London dispersion forces** 伦敦色散力: 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** 偶极-偶极: 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** 氢键: a strong dipole force when H is bonded to N, O, or F.
- **Ion–dipole** 离子-偶极: between an **ion** and a polar molecule (the ion pulls on the oppositely-charged end of the dipole). Their strength depends on ion charge, ion size and the molecular dipole. They help stabilize dissolved ions, although not every ionic solid dissolves readily in water - each Na^+ is surrounded by the $\delta-$ oxygen ends of water molecules.

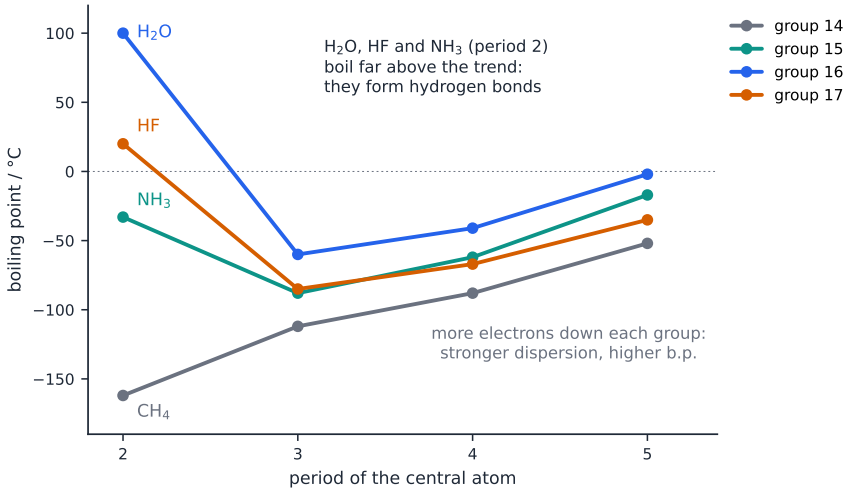


London dispersion: an instantaneous dipole induces a dipole in a neighbour



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

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.



Boiling points rise down each group as dispersion forces grow, except at period 2, where hydrogen bonding lifts NH_3, H_2O and HF far above the trend

Dispersion forces grow with the number of electrons, because a larger electron cloud is more **polarizable** 易极化: it is easier to distort into a temporary dipole. The halogens show this clearly. F_2 boils at −188 °C, Cl_2 at −34 °C and Br_2 at 59 °C, and I_2 is a solid at room temperature. Shape matters too, because a larger **contact area** gives more attraction. Pentane, a long chain, boils at 36 °C; its isomer neopentane, with the same formula C_5H_{12} but a compact ball shape, boils at 9.5 °C. Pi bonds also make electron clouds more polarizable.

A polar molecule can also **induce** a dipole in a nonpolar neighbour (a **dipole–induced dipole** force). This weak attraction is why a little oxygen dissolves in water, enough for fish to breathe.

> **Worked example (rank boiling points).** Rank CH_3CH_2OH (ethanol, 46 g/mol), CH_3OCH_3 (dimethyl ether, 46 g/mol) and $CH_3CH_2CH_3$ (propane, 44 g/mol). All three have similar numbers of electrons, so their dispersion forces are similar. Propane is nonpolar: dispersion only, lowest boiling point (−42 °C). Dimethyl ether is polar but has no H on its O: dipole–dipole added (−24 °C). Ethanol has an O–H, so it hydrogen-bonds: highest (78 °C). When molecules are similar in size, compare the extra forces.

These forces also work inside very large molecules. The two strands of DNA are held together by hydrogen bonds between bases, and a protein folds into its working shape through hydrogen bonds, dipole forces and dispersion forces between different parts of the same long chain.

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.

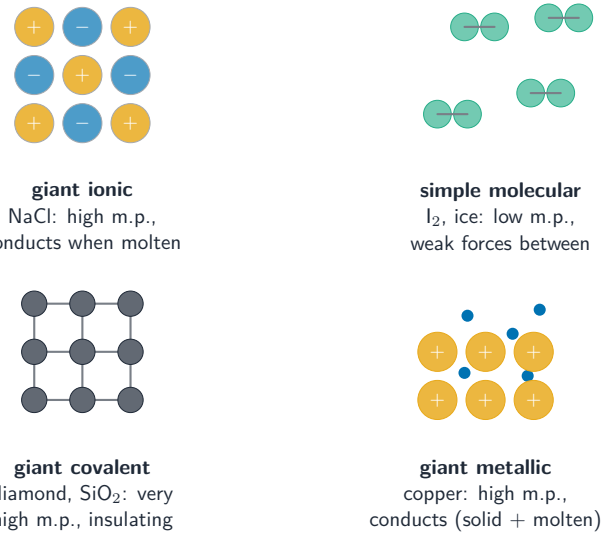
Solid	Particles	Held by	Melting point	Conducts electricity?	Example
ionic	cations and anions	ionic attraction	high	only when melted or dissolved	NaCl
covalent network	atoms	covalent bonds throughout	very high	no (graphite: yes)	diamond, SiO_2
molecular	molecules	intermolecular forces	low	no	ice, sugar, I_2
metallic	cations in an electron sea	metallic bonding	usually high	yes, as a solid	copper

Vaporizing a molecular substance separates its molecules completely, so its boiling point is a direct measure of the forces between them. Strong forces mean a high boiling point and a low **vapor pressure** 蒸气压 (few molecules escape from the liquid).

Metallic solids conduct electricity and heat and are **malleable** 可锻的 and **ductile** 可延展的, all because their **free valence electrons** 自由价电子 move easily and

exercises.lol exercises.com.cn

let the metal ions slide past one another without breaking the bonding. Solids are also either **crystalline** 晶体 (particles in a regular, repeating 3-D arrangement) or **amorphous** 非晶体 (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)

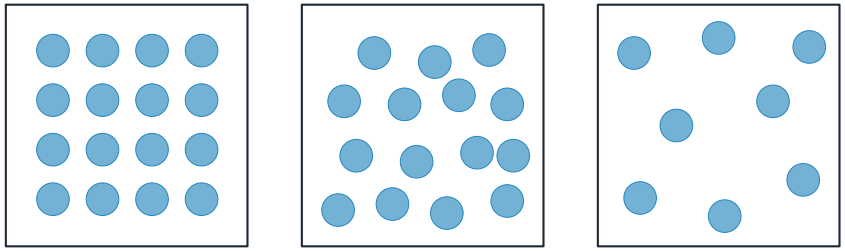
The four solid structures: giant ionic, simple molecular, giant covalent, and metallic

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.

In a solid and in a liquid the particles are in contact, so the two phases have similar volumes per mole: a mole of liquid water (18 mL) and a mole of ice (about 20 mL) are close. A mole of steam at 100 °C and 1 atm fills about 30 L, over 1500 times more. In a gas the spacing and the rate of collisions depend on the temperature, pressure and volume.

exercises.lol exercises.com.cn



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



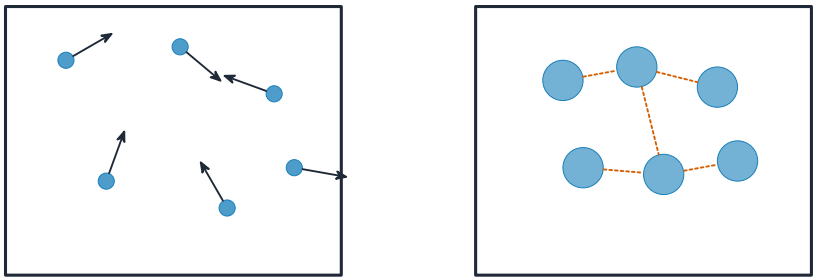
Steam rising from boiling water: gases expand to fill space and obey the ideal gas law at high T and low P

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.

In a mixture of gases, each gas pushes on the walls as if it were alone. Its **partial pressure** is set by its share of the moles, its **mole fraction** 摩尔分数 X:

$$P_A = X_A P_{\text{total}}, \qquad P_{\text{total}} = P_A + P_B + \cdots$$

Worked example (gas collected over water). Hydrogen collected over water at 25 °C has a total pressure of 0.980 atm, but the gas is a mixture of H_2 and water vapor. The vapor pressure of water at 25 °C is 0.031 atm, so $P_{H_2} = 0.980 - 0.031 = 0.949$ atm. Use 0.949 atm, not 0.980, in $PV = nRT$ to find the moles of H_2.

Worked example (partial pressures). A tank holds 2.0 mol O_2 and 6.0 mol He at a total pressure of 8.0 atm, a mixture used by deep-sea divers. $X_{O_2} = 2.0/8.0 = 0.25$, so $P_{O_2} = 0.25 \times 8.0 = 2.0$ atm and $P_{He} = 6.0$ atm. The two add up to 8.0 atm.

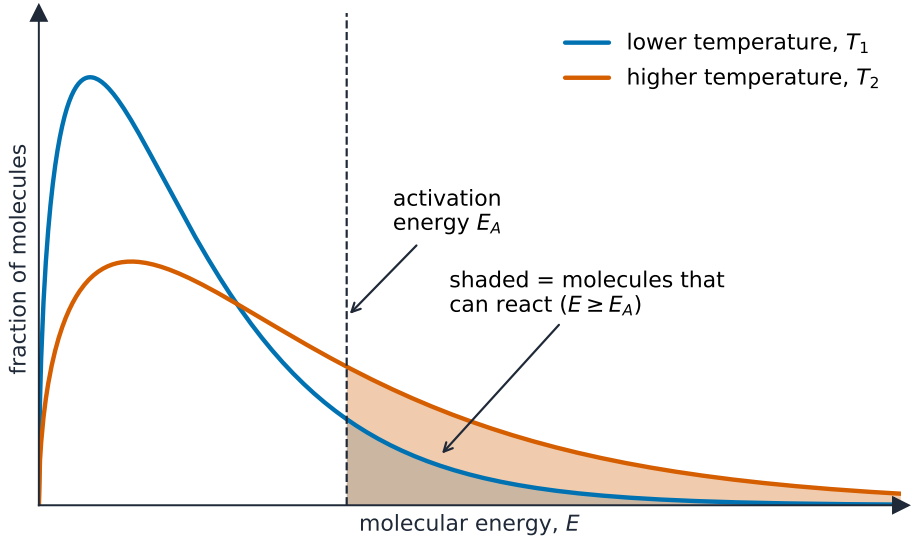
Graphs show the simple relationships hidden in $PV = nRT$. At fixed n and T, P against V is a curve ($P \propto 1/V$: halve the volume, double the pressure). At fixed n and V, P against kelvin temperature is a straight line through the origin.

exercises.lol exercises.com.cn

Kinetic Molecular Theory

Kinetic molecular theory 分子运动论 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).

Worked example (who moves faster?). At the same temperature, H_2 (2 g/mol) and O_2 (32 g/mol) have the **same** average kinetic energy, $\frac{1}{2}mv^2$. Since the oxygen molecule is 16 times heavier, its v^2 must be 16 times smaller, so its average speed is $\sqrt{16} = 4$ times smaller. Hydrogen molecules move about four times faster. This is why a helium balloon goes down faster than an air-filled one: the light atoms escape through tiny holes more often.



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.

Deviations are also larger close to the point where the gas would condense. A gas with strong attractions, such as NH_3 or H_2O (hydrogen bonding), deviates far more than He, whose tiny atoms barely attract each other. At the same temperature and molar volume, NH_3 can show a larger pressure shortfall than He or N_2 when attractions

dominate. At very high density, excluded molecular volume can instead make pressure exceed the ideal value.

Solutions and Mixtures

A **solution** 溶液 is a homogeneous mixture of a **solute** 溶质 dissolved in a **solvent** 溶剂. Concentration is usually **molarity** 摩尔浓度:

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

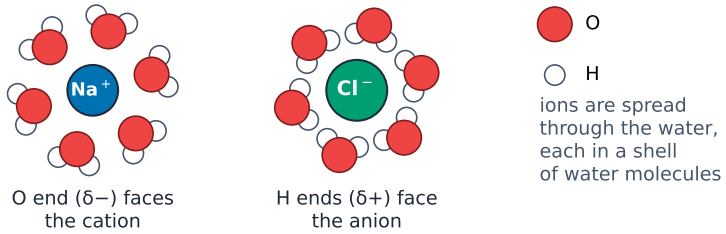
Dilution conserves moles: $M_1V_1 = M_2V_2$.

> **Worked example.** To what final volume must you dilute 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 $V_2 = \dfrac{M_1V_1}{M_2} = \dfrac{6.0 \times 50}{2.0} = 150$ mL. Add water until the solution reaches 150 mL. This takes approximately $150 - 50 = 100$ mL of water; solution volumes are not exactly additive.

> **Worked example (ions in solution).** How many moles of ions are in 250 mL of 0.40 M $CaCl_2$? Moles of $CaCl_2$: $0.250 \times 0.40 = 0.10$ mol. Each formula unit gives one Ca^{2+} and two Cl^-, so $[Cl^-] = 0.80$ M and there are $0.10 + 0.20 = 0.30$ mol of ions in total. In a particle drawing, show twice as many Cl^- as Ca^{2+}.

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.



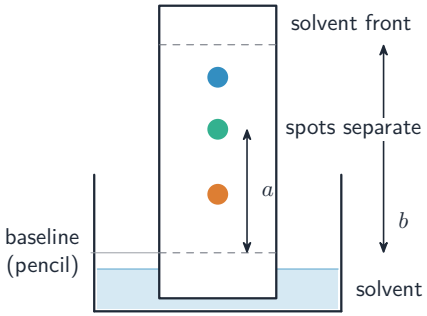
In NaCl(aq) each ion is surrounded by water molecules turned to face it

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** 色谱法 (by how strongly each component sticks to a stationary phase versus moving with a solvent).

Filtration cannot separate a solution, because the dissolved particles are as small as the solvent's. The other two methods both work through intermolecular forces:

- **Distillation**: the component with weaker intermolecular forces has the higher vapor pressure, so the vapour is enriched in that component. Distilling an ethanol–water mixture usually gives a distillate richer in ethanol; both components can enter the vapour.
- **Chromatography**: a component that is attracted more strongly to the **stationary phase** (the paper, or the solid in a column) moves slowly; one attracted more to the moving **mobile phase** (the solvent) travels further. On polar paper with a nonpolar solvent, the most polar dye moves the shortest distance and has the smallest R_f (distance moved by the spot divided by distance moved by the solvent).



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

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

Solubility

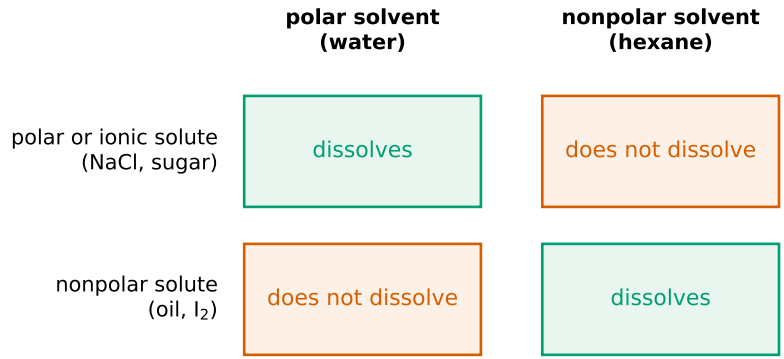
Solubility 溶解度 is how much solute dissolves. "Like dissolves like" is a useful guide: polar solutes often dissolve in polar solvents, and nonpolar solutes in nonpolar solvents. It is not a guarantee, especially for ionic solids. Both interaction energies and entropy affect dissolution.

exercises.lol exercises.com.cn

Worked example (why do some pairs mix?). Ethanol mixes with water in any amount: both hydrogen-bond, and ethanol–water hydrogen bonds replace the ones broken. Hexane does not mix with water. Hexane can only offer dispersion forces, which cannot make up for the strong hydrogen bonds between water molecules that would have to break. NaCl dissolves in water because strong ion–dipole attractions replace the ionic attractions in the crystal, but it does not dissolve in hexane, which offers no such attraction.



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



Like dissolves like: solutes dissolve in solvents with similar intermolecular forces

Spectroscopy and the Electromagnetic Spectrum

Spectroscopy 光谱学 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.

Region	Photon energy	What it changes	Use
microwave	lowest	how fast molecules **rotate**	gas-phase rotational spectroscopy
infrared	medium	how bonds **vibrate**	identifying bonds such as O–H and C=O
ultraviolet–visible	highest of the three	**electron** energy levels	colour, Beer–Lambert analysis

Properties of Photons

Light is carried by **photons** 光子, 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.

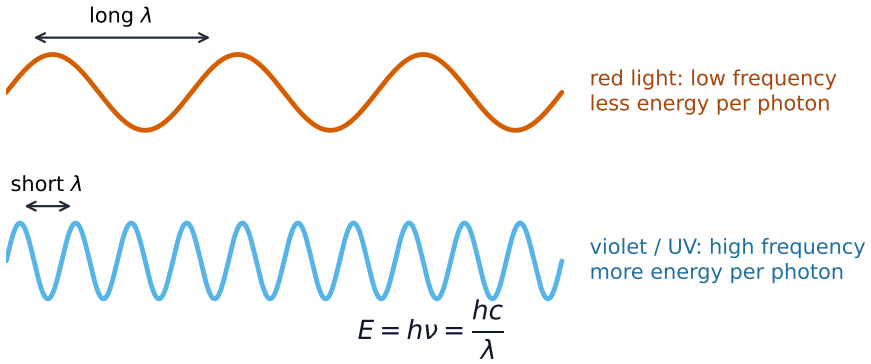
When an atom or molecule absorbs a photon, its energy rises by exactly the photon's energy. When it emits one, its energy falls by the same amount. That is why each element gives a line spectrum of particular colours, as in flame tests.

Worked example (photon energy). Green light has a wavelength of 500 nm. Its frequency is

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{500 \times 10^{-9}\ \text{m}} = 6.00 \times 10^{14}\ \text{s}^{-1},$$

so one photon carries $E = h\nu = (6.626 \times 10^{-34})(6.00 \times 10^{14}) = 3.98 \times 10^{-19}$ J. A mole of such photons carries $3.98 \times 10^{-19} \times 6.022 \times 10^{23} = 2.40 \times 10^{5}$ J, about 240 kJ, similar to the energy of a weak chemical bond. That is why ultraviolet light, with even more energy per photon, can break bonds and damage skin.

exercises.lol exercises.com.cn



Shorter wavelength means higher frequency and more energy per photon

The Beer-Lambert Law

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

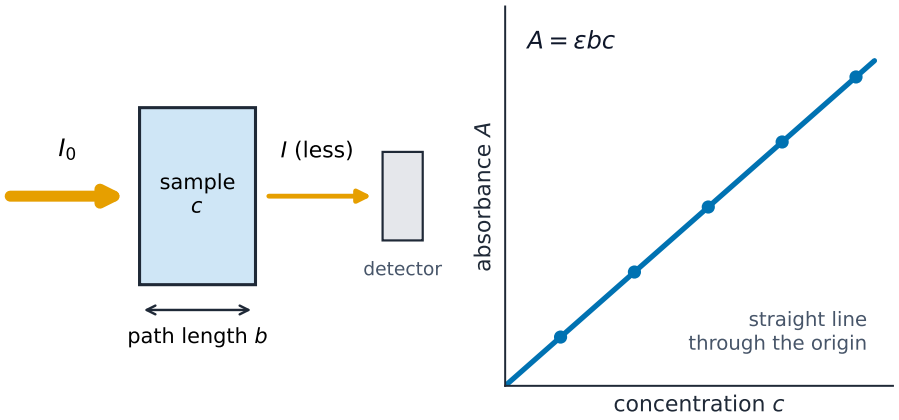
$$A = \varepsilon\, b\, c,$$

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.

In the lab, you usually do not know ε. Instead, you measure the absorbance of several **standard solutions** of known concentration, all in the same cell and at the same wavelength, and plot A against c. The unknown's absorbance is then read off the straight line. Choose the wavelength the substance absorbs **most** strongly: the measurement is then most sensitive. Errors to watch for include fingerprints or scratches on the cell (which make A too high), and a cell not rinsed with the solution being measured.

exercises.lol exercises.com.cn



Absorbance rises in a straight line with concentration: $A = \varepsilon bc$

Exam skill (lab errors). Many free-response questions ask how a mistake changes the result. Follow the error through $A = \varepsilon bc$. Drops of water left in the cuvette dilute the sample, so A is too low and the calculated concentration is too low. Fingerprints or scratches on the cuvette absorb or scatter light, so A is too high. Measuring at a wavelength the substance hardly absorbs makes the line shallow, so small reading errors become large concentration errors: always use the wavelength of maximum absorbance.

Exam skill (making a solution). To make 100.0 mL of 0.340 M NaCl: calculate the mass ($0.1000 \times 0.340 \times 58.44 = 1.99$ g), weigh it on an analytical balance, and dissolve it in less than 100 mL of distilled water in a **100.0 mL volumetric flask**. Then add water up to the mark and mix. To dilute instead, measure the stock with a volumetric pipette or burette into the volumetric flask, then fill to the mark. A beaker or graduated cylinder is not precise enough for the final volume.

Common mistakes.

- Using °C in $PV = nRT$. Convert to **kelvin** first ($T/\mathrm{K} = t/°\mathrm{C} + 273$); at 0 °C the Celsius value would give a volume of zero.
- Saying a hydrogen bond is a bond between the H and the O inside one water molecule. That O–H is a **covalent** bond; the hydrogen bond is the attraction from that H to a lone pair on a **neighbouring** molecule.
- Saying any molecule containing H can hydrogen-bond. The H must be bonded to **N, O or F**; the H atoms in CH_4 cannot.
- Assuming dispersion forces are always the weakest. Between large, highly polarizable molecules, dispersion can outweigh the dipole–dipole forces of a smaller polar molecule.

- Using V_2 as the volume of water to add in a dilution. $M_1V_1 = M_2V_2$ gives the **final** volume; add solvent to reach that final volume; subtraction gives only an approximate volume of water added.
- Saying real gases deviate most at low pressure and high temperature. Deviations are largest at **high pressure and low temperature**, where the particles are close and slow enough for their volume and attractions to matter.
- Reading a higher absorbance as a more dilute solution. In $A = \varepsilon bc$, absorbance is **proportional** to concentration.

Practice

Answer each before reading the answers below.

1. Calculate the moles of CO_2 in a 2.00 L container at 1100 K and 1.04 atm.
2. Explain why HF has a higher boiling point than HCl, but HI has a higher boiling point than HCl.
3. Which gas deviates more from ideal behaviour at high pressure, He or NH_3? Explain.
4. 5.85 g of NaCl (58.44 g/mol) is dissolved to make 250.0 mL of solution. Find the molarity.
5. A calibration line gives $A = (1.5 \times 10^3\ M^{-1})\,c$. A sample has $A = 0.45$. Find c. If the student left a fingerprint on the cuvette, would the calculated concentration be too high or too low?
6. Calculate the energy of one photon of light with wavelength 500. nm.

Answers

1. $n = \dfrac{PV}{RT} = \dfrac{(1.04)(2.00)}{(0.08206)(1100)} = 0.0230$ mol.
2. HF molecules form hydrogen bonds, which are much stronger than the dipole forces in HCl. HI has a larger, more polarizable electron cloud than HCl, so its London dispersion forces are stronger.
3. NH_3: its molecules attract each other (hydrogen bonding) and are larger, so attractions and molecular volume both matter more at high pressure.
4. $5.85 \div 58.44 = 0.100$ mol; $0.100 \div 0.2500 = 0.400\ M$.
5. $c = 0.45 \div (1.5 \times 10^3) = 3.0 \times 10^{-4}\ M$. Too high: the fingerprint absorbs or scatters light, so A is too high.
6. $E = \dfrac{hc}{\lambda} = \dfrac{(6.626 \times 10^{-34})(3.00 \times 10^8)}{5.00 \times 10^{-7}} = 3.98 \times 10^{-19}$ J.

Exam tips

- **Intermolecular forces** (dispersion, dipole–dipole and hydrogen bonding) affect 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" is a guide; check the particular solute and solvent.

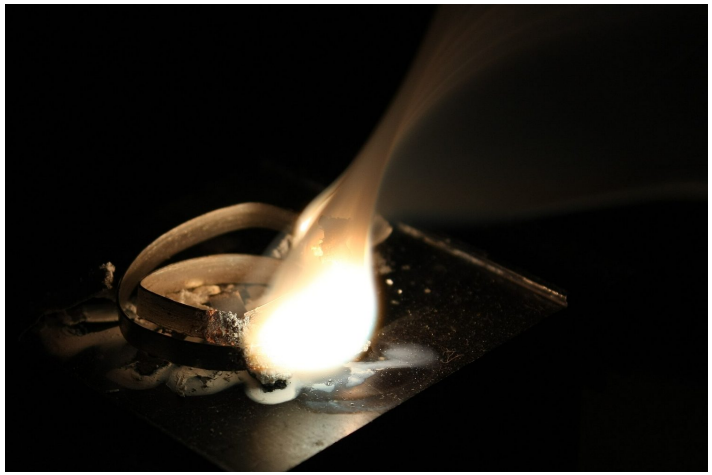
exercises.lol exercises.com.cn

Chemical Reactions

AP Chemistry

Recognizing a Chemical Reaction

In a car crash, an airbag fills in about 0.03 seconds. In early airbag designs, a spark set off a solid, sodium azide, which broke down into nitrogen gas: $2\mathrm{NaN_3}(s) \rightarrow 2\mathrm{Na}(s) + 3\mathrm{N_2}(g)$. Engineers must put in exactly the right mass of solid: too little and the bag is soft, too much and it bursts. That calculation, from a balanced equation to grams of reactant, is the heart of this unit.



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

A **chemical reaction** 化学反应 rearranges atoms into new substances. Possible evidence includes a color change, a gas or **precipitate** 沉淀 forming, or a temperature change. These observations alone do not prove that new substances formed. Atoms are conserved, so an equation must be **balanced** – the same count of each element on both sides.

Physical changes have equations too. Dissolving salt is written $\mathrm{NaCl}(s) \rightarrow \mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq)$, and boiling water is $\mathrm{H_2O}(l) \rightarrow \mathrm{H_2O}(g)$. The state symbols carry the meaning: nothing new is made, but the form changes. A balanced equation must conserve **charge** as well as atoms: the total charge on the left equals the total on the right.

exercises.lol exercises.com.cn

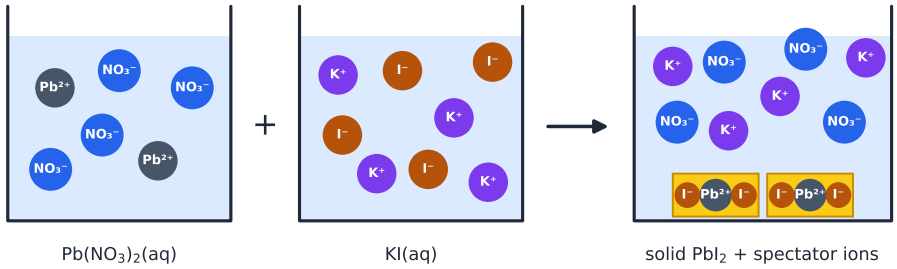
Net Ionic Equations

When writing aqueous ionic equations, split dissolved strong electrolytes into ions; keep insoluble solids and weak electrolytes in their appropriate forms. A **net ionic equation** 净离子方程式 shows only the species that actually change, leaving out the **spectator ions** 旁观离子 that appear unchanged on both sides. It captures the real chemistry (e.g. $\mathrm{Ag^+} + \mathrm{Cl^-} \rightarrow \mathrm{AgCl}(s)$).

> **Worked example (three forms of one equation).** Lead(II) nitrate solution is mixed with potassium iodide solution, and a bright yellow solid forms. Write the three forms.

- **Molecular equation**: $\mathrm{Pb(NO_3)_2}(aq) + 2\mathrm{KI}(aq) \rightarrow \mathrm{PbI_2}(s) + 2\mathrm{KNO_3}(aq)$.
- **Complete ionic equation** 完整离子方程式 (every dissolved strong electrolyte split into ions): $\mathrm{Pb^{2+}} + 2\mathrm{NO_3^-} + 2\mathrm{K^+} + 2\mathrm{I^-} \rightarrow \mathrm{PbI_2}(s) + 2\mathrm{K^+} + 2\mathrm{NO_3^-}$.
- **Net ionic equation**: cross out $\mathrm{K^+}$ and $\mathrm{NO_3^-}$, which appear unchanged on both sides, to leave $\mathrm{Pb^{2+}}(aq) + 2\mathrm{I^-}(aq) \rightarrow \mathrm{PbI_2}(s)$.

How do you know the solid is $\mathrm{PbI_2}$ and not $\mathrm{KNO_3}$? AP expects you to know one solubility rule: **all sodium, potassium, ammonium and nitrate salts are soluble**. So $\mathrm{KNO_3}$ stays dissolved, and the precipitate must be the other product. Check the charge: $+2 + 2(-1) = 0$ on the left and 0 on the right.



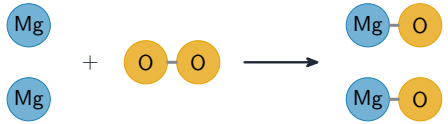
Only Pb^{2+} and I^- leave the solution as solid PbI_2; K^+ and NO_3^- stay dissolved and unchanged, so they are spectator ions

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 good particle drawing follows three rules. It keeps every atom: count each element

before and after. It shows the right ratio of particles, matching the coefficients. And it shows the right form: an ionic solid dissolved in water appears as separate ions, a molecular substance such as sugar stays as whole molecules, and any reactant in excess still appears after the reaction. The limiting-reactant drawing in the Stoichiometry section shows 4 H_2 and 1 O_2: only one O_2 can react, so 2 H_2 remain.



$2Mg + O_2 \rightarrow 2MgO$

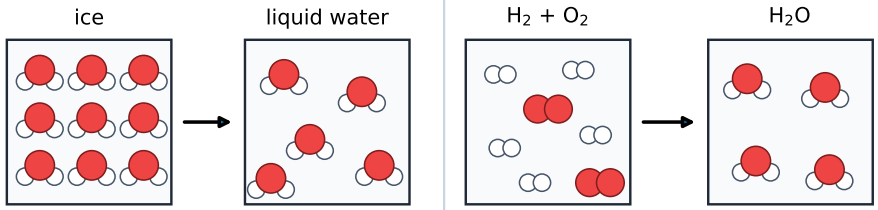
2 Mg and 2 O on each side: balanced

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

Physical Changes versus Chemical Changes

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

At the particle level, the test is **which forces change**. A chemical process breaks or forms chemical bonds (covalent, ionic or metallic). For molecular substances, a physical process can change intermolecular forces without changing the molecules, as when ice melts: the H_2O molecules stay whole, and only the hydrogen bonds between them break. Some cases sit on the line. Dissolving salt breaks ionic bonds in the crystal, yet the salt comes back when the water evaporates. You can argue it either way, as long as your argument uses the particle model.

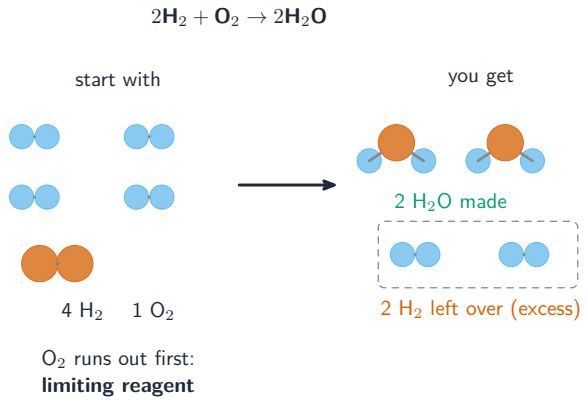


A physical change rearranges the same molecules; a chemical change makes new ones

exercises.lol exercises.com.cn

Stoichiometry

Stoichiometry 化学计量 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** 限量反应物 runs out first and sets the maximum product (the **theoretical yield** 理论产量); 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: $n(N_2) = 10.0/28.0 = 0.357$, $n(H_2) = 5.0/2 = 2.5$. The reaction needs 3 H_2 per N_2; you have $2.5/0.357 = 7.0$, far more than 3, so **N_2 is limiting**. It makes $2 \times 0.357 = 0.714$ mol of ammonia (12.1 g), with hydrogen left over.

Worked example (percent yield). In the same experiment, only 8.5 g of ammonia is collected. The **percent yield** 产率 is

$$\frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{8.5}{12.1} \times 100\% = 70\%.$$

A yield below 100% can come from an incomplete reaction, side reactions, or product lost while collecting it. A yield above 100% means an error, often a product that is

still wet.

Worked example (the airbag). An airbag must fill with 60.0 L of nitrogen at 1.00 atm and 298 K. What mass of NaN_3 ($M = 65.0$ g/mol) is needed? Use the ideal gas law for the gas, then the mole ratio:

$$n(N_2) = \frac{PV}{RT} = \frac{(1.00)(60.0)}{(0.08206)(298)} = 2.45 \text{ mol}, \qquad n(NaN_3) = \frac{(1.00)(60.0)}{(0.08206)(298)} \times \frac{2}{3} = 1.6357\ldots \text{ mol}.$$

Using the unrounded amount, the mass is $1.6357\ldots \times 65.0 = 106$ g, which fits in your palm.

Worked example (solution stoichiometry). What mass of PbI_2 ($M = 461$ g/mol) forms when 50.0 mL of 0.200 M $Pb(NO_3)_2$ is mixed with 50.0 mL of 0.300 M KI? Moles: $n(Pb^{2+}) = 0.0500 \times 0.200 = 0.0100$ mol and $n(I^-) = 0.0500 \times 0.300 = 0.0150$ mol. The net ionic equation needs 2 I^- per Pb^{2+}, so 0.0100 mol of lead needs 0.0200 mol of iodide. There is only 0.0150 mol, so **iodide is limiting**. It gives $0.0150/2 = 0.00750$ mol of PbI_2, or $0.00750 \times 461 = 3.46$ g.

Worked example (gravimetric analysis). A 1.250 g tablet containing iodide is dissolved, and excess $AgNO_3$ precipitates all the iodide as AgI ($M = 234.8$ g/mol). The dried precipitate has a mass of 0.4110 g. Moles of AgI $= 0.4110/234.8 = 1.750 \times 10^{-3}$ mol, which is also the moles of I^- (a 1 : 1 ratio). Mass of $I^- = 1.750 \times 10^{-3} \times 126.9 = 0.2221$ g, so the tablet is $0.2221/1.250 \times 100\% = 17.8\%$ iodide by mass.

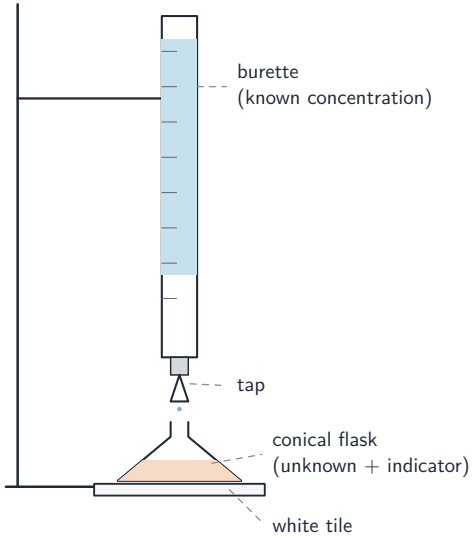
Exam skill (gravimetric errors). The precipitate is dried, weighed, and dried again until two weighings agree: drying to **constant mass**. That provides evidence that drying is complete under the chosen conditions. A precipitate weighed while still wet has too large a mass, so the calculated percent is too *high*. If some precipitate passes through the filter paper, the mass is too low, so the percent is too *low*. Adding the precipitating reagent in **excess** makes sure all of the ion you are measuring comes out of solution.

Introduction to Titration

A **titration** 滴定 finds an unknown concentration by reacting it with a solution of known concentration until they reach the **equivalence point** 等当点 (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.

The solution in the burette, whose concentration you know, is the **titrant** 滴定剂. The substance in the flask, whose amount you want, is the **analyte** 被测物. At the equivalence point the analyte has just been used up. Any property that changes sharply there can show it: the colour of an indicator, the pH, or the electrical conductivity.

exercises.lol exercises.com.cn

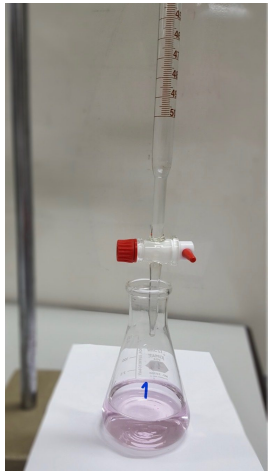


Titration apparatus: a burette delivers a known solution into a conical flask

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:

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

Worked example (a 1:2 titration). 20.0 mL of sulfuric acid needs 32.0 mL of 0.150 M NaOH: $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$. Moles of NaOH are $0.0320 \times 0.150 = 4.80 \times 10^{-3}$. Each acid molecule uses *two* hydroxide ions, so $n(H_2SO_4) = 2.40 \times 10^{-3}$ mol and $[H_2SO_4] = 2.40 \times 10^{-3}/0.0200 = 0.120$ M. Forgetting the 2 gives an answer twice too large.



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.

AP focuses on three types and how to tell them apart:

Type	What moves	How to spot it
Acid–base	a proton, H^+	an acid such as HCl meets a base such as OH^- or NH_3
Redox	electrons	oxidation numbers change; an element appears alone on one side
Precipitation	ions out of solution	two ionic solutions give an (s) product

Combustion 燃烧 is a kind of redox: a substance reacts with oxygen gas. A hydrocarbon burned completely gives carbon dioxide and water, as in $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$. Carbon's average oxidation number goes from $-\frac{8}{3}$ to $+4$ (oxidized) and oxygen from 0 to -2 (reduced).

exercises.lol exercises.com.cn

	what is transferred	*example*
ACID-BASE	a proton (H^+) moves	$HCl + NH_3 \rightarrow NH_4^+ + Cl^-$
REDOX	electrons move; oxidation no. changes	$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$
PRECIPITATION	ions join into an insoluble solid	$Ag^+ + Cl^- \rightarrow AgCl(s)$

Acid-base reactions move protons; redox moves electrons; precipitation forms a solid

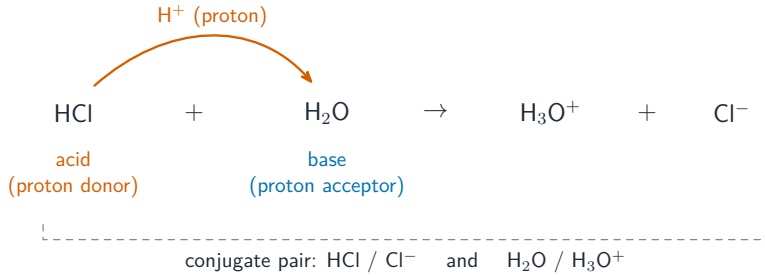
Acid-Base Reactions

An **acid** 酸 donates a proton (H^+); a **base** 碱 accepts one (Brønsted–Lowry). For an aqueous acid reacting with a hydroxide base, the net neutralisation is: $H^+ + OH^- \rightarrow H_2O$. Strong acids ionise essentially completely in dilute water; soluble strong hydroxide bases dissociate into ions. Weak acids and bases establish equilibria.

Water can play either role. With ammonia it gives a proton, acting as an acid:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq).$$

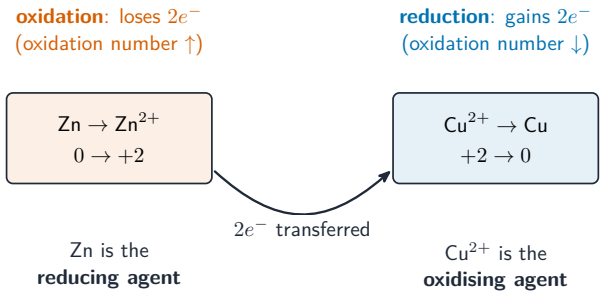
With hydrogen chloride it takes one, acting as a base: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$. Each acid–base reaction makes two **conjugate acid–base pairs** 共轭酸碱对, which differ by one H^+. In the ammonia equation, NH_4^+/NH_3 is one pair and H_2O/OH^- is the other. To find the conjugate base of an acid, remove one H^+; to find the conjugate acid of a base, add one.



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

Oxidation-Reduction (Redox) Reactions

In a **redox** 氧化还原 reaction, electrons transfer between species. **Oxidation** 氧化 is loss of electrons (oxidation number rises); **reduction** 还原 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 $(+1) + \mathrm{Mn} + (-8) = 0$, giving $\mathrm{Mn} = +7$ – its maximum, which is why permanganate is a powerful oxidizing agent (it can only gain electrons).

A redox equation can be built from two **half-reactions** 半反应, one for oxidation and one for reduction. Balance each half for atoms and charge, then multiply so that the electrons lost equal the electrons gained.

Worked example (balancing with half-reactions). Permanganate oxidizes iron(II) in acid solution to give Mn^{2+} and Fe^{3+}.

1. Oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$.
2. Reduction: balance Mn, then add H_2O to balance O, then H^+ to balance H, then electrons to balance charge: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$.
3. Multiply the oxidation by 5 so both halves involve 5 electrons, then add and cancel the electrons:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O.$$

Check the charge: on the left $-1 + 8 + 10 = +17$; on the right $+2 + 15 = +17$. Balanced.

Common mistakes.

exercises.lol exercises.com.cn

- Splitting a precipitate or a weak acid into ions. In a net ionic equation only **dissolved strong electrolytes** are written as ions; $AgCl(s)$, water and CH_3COOH stay whole.
- Choosing the limiting reactant by the smaller **mass**. Compare **moles**, divided by the coefficients: in the example above, 10.0 g of N_2 is the larger mass but it runs out first.
- Rounding moles early. Carry an extra figure through the working (0.357, not 0.36) and round only the final answer.
- Using mL in $n = cV$. Change to litres first: 30.0 mL = 0.0300 L.
- Calling every "disappearing" solid a chemical change. Dissolving sugar is **physical**: the molecules are unchanged and the sugar comes back when the water evaporates. Judge by which bonds or forces break, not by what you see.
- Mixing up oxidation and reduction. **Oxidation** is loss of electrons (the oxidation number rises); the species oxidised is the **reducing agent**.

Practice

Answer each before reading the answers below.

1. Write the balanced net ionic equation for the reaction of $Pb(NO_3)_2(aq)$ with $KI(aq)$, and explain why a net ionic equation is the best representation.
2. 2.00 g of H_2 reacts with 16.0 g of O_2. Identify the limiting reactant and find the mass of water formed.
3. 25.00 mL of HCl is titrated to the equivalence point with 18.40 mL of 0.1000 M NaOH. Find [HCl].
4. In $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$, which species is oxidized, which is reduced, and which is the reducing agent?
5. In a precipitation lab, the student does not dry the precipitate completely. Is the calculated mass percent of the ion too high, too low, or unchanged? Explain.
6. Explain why boiling water is a physical change but the electrolysis of water is a chemical change.

Answers

1. $Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$. K^+ and NO_3^- stay dissolved and do not take part (spectator ions).
2. H_2: $2.00 \div 2.016 = 0.992$ mol; O_2: $16.0 \div 32.00 = 0.500$ mol. 0.992 mol H_2 needs only 0.496 mol O_2, so H_2 is limiting. Water: $0.992 \times 18.02 = 17.9$ g.
3. $n(OH^-) = 0.01840 \times 0.1000 = 1.840 \times 10^{-3}$ mol $= n(H^+)$; $[HCl] = 1.840 \times 10^{-3} \div 0.02500 = 0.07360$ M.
4. Al is oxidized ($0 \rightarrow +3$) and is the reducing agent; Cu^{2+} is reduced ($+2 \rightarrow 0$).

5. Too high: the measured mass includes water, so the calculated moles and mass of the ion are too large.
6. Boiling overcomes intermolecular forces only; the molecules are still H_2O. Electrolysis breaks O–H covalent bonds and forms new substances, H_2 and O_2.

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.

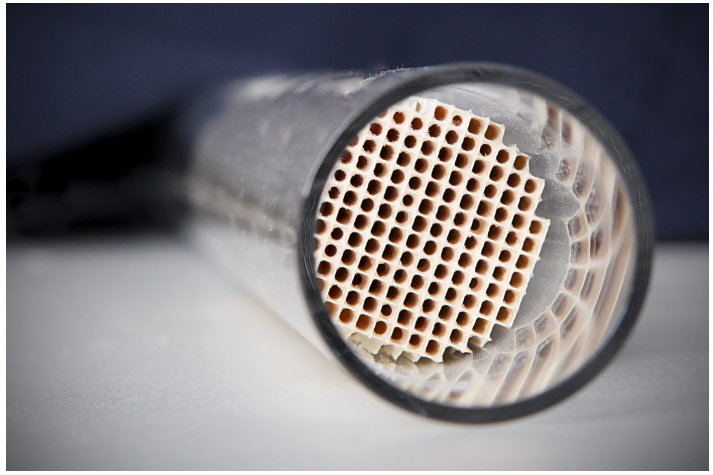
exercises.lol exercises.com.cn

Kinetics

AP Chemistry

How Fast a Reaction Goes

Snap a glow stick and drop it into hot water: it shines brightly but fades within an hour. Put an identical one in the freezer and it glows dimly, but for many hours. The same chemicals react in both, and only the speed differs. Food in a fridge, iron rusting and the engine of a car all depend on the same question: how fast? This unit measures reaction speed, explains it with colliding particles, and uses it to work out the steps a reaction really takes.

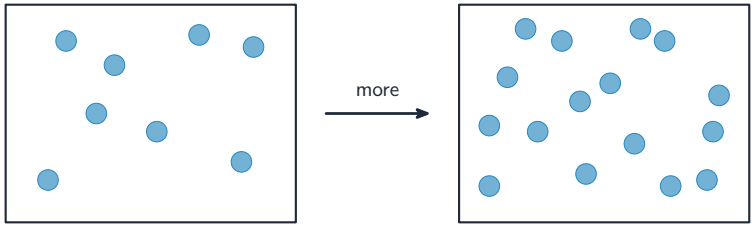


A catalytic converter: catalysts speed rates by lowering activation energy without being consumed

Kinetics 动力学 studies **reaction rate** 反应速率 – how fast reactants become products. Rate is the change in **concentration** 浓度 per unit time, and it typically **decreases** as reactants are used up. Higher **temperature** 温度 and a suitable catalyst usually increase rate. Concentration effects depend on the rate law; greater exposed **surface area** 表面积 matters for reactions involving a solid.

The balanced equation links the rates of the different species. For $2N_2O_5 \rightarrow 4NO_2+O_2$, for every 2 mol of N_2O_5 used, 4 mol of NO_2 and 1 mol of O_2 form. If N_2O_5 is used up at 0.010 M/s, then NO_2 forms at 0.020 M/s and O_2 at 0.0050 M/s. Always say which species a rate refers to.

To measure a rate in the lab, follow something that changes as the reaction goes: the volume of gas given off, the mass lost as gas escapes, a colour (with a colorimeter), the pressure, or the pH.



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



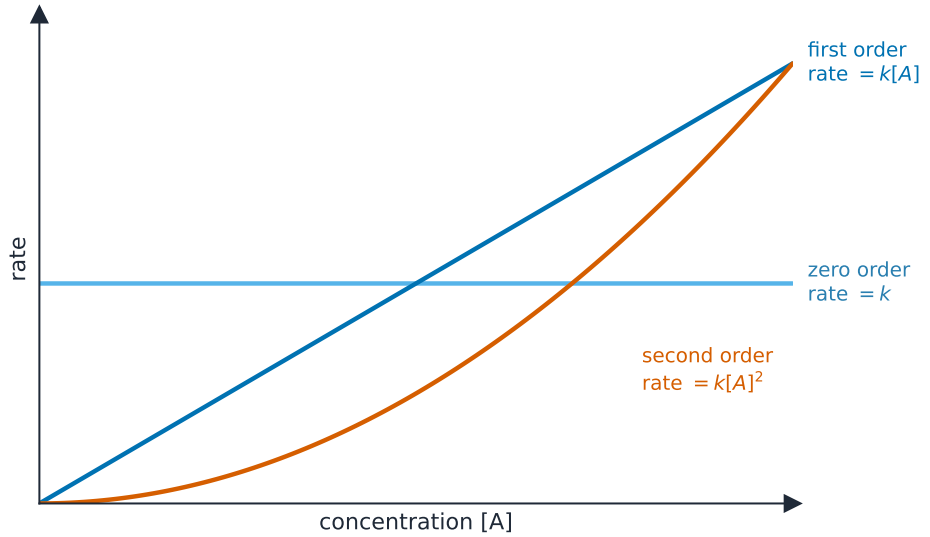
A gas syringe: measuring gas volume over time gives reaction rate from the slope

Writing the Rate Law

The **rate law** 速率方程 relates rate to reactant concentrations:

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

where k is the **rate constant** 速率常数 and m, n are the **orders** 级数. 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** 二级 in A ($2^2 = 4$) and **zero order** 零级 in B, giving rate $= k[\text{A}]^2$. The **overall order** 总级数 is $2+0=2$. Never read the orders off the balanced coefficients – only experiment gives them.

Worked example (method of initial rates). For $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$:

Experiment	$[\text{NO}]_0$ / M	$[\text{O}_2]_0$ / M	Initial rate / M s^{-1}
1	0.010	0.010	2.5×10^{-5}
2	0.020	0.010	1.0×10^{-4}
3	0.010	0.020	5.0×10^{-5}

From 1 to 2, [NO] doubles and the rate goes up 4 times: second order in NO. From 1 to 3, $[\text{O}_2]$ doubles and the rate doubles: first order in O_2. So rate $= k[\text{NO}]^2[\text{O}_2]$, third order overall. Using experiment 1:

$$k = \frac{2.5 \times 10^{-5}}{(0.010)^2(0.010)} = 25\ \text{M}^{-2}\,\text{s}^{-1}.$$

The units of k depend on the overall order: M s^{-1} for zero order, s^{-1} for first, $\text{M}^{-1}\text{s}^{-1}$ for second, $\text{M}^{-2}\text{s}^{-1}$ for third. The value of k changes with temperature, but not with

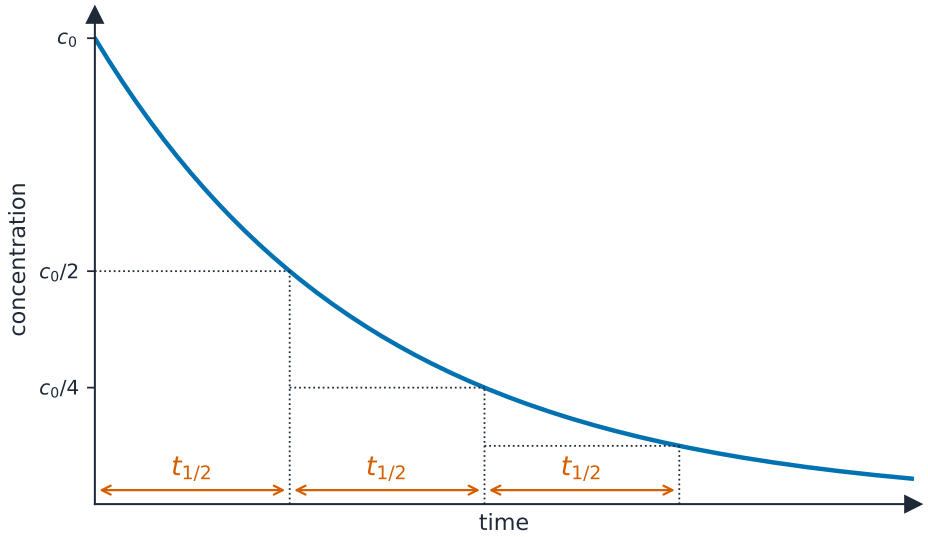
exercises.lol exercises.com.cn

concentration.

Concentration Over Time

The **integrated rate laws** 积分速率方程 describe how concentration falls with time and give straight-line tests:

- **Zero order:** [A] vs t is linear.
- **First order** 一级: $\ln[\mathrm{A}]$ vs t is linear; constant **half-life** 半衰期.
- **Second order:** $\dfrac{1}{[\mathrm{A}]}$ vs t is linear.



A first-order reaction has a constant half-life

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

> **Worked example.** A first-order reaction has rate constant $k = 0.030\ \mathrm{s}^{-1}$. Its half-life is
>
> $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.030} = 23\ \mathrm{s},$$
>
> 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.

For times that are not whole half-lives, use the integrated law, $\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_0 = -kt$. For this reaction, starting at 0.50 M, after 60 s:

$$\ln[\mathrm{A}]_t = \ln(0.50) - (0.030)(60) = -0.693 - 1.80 = -2.49, \qquad [\mathrm{A}]_t = e^{-2.49} = 0.083\ \mathrm{M}.$$

exercises.lol exercises.com.cn

Radioactive decay 放射性衰变 is always first order. Carbon-14 has a half-life of 5730 years. A piece of wood with one-eighth of the carbon-14 of living wood has passed through 3 half-lives ($\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{8}$), so it is about $3 \times 5730 \approx 17{,}000$ years old. That is how carbon dating works.

> **Worked example (which plot is straight?).** A reactant is measured at 0, 10, 20 and 30 s: 0.80, 0.40, 0.20 and 0.10 M. The concentration halves every 10 s, which is a constant half-life, so the reaction is first order and a plot of $\ln[\mathrm{A}]$ against t is a straight line. Its slope is $-k$, with $k = 0.693/10 = 0.069\ \mathrm{s}^{-1}$. For a second-order reaction, each half-life is twice as long as the one before.

The Steps a Reaction Really Takes

A **reaction mechanism** 反应机理 is the sequence of **elementary steps** 基元反应 that actually occur. Their **molecularity** 分子数 (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** 中间体.

For an elementary step, and **only** for an elementary step, the rate law comes straight from the equation for that step:

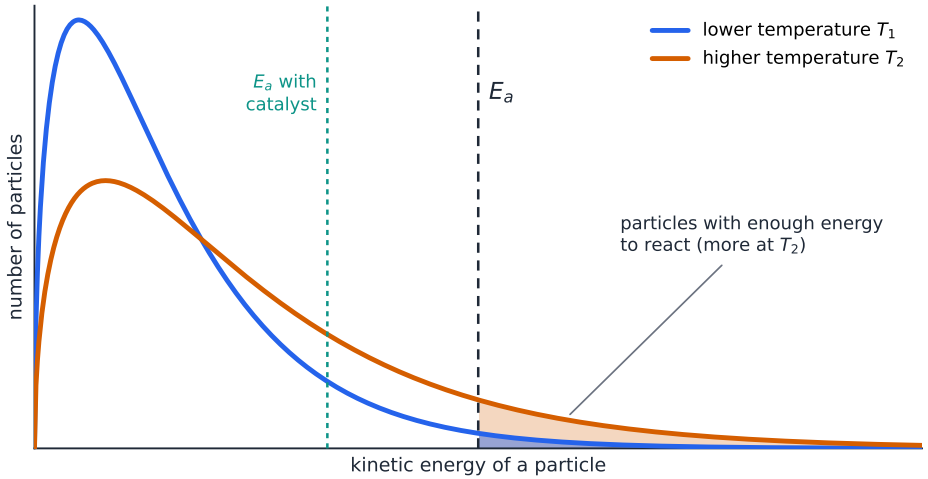
Elementary step	Molecularity	Rate law
$\mathrm{A} \rightarrow$ products	unimolecular	$k[\mathrm{A}]$
$\mathrm{A} + \mathrm{B} \rightarrow$ products	bimolecular	$k[\mathrm{A}][\mathrm{B}]$
$2\mathrm{A} \rightarrow$ products	bimolecular	$k[\mathrm{A}]^2$

A step in which three particles must collide at the same moment is very rare, because three particles almost never meet at one point at the same time.

Why Collisions Do or Do Not React

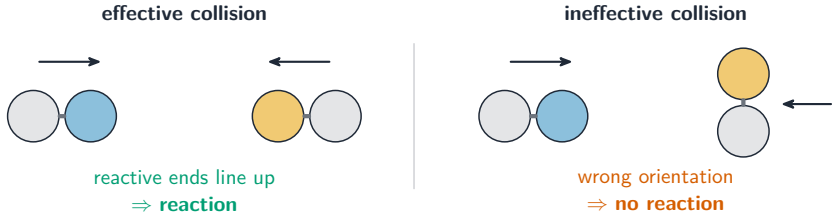
Collision theory 碰撞理论: molecules must collide with enough energy (the **activation energy** 活化能, E_a) and the correct **orientation** 取向 to react. Higher temperature means more molecules exceed E_a, so the reaction speeds up sharply.

Most collisions do not lead to a reaction. In a gas at room temperature each molecule collides billions of times per second, so if every collision worked, every reaction would be over almost instantly. The **Maxwell-Boltzmann distribution** 麦克斯韦-玻尔兹曼分布 shows the spread of particle energies.



At a higher temperature the curve flattens and spreads out, and the shaded fraction of particles above Ea grows much larger; a catalyst moves Ea to the left instead

Raising the temperature makes particles collide a little more often, but the main effect is that a much larger **fraction** of collisions now have energy above E_a. That is why, for many reactions near room temperature, a rise of just 10 °C roughly doubles the rate. The Arrhenius equation describes this link between k, E_a and temperature; AP asks you to explain it, not to calculate with it.

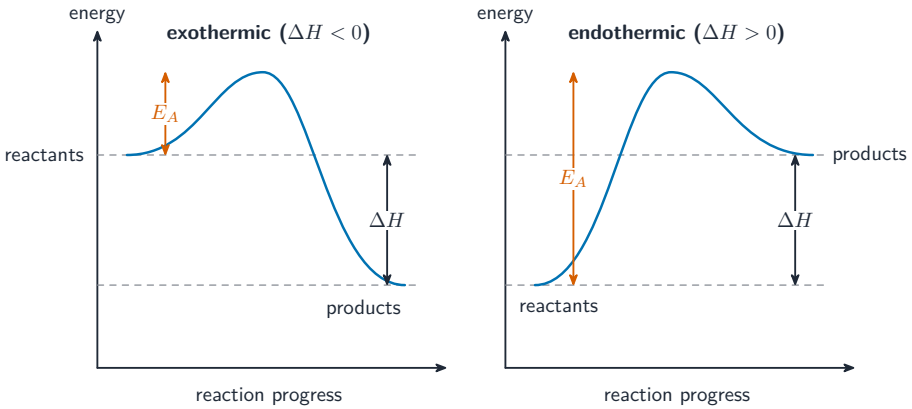


A collision only reacts with the right orientation and enough energy

Reading an Energy Profile

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

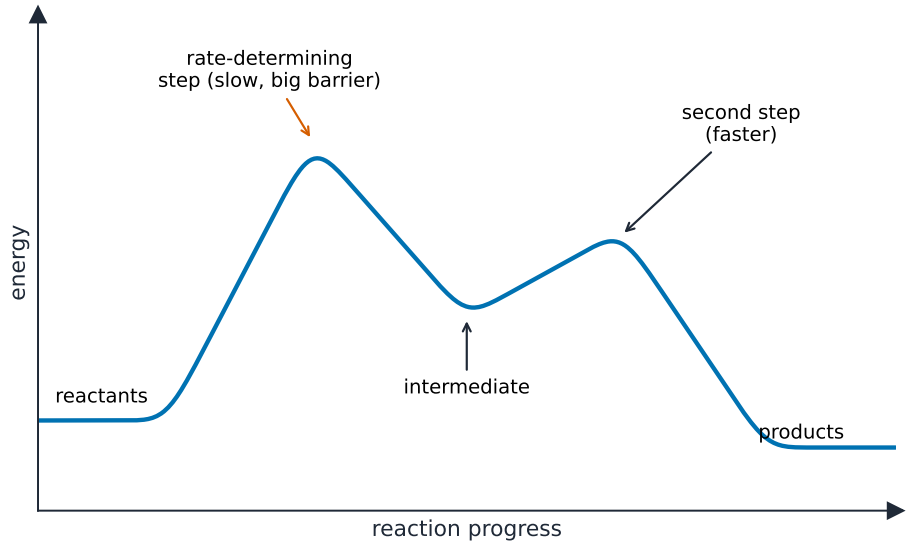
exercises.lol exercises.com.cn



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 barrier, measured from the preceding minimum. A diagram helps suggest a controlling step, but the full mechanism and concentrations determine the rate.



The slow step with the higher barrier is rate-determining

Finding the Rate Law From a Mechanism

The **rate-determining step** 决速步骤 is the slow step that controls rate in a suitable mechanism model. Its elementary rate law follows its molecularity. If this law contains an intermediate, use a justified relation, such as a fast pre-equilibrium, to express it in observable species before predicting 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** 双分子 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.

step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ **slow** → rate $= k[NO_2]^2$

step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ **fast**

from the slow step's reactants, not the overall equation

overall: $NO_2 + CO \rightarrow NO + CO_2$

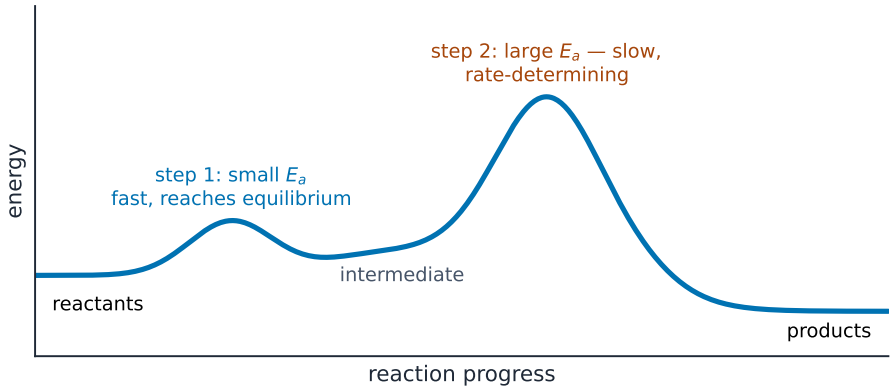
NO_3 is an intermediate: made in step 1, used in step 2

The rate law comes from the slow step of the mechanism

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** 快速预平衡 to rewrite that intermediate in terms of reactants, so the final rate law contains only measurable species.

exercises.lol exercises.com.cn



rate $= k_2$[intermediate]; replace the intermediate using step 1's K

A fast reversible first step followed by a slow rate-determining step

> **Worked example (a fast first step).** For $2NO + Br_2 \rightarrow 2NOBr$, this mechanism is proposed:

- Step 1 (fast, reversible): $NO + Br_2 \rightleftharpoons NOBr_2$
- Step 2 (slow): $NOBr_2 + NO \rightarrow 2NOBr$

1. Check the sum: $NOBr_2$ appears on both sides and cancels, leaving $2NO + Br_2 \rightarrow 2NOBr$. ✓
2. Write the rate law of the slow step from its molecularity: rate $= k_2[NOBr_2][NO]$.
3. $NOBr_2$ is an intermediate, so it cannot stay in the answer. Step 1 is at equilibrium, so $K_1 = \dfrac{[NOBr_2]}{[NO][Br_2]}$, which gives $[NOBr_2] = K_1[NO][Br_2]$.
4. Substitute: rate $= k_2K_1[NO]^2[Br_2] = k[NO]^2[Br_2]$.

The predicted law is second order in NO and first order in Br_2, which matches experiment. Notice that it looks as if three particles collide at once, but no single step has three particles.

Derive the rate law by substituting the fast pre-equilibrium expression into the slow-step law. Simply counting reactants up to the slow step is not a general rule: a pre-equilibrium can also introduce concentration terms in the denominator.

Energy Profiles for Many Steps

A multi-step reaction's profile shows several peaks (one per step) with valleys (intermediates) between them. Measure each barrier from its preceding minimum, and test any proposed controlling step against the observed rate law. The highest absolute peak alone does not establish the rate-determining step.

How Catalysts Speed Things Up

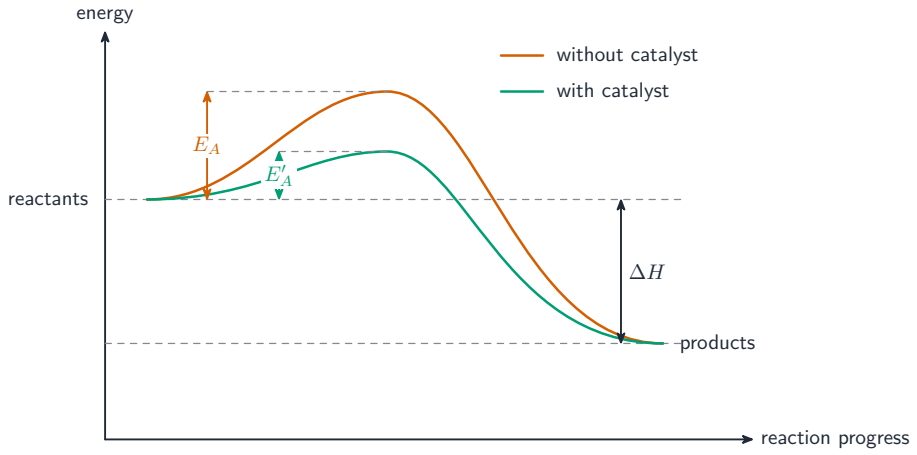
A **catalyst** 催化剂 speeds a reaction by providing a new pathway with a **lower activation energy**, without being consumed. It does not change ΔH or the **equilibrium position** 平衡位置 – only how fast equilibrium is reached. On an energy profile, a catalyst lowers the peak(s).

Catalysts work in different ways:

Type	How it works	Example
Binding (enzyme)	holds reactants in the right orientation, lowering E_a	enzymes in living cells
Acid–base	a reactant gains or loses a proton, giving a new, easier intermediate	H^+ speeding up the making of esters
Surface	reactants bond to a metal surface, which weakens their bonds	platinum in a car's catalytic converter; iron in the Haber process

In each case the catalyst is used in one step, often the slow one, and made again in a later step, so its total amount does not change.

exercises.lol exercises.com.cn



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

Catalyst or intermediate? Both cancel from the overall equation, so look at **where** each one first appears:

- an **intermediate** is **made** in an early step and **used up** in a later step.
- a **catalyst** is **used up** in an early step and **made again** in a later step, so it is there at the start.

Worked example. Iodide ions speed up the decomposition of hydrogen peroxide:

- Step 1 (slow): $H_2O_2 + I^- \rightarrow H_2O + IO^-$
- Step 2 (fast): $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$

Adding the steps gives $2H_2O_2 \rightarrow 2H_2O + O_2$. I^- is used in step 1 and returned in step 2, so it is the **catalyst**. IO^- is made in step 1 and used in step 2, so it is an **intermediate**. The slow step gives rate $= k[H_2O_2][I^-]$: a catalyst **can** appear in the rate law, even though it is not in the overall equation.

Common mistakes.

- Writing the rate law from the coefficients of the **overall** equation. Orders come from experiment, or from the slow step of a mechanism, never from the balanced equation.
- Leaving an intermediate in a final rate law. Replace it using the fast equilibrium.
- Using the orders of the slow step when a fast step comes **before** it, without substituting.
- Calling the highest point on the profile the "intermediate". Peaks are **transition states**; intermediates sit in the valleys between peaks.

- Saying a catalyst "lowers ΔH" or "shifts the equilibrium". It only lowers E_a, for both directions equally.

Practice

Answer each before reading the answers below.

1. The concentration of A halves every 20 s, whatever the starting concentration. State the order and find k.
2. Initial-rate data: trial 1, [A] = 0.10, [B] = 0.10, rate 2.0×10^{-3}; trial 2, [A] = 0.20, [B] = 0.10, rate 8.0×10^{-3}; trial 3, [A] = 0.10, [B] = 0.20, rate 4.0×10^{-3} (concentrations in M, rates in $M\,\mathrm{s}^{-1}$). Find the rate law and k with units.
3. Which plot is linear for a first-order reaction, and which for a second-order reaction?
4. Mechanism: step 1 (slow) $\mathrm{NO_2} + \mathrm{NO_2} \rightarrow \mathrm{NO_3} + \mathrm{NO}$; step 2 (fast) $\mathrm{NO_3} + \mathrm{CO} \rightarrow \mathrm{NO_2} + \mathrm{CO_2}$. Give the overall equation, the intermediate and the rate law.
5. Explain how a catalyst increases the rate. Does it change ΔH?
6. A first-order reaction has $k = 0.0231\ \mathrm{min}^{-1}$. Find the half-life and the fraction left after 90.0 min.

Answers

1. A constant half-life means first order. $k = \dfrac{0.693}{20\ \mathrm{s}} = 0.035\ \mathrm{s}^{-1}$.
2. Doubling [A] multiplies the rate by 4: second order in A. Doubling [B] doubles the rate: first order in B. Rate $= k[\mathrm{A}]^2[\mathrm{B}]$; $k = \dfrac{2.0 \times 10^{-3}}{(0.10)^2(0.10)} = 2.0\ M^{-2}\,\mathrm{s}^{-1}$.
3. First order: ln[A] against time. Second order: 1/[A] against time.
4. $\mathrm{NO_2} + \mathrm{CO} \rightarrow \mathrm{NO} + \mathrm{CO_2}$; intermediate $\mathrm{NO_3}$; rate $= k[\mathrm{NO_2}]^2$ (from the slow step).
5. It provides a different pathway with a lower activation energy, so a larger fraction of collisions have enough energy. It does not change ΔH (or K).
6. $t_{1/2} = 0.693 \div 0.0231 = 30.0$ min. 90.0 min is three half-lives: $\left(\frac{1}{2}\right)^3 = \frac{1}{8}$ is left.

Exam tips

- Use **collision theory** to explain temperature and suitable catalyst effects; check the rate law for concentration effects and whether a solid surface is involved.
- 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.

exercises.lol exercises.com.cn

- 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

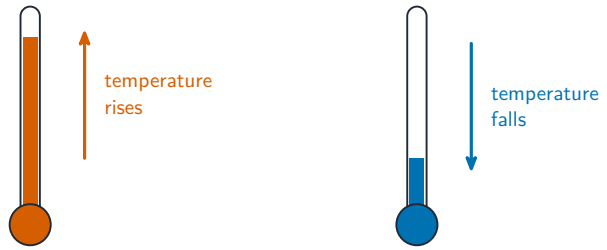
Squeeze an instant cold pack and within seconds it is cold enough to soothe a sprained ankle. Nothing was plugged in and no ice was added. Inside, a bag of water breaks and ammonium nitrate dissolves, and that process takes energy *from* its surroundings, including your skin. A hand warmer does the opposite: iron powder rusts and gives energy out. This unit measures those energy flows and predicts them from bonds.



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

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

The **system** 体系 is the part you study, such as the reacting chemicals. Everything else, including the water they are dissolved in, is the surroundings. A thermometer in the solution reads the surroundings, so a rising temperature means the system gave energy out. Physical processes have a sign too. Dissolving can go either way, depending on the forces broken and made. Ammonium nitrate dissolving is endothermic: the energy needed to separate its ions and rearrange water exceeds the energy released by ion–water attractions. Calcium chloride dissolving is exothermic, and it is used in hot packs.



exothermic

heat given out, so the surroundings get hotter ($\Delta H < 0$)

endothermic

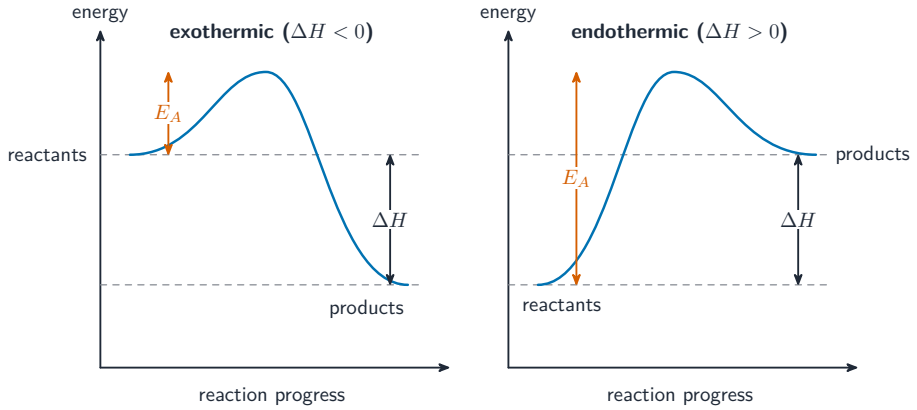
heat taken in, so the surroundings get colder ($\Delta H > 0$)

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

Energy Diagrams

An **energy diagram** 能量图 plots energy from **reactants** 反应物 to **products** 生成物. Reactants above products means exothermic; below means endothermic. The vertical gap between them is the **enthalpy change** 焓变 ΔH.

To draw one, mark the reactants on the left and the products on the right at the right heights, then join them with a curve that rises to a hump. The hump is the energy needed to start the reaction; it does not change ΔH. Label the arrow from reactants to products with its sign and size, for example $\Delta H = -891$ kJ for burning one mole of methane.



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

exercises.lol exercises.com.cn

Heat Transfer and Thermal Equilibrium

Heat 热量 flows from hot to cold until objects reach **thermal equilibrium** 热平衡 (equal temperature). **Energy is conserved** 能量守恒: for an **isolated** 孤立的 pair, the heat lost by the hot object equals the heat gained by the cold one.

At the particle level, temperature measures the **average kinetic energy** of the particles. When a hot metal block touches cooler water, interactions between particles transfer thermal energy to the water. Net heat transfer continues until both have the same temperature. Then energy still moves in both directions, but there is no net flow.

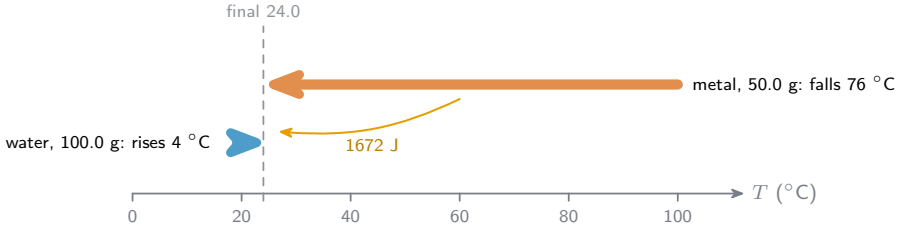
> **Worked example (identify a metal).** A 50.0 g metal block at 100.0 °C is dropped into 100.0 g of water at 20.0 °C in an insulated cup. The final temperature is 24.0 °C. The water gains

$$q_{\text{water}} = (100.0)(4.18)(24.0 - 20.0) = 1672 \text{ J}.$$

The metal loses the same amount, so

$$c_{\text{metal}} = \frac{1672}{(50.0)(100.0 - 24.0)} = 0.44 \text{ J/(g °C)}.$$

That matches iron, 0.45. Note how differently the two temperatures changed: the metal fell 76 °C while the water rose only 4 °C, because water's specific heat is about nine times larger and there is twice as much water by mass.



same energy, very different ΔT: water's c is about 9 times larger, and there is twice the mass

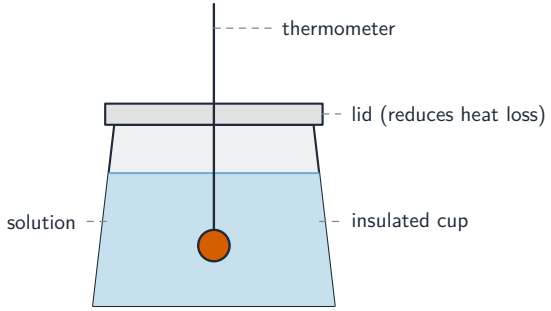
The same 1672 J leaves the metal and enters the water, but the metal falls 76 degrees while the water rises only 4

Heat Capacity and Calorimetry

The heat to change a substance's temperature is

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

where c is the **specific heat** 比热容 (energy per gram per degree). **Calorimetry** 量热法 measures a reaction's heat by tracking the temperature change of surrounding water: in a simple **insulated** 隔热的 model, the heat the water gains equals the heat the reaction releases. Include heat absorbed by the container and any losses when they matter.



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

> **Worked example.** A reaction in a coffee-cup **calorimeter** 量热计 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).

The same heat gives different temperature changes in different materials. This is why a sandy beach is too hot to walk on at noon while the sea stays cool: sand's specific heat is about one-fifth of water's. Tables also give the **molar heat capacity** 摩尔热容, the energy to warm one *mole* by one degree. For water it is $18.0 \times 4.18 = 75.2$ J/(mol °C).

> **Worked example (enthalpy of dissolving).** 5.00 g of NH_4NO_3 ($M = 80.0$ g/mol) dissolves in 100.0 g of water. The temperature falls from 22.0 °C to 18.4 °C. Use the mass of the whole solution, 105.0 g, and assume it has the specific heat of water:

$$q_{\text{solution}} = (105.0)(4.18)(18.4 - 22.0) = -1580 \text{ J}.$$

The solution lost 1580 J, so the dissolving absorbed +1580 J. With $n = 5.00/80.0 = 0.0625$ mol,

$$\Delta H_{\text{soln}} = \frac{+1.58 \text{ kJ}}{0.0625 \text{ mol}} = +25.3 \text{ kJ/mol}.$$

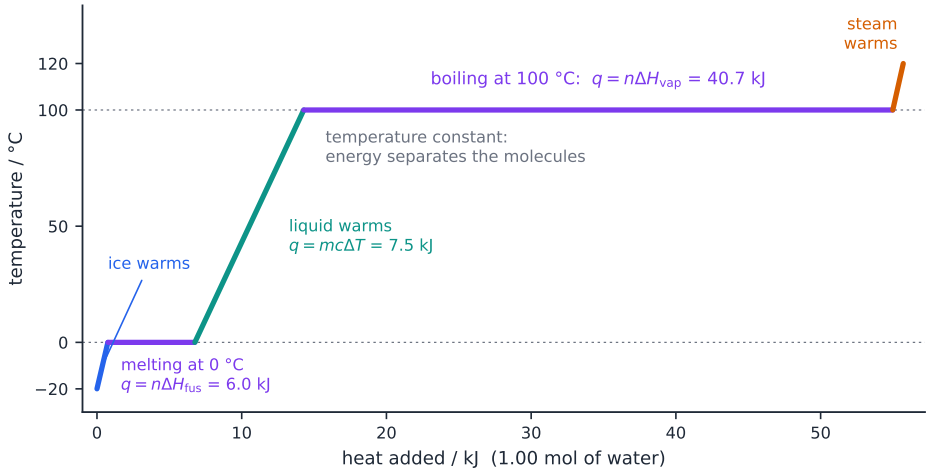
exercises.lol exercises.com.cn

A falling temperature means an endothermic process; the sign of ΔH is opposite to the sign of the solution's q.

Exam skill (calorimetry errors). A real coffee cup is not perfectly insulated. In an exothermic reaction some heat escapes to the room, so the measured ΔT is too small and the *magnitude* of ΔH comes out too small. In an endothermic one, heat leaks *in* from the room, so again the measured temperature change is too small and the magnitude of ΔH too small. Other errors follow the same path through $q = mc\Delta T$: a metal calorimeter that absorbs heat, or a thermometer read before the temperature has finished changing, also makes $|\Delta T|$ too small. To give ΔH per mole of *reaction*, divide q by the moles of the **limiting** reactant (scaled by its coefficient), not by the moles of the reactant in excess.

Energy of Phase Changes

During a **phase change** 相变 (**melting** 熔化, **boiling** 沸腾) of a pure substance at fixed pressure, the temperature stays **constant**. For a molecular substance, heat overcomes **intermolecular forces** 分子间作用力 rather than raising the average **kinetic energy** 动能. 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** 加热曲线.



Drawn to scale for one mole of water: boiling takes almost seven times as much energy as melting, because the molecules must be pulled completely apart

The reverse changes give out the same amount of energy. Freezing releases ΔH_{fus} per mole, and condensing releases ΔH_{vap}: $\Delta H_{\text{cond}} = -\Delta H_{\text{vap}}$. That is why a steam burn is worse than a burn from boiling water at the same 100 °C: the steam releases 40.7 kJ/mol as it condenses on your skin before it even starts to cool.

exercises.lol exercises.com.cn

Worked example (ice to steam). How much energy turns 18.0 g (1.00 mol) of ice at 0 °C into steam at 100 °C? Use $\Delta H_{\text{fus}} = 6.01$ kJ/mol and $\Delta H_{\text{vap}} = 40.7$ kJ/mol. Add the three steps:

$$q = \underbrace{(1.00)(6.01)}_{\text{melt}} + \underbrace{\frac{(18.0)(4.18)(100)}{1000}}_{\text{warm the liquid}} + \underbrace{(1.00)(40.7)}_{\text{boil}} = 6.01 + 7.52 + 40.7 = 54.2 \text{ kJ}.$$

Boiling accounts for three-quarters of the total. Use $q = mc\Delta T$ on the sloped parts and $q = n\Delta H$ on the flat parts, and keep all terms in the same unit.



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

Introduction to Enthalpy of Reaction

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

ΔH is given per mole of reaction *as written*, so the heat scales with the amount that reacts: $q = n\Delta H$.

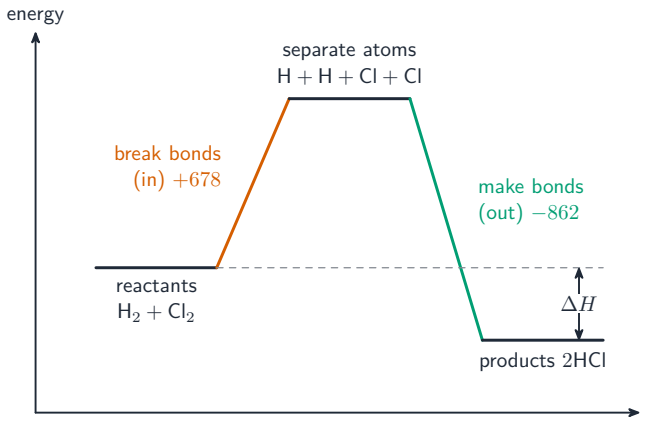
Worked example (heat from burning). For $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, $\Delta H = -891$ kJ/mol. Burning 4.00 g of methane ($M = 16.0$ g/mol) means $n = 0.250$ mol, so the heat released is $0.250 \times 891 = 223$ kJ. That energy appears first as faster-moving product molecules, a high temperature, and then passes to the surroundings as the products cool.

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** 键焓 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 $H_2 + Cl_2 \to 2HCl$ 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.

Worked example (comparing two methods). Estimate ΔH for burning methane from bond enthalpies: C–H 413, O=O 495, C=O 799, O–H 467 kJ/mol. Draw the molecules to count the bonds. One CH_4 has four C–H; two O_2 have two O=O; one CO_2 has two C=O; two H_2O have four O–H.

$$\text{broken} = 4(413) + 2(495) = 2642, \qquad \text{formed} = 2(799) + 4(467) = 3466,$$

$$\Delta H \approx 2642 - 3466 = -824 \text{ kJ}.$$

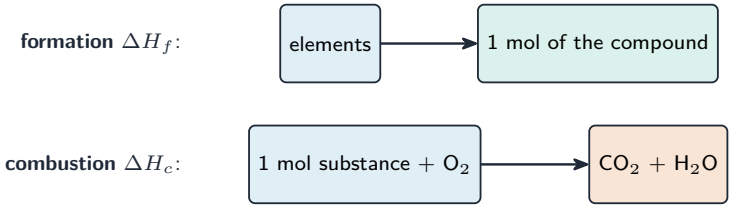
exercises.lol exercises.com.cn

The formation-enthalpy method below gives −891 kJ. The two differ for two reasons. Bond enthalpies are averages over many molecules. And they are for gases, so the estimate makes water vapour, not liquid water, and misses the energy released when the vapour condenses.

Enthalpy of Formation

The **standard enthalpy of formation** 生成焓 ΔH_f° is the enthalpy to make one mole of a compound from its **elements** 单质 (zero for an element in its most stable form at the stated temperature and standard pressure, its reference **standard state** 标准状态). Then

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



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

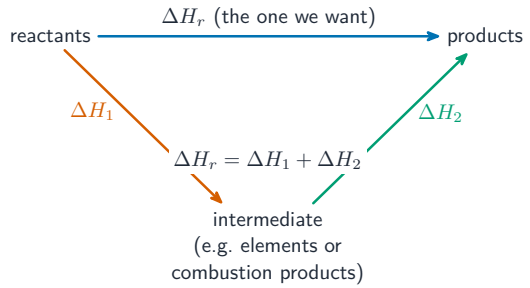
Worked example. Find $\Delta H^\circ_{\text{rxn}}$ for burning methane, $CH_4 + 2O_2 \to CO_2 + 2H_2O$, given ΔH_f°: $CH_4 = -75$, $CO_2 = -394$, $H_2O = -286$ kJ/mol ($O_2 = 0$). Products minus reactants:

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

a large release, as expected for a **combustion** 燃烧.

Hess's Law

Hess's law 盖斯定律: 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

Worked example. Find ΔH for $\mathrm{C}(s) + \tfrac{1}{2}\mathrm{O_2}(g) \to \mathrm{CO}(g)$, which cannot be measured directly because some $\mathrm{CO_2}$ always forms. You are given

$$\mathrm{C}(s) + \mathrm{O_2}(g) \to \mathrm{CO_2}(g) \qquad \Delta H_1 = -394 \text{ kJ}$$

$$\mathrm{CO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \to \mathrm{CO_2}(g) \qquad \Delta H_2 = -283 \text{ kJ}$$

Keep step 1 as written (it has C on the left). Reverse step 2 so that CO is a product: $\mathrm{CO_2} \to \mathrm{CO} + \tfrac{1}{2}\mathrm{O_2}$, $\Delta H = +283$ kJ. Add the two: $\mathrm{CO_2}$ cancels, and $\mathrm{O_2} - \tfrac{1}{2}\mathrm{O_2}$ leaves $\tfrac{1}{2}\mathrm{O_2}$ on the left, which is the target. So

$$\Delta H = -394 + 283 = -111 \text{ kJ}.$$

Check that every species left over matches the target equation before you add the numbers.

Common mistakes.

- Losing the sign in calorimetry. The water **gains** heat ($q_{\text{water}} > 0$), so the reaction **releases** it: $q_{\text{rxn}} = -q_{\text{water}}$.
- Using the mass of the solid that dissolved, not of the solution, in $q = mc\,\Delta T$. The temperature change is of the **water or solution**, so use its mass.
- Turning a bond-enthalpy calculation upside down. It is **broken − formed**; with products − reactants (the ΔH_f° order) you get the right size but the wrong sign.
- Counting bonds per molecule, not per equation. In $\mathrm{H_2} + \mathrm{Cl_2} \to 2\mathrm{HCl}$ there are **two** H–Cl bonds formed.
- Giving $\mathrm{O_2}(g)$ or another element in its standard state a non-zero ΔH_f°. It is **zero** by definition.
- Forgetting the coefficients with ΔH_f°. Multiply each value by its coefficient: $2(-286)$ for two moles of water.

exercises.lol exercises.com.cn

- Saying bond breaking releases energy. Breaking bonds always **costs** energy; energy is released only when bonds form.

Practice

Answer each before reading the answers below.

1. 10.0 g of LiCl (42.39 g/mol) dissolves in 100.0 g of water in a calorimeter, and the temperature rises from 15.0°C to 33.0°C. Taking $c = 4.18$ J/(g·°C) for all 110.0 g of solution, find ΔH_{soln} in kJ/mol.
2. How much heat is needed to warm 1.00 mol of Al from 298 K to its melting point, 933 K, and melt it? Molar heat capacity 24 J/(mol·K); $\Delta H_{\text{fus}} = 10.7$ kJ/mol.
3. Use bond enthalpies (H–H 436, Cl–Cl 242, H–Cl 431 kJ/mol) to estimate ΔH for $\mathrm{H_2} + \mathrm{Cl_2} \to 2\mathrm{HCl}$.
4. Given $\mathrm{C} + \mathrm{O_2} \to \mathrm{CO_2}$, $\Delta H = -393.5$ kJ, and $\mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \to \mathrm{CO_2}$, $\Delta H = -283.0$ kJ, find ΔH for $\mathrm{C} + \tfrac{1}{2}\mathrm{O_2} \to \mathrm{CO}$.
5. Use ΔH_f° values ($\mathrm{CH_4}$ −74.8, $\mathrm{CO_2}$ −393.5, $\mathrm{H_2O}(l)$ −285.8 kJ/mol) to find ΔH° for the combustion of methane.
6. 50.0 g of a metal at 100.0°C is placed in 100.0 g of water at 20.0°C. The final temperature is 23.0°C. Find the specific heat of the metal.

Answers

1. $q = (110.0)(4.18)(18.0) = 8.28 \times 10^3$ J released by the process. $n = 10.0 \div 42.39 = 0.236$ mol. $\Delta H_{\text{soln}} = -\dfrac{8.28 \text{ kJ}}{0.236 \text{ mol}} = -35.1$ kJ/mol (negative: the temperature rose).
2. Warming: $(1.00)(24)(635) = 15.2$ kJ; melting: 10.7 kJ; total 25.9 kJ.
3. $\Delta H = (436 + 242) - 2(431) = -184$ kJ/mol.
4. Reverse the second equation and add: $-393.5 + 283.0 = -110.5$ kJ.
5. $\mathrm{CH_4} + 2\mathrm{O_2} \to \mathrm{CO_2} + 2\mathrm{H_2O}(l)$: $[-393.5 + 2(-285.8)] - [-74.8] = -890.3$ kJ/mol.
6. Heat gained by water $= (100.0)(4.18)(3.0) = 1254$ J $=$ heat lost by metal $= (50.0)\,c\,(77.0)$, so $c = 0.326$ J/(g·°C).

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 and calorimeter gain in an insulated model.
- Bond enthalpies: $\Delta H \approx \sum$(bonds broken) $- \sum$(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** of a pure substance at fixed pressure, temperature stays constant while energy changes the interactions between particles.

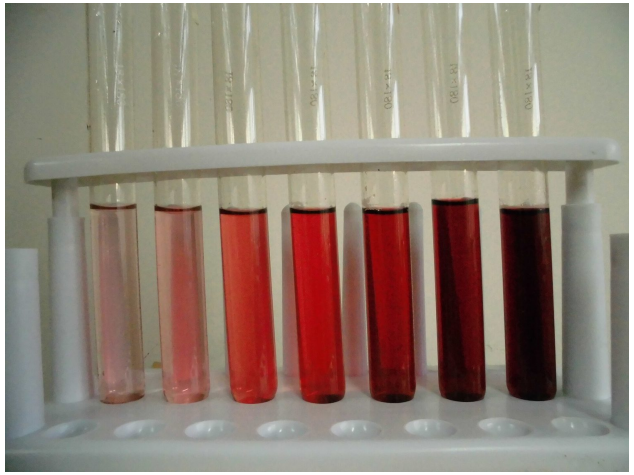
exercises.lol exercises.com.cn

Equilibrium

AP Chemistry

Introduction to Equilibrium

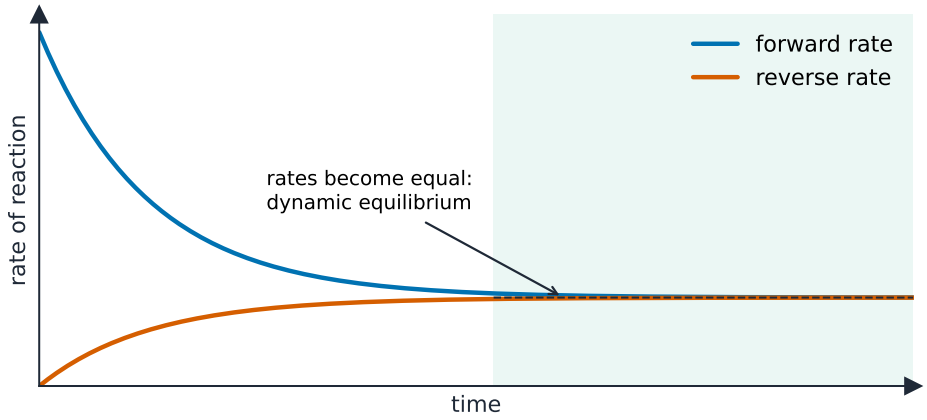
Some souvenir "weather" figures change colour: blue on a dry day, pink on a damp one. The colour comes from cobalt chloride, and it is a window into equilibrium. In solution, a pink cobalt ion and a blue one turn into each other all the time, in both directions at once. Change the conditions (water, chloride, temperature) and the balance between them moves, so the colour moves too. This unit explains how to predict where such a balance sits and which way it will move.



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

A **reversible reaction** 可逆反应 runs both ways. **Chemical equilibrium** 化学平衡 is reached when the **forward reaction** 正反应 and **reverse reaction** 逆反应 rates become **equal**, so **concentrations** 浓度 stop changing. Equilibrium is **dynamic** 动态的 – both reactions continue, but at matching rates, so nothing appears to change.

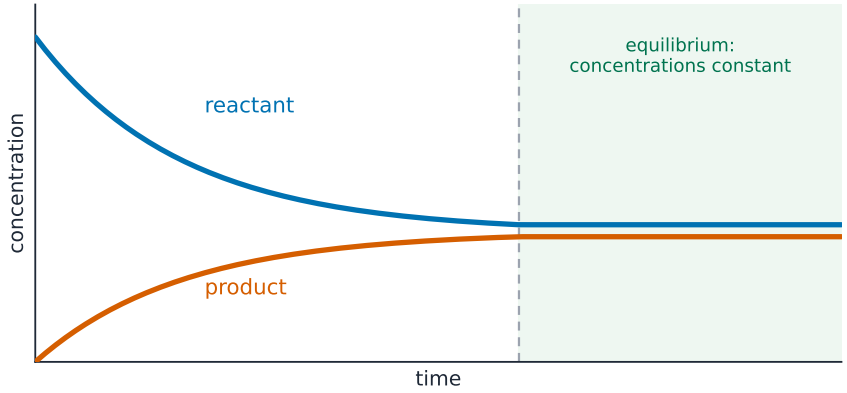
Physical processes can reach equilibrium too. In a closed water bottle, water evaporates and water vapour condenses. Once the two rates are equal, the amount of liquid stops changing even though molecules keep crossing the surface. A saturated salt solution, where dissolving and crystallising run at equal rates, is another example.



at equilibrium: $\text{rate}_f = \text{rate}_r \cdot K_c = \frac{[\text{products}]}{[\text{reactants}]}$

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** 反应物 fall and **products** 生成物 rise until, once the rates match, both hold constant (they need not be equal).



at equilibrium: $r_f = r_r \cdot K_c = \frac{[\text{products}]}{[\text{reactants}]}$

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.

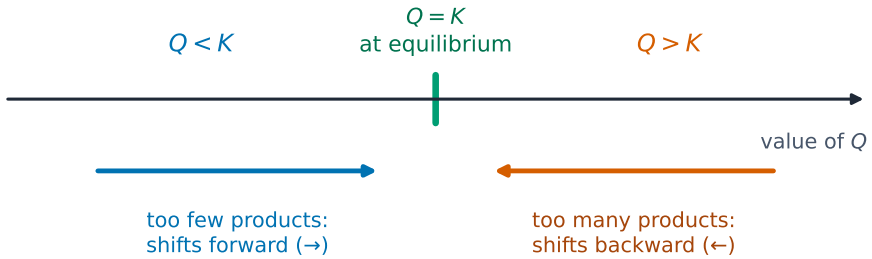
Think in terms of rates. If the forward rate is greater than the reverse rate, there is a net change from reactants to products. If the reverse rate is greater, the net change goes the other way. Starting with only reactants, the forward rate is high and the reverse rate is zero. As products build up, the forward rate falls and the reverse rate rises, until they meet.

The Reaction Quotient and Equilibrium Constant

The **reaction quotient** 反应商 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** 平衡常数 K. Comparing them predicts direction: $Q < K$ shifts **forward** (toward products); $Q > K$ shifts **reverse**; $Q = K$ means already at equilibrium.



Compare Q with K to tell which way a reaction will shift

Calculating the Equilibrium Constant

Write K from the **balanced equation** 配平方程式 (pure solids and liquids are left out). From equilibrium concentrations (or **partial pressures** 分压 for K_p), plug in and compute. K_c uses **molarities** 摩尔浓度; K_p uses pressures.

exercises.lol exercises.com.cn

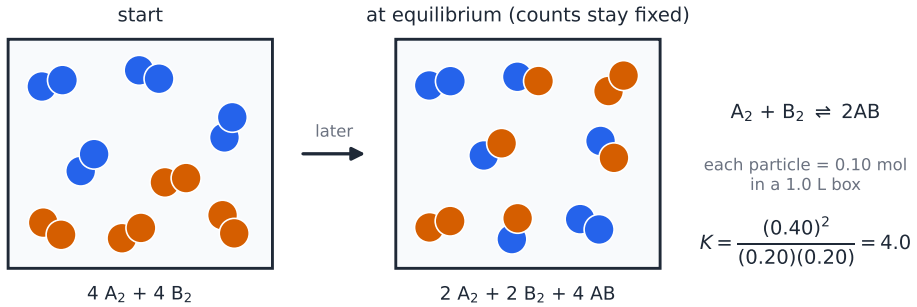
Worked example. For $N_2O_4 \rightleftharpoons 2NO_2$, the equilibrium concentrations are $[N_2O_4] = 0.20$ M and $[NO_2] = 0.10$ M. Then

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

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

Worked example (leave out solids and liquids). For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, the expression is simply $K_p = P_{CO_2}$. The two solids do not appear: adding more solid does not change its concentration. If the equilibrium pressure of CO_2 is 0.22 atm at some temperature, then $K_p = 0.22$, provided both solid phases remain present.

AP will not ask you to convert between K_c and K_p, but read each question carefully to see which one it uses.



Counting particles gives the equilibrium concentrations, and from them K; the average counts stay constant at equilibrium

Worked example (K from a particle picture). In the drawing above, the box starts with 4 A_2 and 4 B_2. At equilibrium it holds 2 A_2, 2 B_2 and 4 AB. If each particle stands for 0.10 mol in 1.0 L, the concentrations are 0.20, 0.20 and 0.40 M, so

$$K = \frac{[AB]^2}{[A_2][B_2]} = \frac{(0.40)^2}{(0.20)(0.20)} = 4.0.$$

Check the atoms: 8 A atoms and 8 B atoms before, and 8 of each after.

exercises.lol exercises.com.cn

Magnitude of the Equilibrium Constant

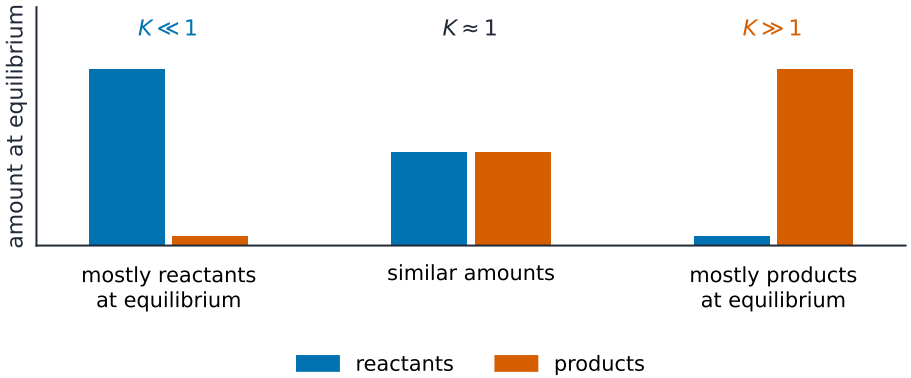
- $K \gg 1$: products strongly favored (reaction nearly complete).
- $K \ll 1$: reactants favored (little reaction).
- $K \approx 1$: significant amounts of both.

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

Worked example. At 25 °C, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ has $K \approx 10^{-30}$. What does this mean for a sample of air? $K \ll 1$, so at equilibrium almost no NO is present: the nitrogen and oxygen in air do not react to a measurable extent at room temperature. The reverse reaction, $2NO \rightleftharpoons N_2 + O_2$, has $K = \frac{1}{10^{-30}} = 10^{30}$, so it is strongly product-favored.

The size of K says nothing about speed. A reaction with a huge K can still be extremely slow: K describes where the reaction ends up, not how fast it gets there, which depends on the activation energy. Saying "a large K means a fast reaction" loses the point.

Using a small K in a calculation. When K is very small and the mixture starts with reactants only, the amount that reacts, x, may be small compared with the starting concentrations. Check this before using $[A]_0 - x \approx [A]_0$. A valid approximation makes the calculation of equilibrium concentrations much simpler (see *Calculating Equilibrium Concentrations* below).



A large K means mostly products at equilibrium; a small K means mostly reactants

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.

> **Worked example (changing K with the equation).** For $N_2O_4 \rightleftharpoons 2NO_2$, $K = 0.050$.

- Reversed, $2NO_2 \rightleftharpoons N_2O_4$: $K = 1/0.050 = 20$.
- Halved, $NO_2 \rightleftharpoons \frac{1}{2}N_2O_4$: $K = 20^{1/2} = 4.5$.
- Added steps: if reaction 1 has K_1 and reaction 2 has K_2, their sum has $K = K_1K_2$. For example, $N_2 + O_2 \rightleftharpoons 2NO$ (K_1) plus $2NO + O_2 \rightleftharpoons 2NO_2$ (K_2) gives $N_2 + 2O_2 \rightleftharpoons 2NO_2$ with $K = K_1K_2$.

These rules follow from the expressions: write them out and you can see why. Compare Hess's law, where the ΔH values *add*; here the K values *multiply*.

Calculating Equilibrium Concentrations

Use an **ICE table** 三段式 (Initial, Change, Equilibrium): fill in starting amounts, express the change with x using the **mole ratios** 摩尔比, then substitute into the K expression and solve for x. When K is small, the approximation "x is **negligible** 可忽略的 " 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.

> **Worked example (when x is small).** For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at a certain temperature, $K_c = 1.0 \times 10^{-5}$. Start with 0.50 M PCl_5. At equilibrium $[PCl_5] = 0.50 - x$ and $[PCl_3] = [Cl_2] = x$:
>
> $$\frac{x^2}{0.50-x} = 1.0 \times 10^{-5}.$$

Because K is so small, very little reacts, so $0.50 - x \approx 0.50$. Then $x^2 = 5.0 \times 10^{-6}$ and $x = 2.2 \times 10^{-3}$ M. Check: 0.0022 is under 1% of 0.50, so the approximation was safe. If x came out bigger than about 5% of the starting value, you would have to solve the full quadratic.

exercises.lol exercises.com.cn

	H_2	I_2	2 HI
I initial	0.100	0.100	0
C change	$-x$	$-x$	$+2x$
E equilibrium	$0.100 - x$	$0.100 - x$	$2x$

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

An ICE table organises initial amounts, changes and equilibrium amounts

Representations of Equilibrium

A **particulate** 微粒 picture at equilibrium shows the equilibrium proportions of reactant and product particles; individual particles still react. Graphs of concentration vs time level off (never reaching zero) once equilibrium is reached – both curves flatten at the same moment.

A particle picture can also tell you which way a mixture will go. Count the particles to find Q, and compare it with K. Suppose $K = 4.0$ for $A_2 + B_2 \rightleftharpoons 2AB$, and a box (0.10 mol per particle, 1.0 L) holds 1 A_2, 1 B_2 and 6 AB. Then $Q = (0.60)^2/[(0.10)(0.10)] = 36 > K$, so some AB must break up: the mixture shifts toward reactants.

Introduction to Le Chatelier's Principle

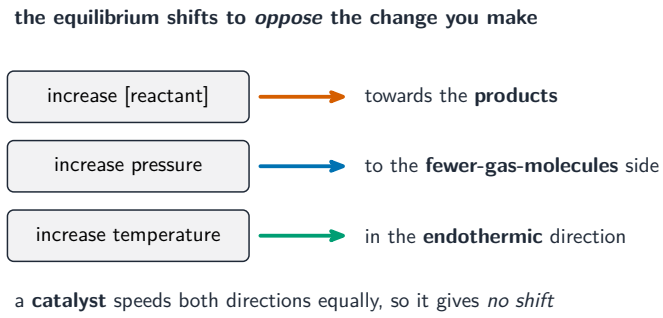
Le Chatelier's principle 勒沙特列原理: if you disturb a system at equilibrium, it shifts to **partly counteract** the change. Adding a reactant shifts forward; removing product shifts forward; increasing pressure (by reducing volume) shifts toward the side with fewer gas moles; raising temperature shifts in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

> **Worked example (a colour change).** In the cobalt solution,

$$[Co(H_2O)_6]^{2+}(aq)\ \text{(pink)} + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq)\ \text{(blue)} + 6H_2O(l) \qquad \Delta H > 0.$$

- Add concentrated HCl (more Cl^-): the mixture shifts forward and turns **bluer**.
- Add water: it shifts back and turns **pinker**. Dilution lowers every ion concentration, and the left side has 5 dissolved particles against 1 on the right.
- Heat it: the forward direction is endothermic, so it turns **blue**. Put it in ice and it turns **pink**.

Le Chatelier's principle also predicts other things you can measure, such as pH and temperature. For example, removing H^+ from an equilibrium that makes H^+ shifts it to make more, which partly restores the pH.



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

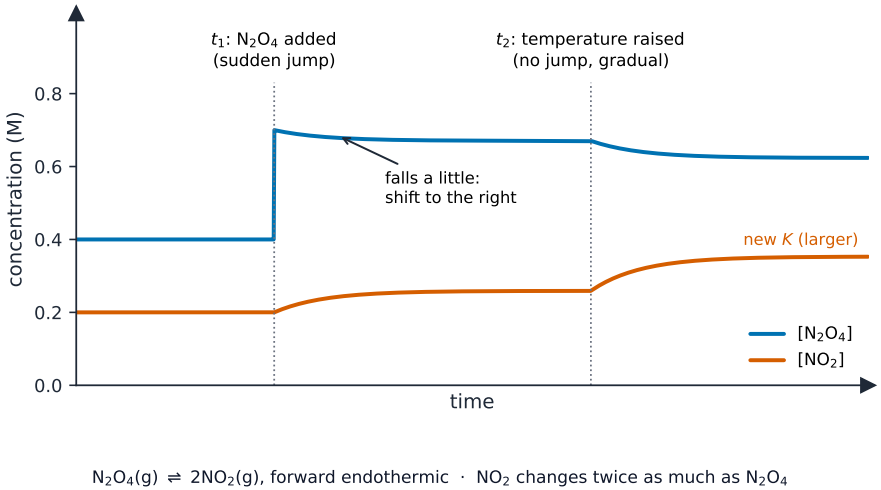
The Reaction Quotient and Le Chatelier's Principle

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.

> **Worked example.** For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (forward endothermic), an equilibrium mixture in a rigid vessel has $[N_2O_4] = 0.40\ M$ and $[NO_2] = 0.20\ M$, so

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.20^2}{0.40} = 0.10$$

- **Add N_2O_4** until $[N_2O_4] = 0.70\ M$: $Q = \dfrac{0.20^2}{0.70} = 0.057 < K$, so the reaction runs **forward** until $Q = 0.10$ again.
- **Halve the volume**: every concentration doubles, so $Q = \dfrac{0.40^2}{0.80} = 0.20 > K$. The reaction runs **in reverse**, towards the side with fewer moles of gas. This works because the top of Q is squared and the bottom is not.
- **Add argon at constant volume**: no concentration in Q changes, so $Q = K$ and there is **no shift**, even though the total pressure rises.
- **Raise the temperature**: this time Q does not change, but K does. Heat favours the endothermic (forward) direction, so K increases and now $Q < K$.



Adding a substance makes its line jump at once; a temperature change makes both lines move gradually, because it changes K

Common mistakes.

- Saying that adding a reactant "changes K". Only temperature changes K; other disturbances change Q.
- Saying that any pressure increase causes a shift. Adding an inert gas at constant volume does not change Q.
- Drawing the graph with every line jumping at a temperature change, or with the system returning to the **original** concentrations.
- Forgetting that a catalyst changes neither Q nor K, so it causes no shift.

exercises.lol exercises.com.cn

Introduction to Solubility Equilibria

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

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

Compare K_{sp} values directly only for salts with the same dissolution **stoichiometry** 化学计量 under the same conditions. For different stoichiometries, calculate **molar solubility** 摩尔溶解度 from each balanced equilibrium expression. The **common-ion effect** 同离子效应 – 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.

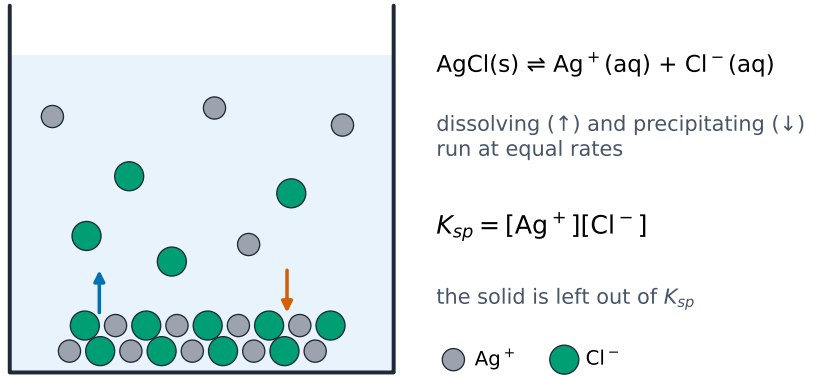
> **Worked example (a 1:2 salt).** Calcium fluoride has $K_{sp} = 3.9 \times 10^{-11}$. Each $\mathrm{CaF_2}$ that dissolves gives one Ca^{2+} and **two** F^-, so $[\mathrm{Ca}^{2+}] = s$ and $[\mathrm{F}^-] = 2s$:
>
> $$K_{sp} = s(2s)^2 = 4s^3, \qquad s = \sqrt[3]{\frac{3.9 \times 10^{-11}}{4}} = 2.1 \times 10^{-4}\ \mathrm{M}.$$

$\mathrm{CaF_2}$ has the *smaller* K_{sp} but the *larger* molar solubility, which is why K_{sp} values can only be compared directly for salts of the same type. The calculation also runs backwards: a measured molar solubility gives K_{sp}. AP relates $K_{sp} > 1$ to soluble salts and treats sodium, potassium, ammonium and nitrate salts as soluble for its qualitative solubility rules.

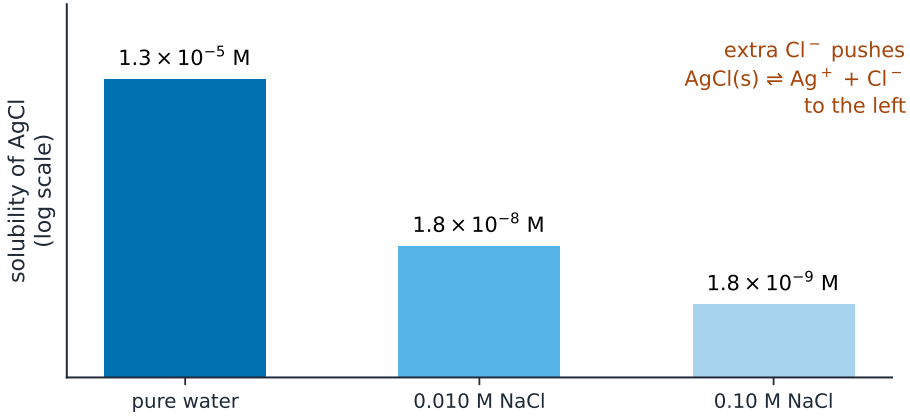
> **Worked example (common ion, with numbers).** How much AgCl dissolves in 0.10 M NaCl? Now $[\mathrm{Cl}^-] = 0.10 + s \approx 0.10$, because s is tiny:
>
> $$s = \frac{K_{sp}}{[\mathrm{Cl}^-]} = \frac{1.8 \times 10^{-10}}{0.10} = 1.8 \times 10^{-9}\ \mathrm{M}.$$

That is about 7000 times less than in pure water (1.3×10^{-5} M).

exercises.lol exercises.com.cn



In a saturated solution dissolving and precipitating run at equal rates



Adding a common ion lowers the solubility of a salt

Practice

Answer each before reading the answers below.

1. Write the K_c expression for $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$.
2. For the reaction in question 1, $K_c = 0.50$. A mixture has $[\mathrm{N_2}] = [\mathrm{H_2}] = [\mathrm{NH_3}] = 1.0\ M$. Which way does the reaction go?
3. For $\mathrm{H_2} + \mathrm{I_2} \rightleftharpoons 2\mathrm{HI}$, $K_c = 49.0$. Starting from 0.100 M each of $\mathrm{H_2}$ and $\mathrm{I_2}$ and no HI, find all equilibrium concentrations.

4. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ at constant temperature, extra CO_2 is injected. What is the final pressure of CO_2 compared with before? What if extra $CaCO_3(s)$ is added instead?
5. For $A \rightleftharpoons 2B$, $K = 4.0$. Find K for $4B \rightleftharpoons 2A$.
6. For AgCl, $K_{sp} = 1.8 \times 10^{-10}$. Find the molar solubility in pure water and in 0.10 M NaCl.

Answers

1. $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$.
2. $Q = \dfrac{1.0^2}{(1.0)(1.0)^3} = 1.0 > K$, so the reaction shifts left, toward N_2 and H_2.
3. $\dfrac{(2x)^2}{(0.100-x)^2} = 49.0$, so $\dfrac{2x}{0.100-x} = 7.00$ and $x = 0.0778$. $[HI] = 0.156\ M$; $[H_2] = [I_2] = 0.022\ M$.
4. $K_p = P_{CO_2}$, so added CO_2 reacts with CaO and restores the original equilibrium pressure, provided some CaO remains. If all CaO is consumed first, the pressure can remain higher. Adding $CaCO_3$ changes nothing when both solid phases are already present.
5. Reverse (giving 1/4.0), then double the coefficients (square it): $K = (0.25)^2 = 0.0625$.
6. Pure water: $s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}\ M$. In 0.10 M NaCl: $s = 1.8 \times 10^{-10} \div 0.10 = 1.8 \times 10^{-9}\ M$ (common-ion effect).

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; compress the gas → shift toward fewer gas moles; raise temperature → shift in the **endothermic** 吸热 direction.
- A **catalyst** 催化剂 **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.

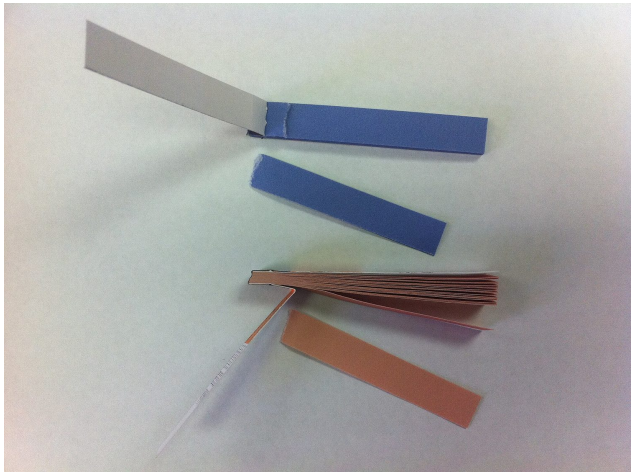
exercises.lol exercises.com.cn

Acids and Bases

AP Chemistry

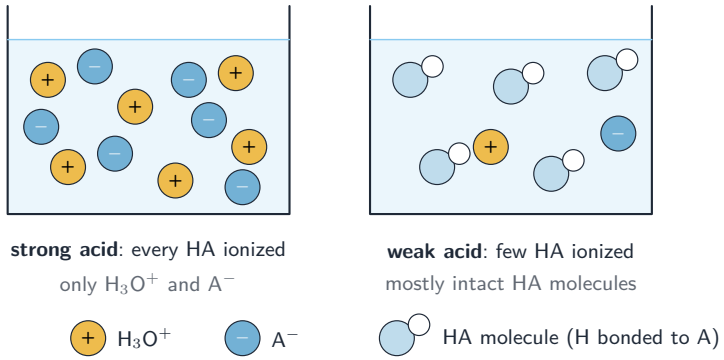
Introduction to Acids and Bases

Your blood stays between pH 7.35 and 7.45. Below about 7.0 or above 7.8, cells stop working and a person can die. Yet every minute your muscles release acid and your lungs remove carbon dioxide, so the amount of acid in your blood is always changing. The pH stays steady because blood is a **buffer**, a mixture of carbonic acid and hydrogen carbonate ions. This unit builds up the ideas you need to understand it: pH, strong and weak acids, titrations and buffers.



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

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



A strong acid is fully dissociated; in this weak-acid sample, only a small fraction ionizes and most stays as HA molecules



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** 自偶电离:

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

One water molecule passes a proton to another, making a **hydronium ion** 水合氢离子 (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** 水的离子积:

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

exercises.lol exercises.com.cn

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.

At 25 °C, 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** 中性 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.

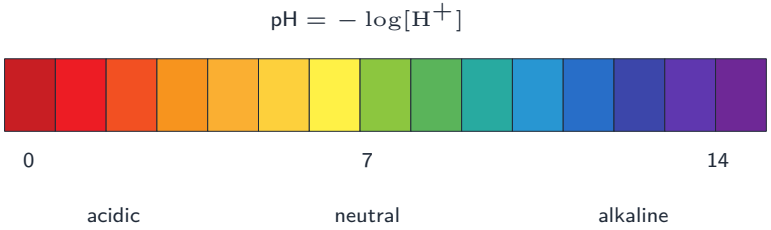
K_w is **temperature dependent**: autoionization is endothermic, so heating water shifts it forward and raises K_w. At 50 °C, $K_w > 1.0 \times 10^{-14}$, so neutral water has $\text{pH} = \text{pOH} < 7.0$. It is still neutral, because the ion concentrations are still equal – neutral means equal ions,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



pH strips: water autoionizes so pure water is pH 7 at 25 °C; acids and bases shift H+ and OH-

pH and pOH of Strong Acids and Bases

The **pH** pH 值 scale measures acidity: $\mathrm{pH} = -\log[\mathrm{H}^+]$, with $\mathrm{pH} + \mathrm{pOH} = 14$ at 25 °C. A **strong acid** 强酸 ionises essentially completely in dilute water; a soluble **strong base** 强碱 such as NaOH dissociates. For a monoprotic acid or a base supplying one hydroxide per formula unit, the ion concentration is approximately the analytical concentration when water autoionisation is negligible. Otherwise use the balanced stoichiometric ratio. 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, $\mathrm{pOH} = 2.0$, so $\mathrm{pH} = 14 - 2.0 = 12.0$.

Learn the six strong acids AP names: HCl, HBr, HI, $\mathrm{HClO_4}$, $\mathrm{H_2SO_4}$ and $\mathrm{HNO_3}$. Common strong bases are the group 1 hydroxides and the dissolved hydroxides of calcium, strontium and barium. Watch the formula: $\mathrm{Ba(OH)_2}$ gives **two** hydroxide ions per formula unit. In 0.0050 M $\mathrm{Ba(OH)_2}$, $[\mathrm{OH}^-] = 0.010$ M, so $\mathrm{pOH} = 2.0$ and $\mathrm{pH} = 12.0$, the same as 0.010 M NaOH.

Weak Acid and Base Equilibria

A **weak acid** 弱酸 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. Find $[\mathrm{H}^+]$ with an ICE table and the K_a expression. Use a small-x approximation only after checking that the dissociated fraction is small.

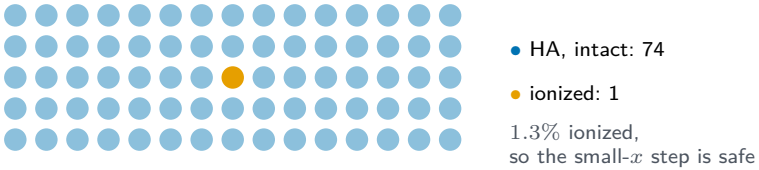
exercises.lol exercises.com.cn

> **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
>
> $$x = \sqrt{K_a \times 0.10} = \sqrt{1.8 \times 10^{-6}} = 1.3 \times 10^{-3}\ \text{M} \ \Rightarrow\ \mathrm{pH} = -\log(1.3 \times 10^{-3}) = 2.9.$$
>
> The weak acid is far less acidic than a strong acid of the same concentration (which would be pH 1.0).

The **percent ionization** 电离百分比 shows how weak it is:

$$\frac{[\mathrm{H_3O^+}]}{[\mathrm{HA}]_0} \times 100\% = \frac{1.3 \times 10^{-3}}{0.10} \times 100\% = 1.3\%.$$

Only about 1 molecule in 75 has given up its proton. The small-x approximation was safe, because 1.3% is under 5%.



At 0.10 M, acetic acid is 1.3 percent ionized: about one molecule in 75

Exam skill (dilution and particle diagrams). Diluting a weak acid makes its percent ionization go *up*, even though $[\mathrm{H_3O^+}]$ goes down. Adding water lowers every concentration, so $Q = \dfrac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$ falls below K_a, and more HA ionizes to restore equilibrium. For 0.035 M HF diluted to 0.0175 M, the ionized fraction rises. In a particle diagram of a weak acid, most particles are intact HA, with only a few $\mathrm{H_3O^+}$ and $\mathrm{A^-}$. In a buffer drawing, compare HA with $\mathrm{A^-}$: more HA means $\mathrm{pH} < \mathrm{p}K_a$, equal numbers mean $\mathrm{pH} = \mathrm{p}K_a$, and more $\mathrm{A^-}$ means $\mathrm{pH} > \mathrm{p}K_a$.

> **Worked example (a weak base).** Find the pH of 0.10 M ammonia, $K_b = 1.8 \times 10^{-5}$:
>
> $$\mathrm{NH_3} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_4^+} + \mathrm{OH^-}, \qquad K_b = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}.$$
>
> So $x = [\mathrm{OH}^-] = 1.3 \times 10^{-3}$ M, $\mathrm{pOH} = 2.87$ and $\mathrm{pH} = 14.00 - 2.87 = 11.13$. A weak base gives you $[\mathrm{OH}^-]$ first; remember to convert to pH at the end. The conjugate acid, $\mathrm{NH_4^+}$, has $K_a = K_w/K_b = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$.

Acid-Base Reactions and Buffers

A **buffer** 缓冲溶液 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.

When a strong acid or strong base neutralizes another acid or base, first do the stoichiometry, then examine what remains. A weak acid with a weak base instead needs an equilibrium calculation. Four cases come up:

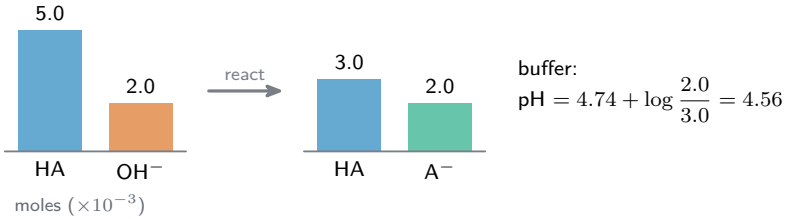
You mix	What happens	What sets the pH
strong acid + strong base	$H^+ + OH^- \rightarrow H_2O$	whichever is in excess; at equivalence, water sets the neutral pH
weak acid + strong base	$HA + OH^- \rightarrow A^- + H_2O$	excess HA with A^-: buffer; at equivalence, A^- hydrolysis; beyond it, excess OH^-
weak base + strong acid	$B + H_3O^+ \rightarrow HB^+ + H_2O$	excess B with HB^+: buffer; at equivalence, HB^+ hydrolysis; beyond it, excess strong acid
weak acid + weak base	an equilibrium, $HA + B \rightleftharpoons A^- + HB^+$	the equilibrium mixture

Worked example (strong + strong). Mix 25.0 mL of 0.100 M HCl with 15.0 mL of 0.100 M NaOH. Moles: H^+ 2.50×10^{-3}, OH^- 1.50×10^{-3}. After reaction, 1.00×10^{-3} mol of H^+ is left in 40.0 mL, so $[H^+] = 0.0250$ M and pH = 1.60. Do not forget the total volume.

exercises.lol exercises.com.cn

Worked example (weak + strong makes a buffer). Add 2.0×10^{-3} mol NaOH to 5.0×10^{-3} mol acetic acid ($pK_a = 4.74$). The hydroxide converts 2.0×10^{-3} mol of HA into A^-, leaving 3.0×10^{-3} mol HA. Both are in the same volume, so the mole ratio is the concentration ratio:

$$\text{pH} = 4.74 + \log \frac{2.0}{3.0} = 4.74 - 0.18 = 4.56.$$



Stoichiometry first, then Henderson-Hasselbalch: 2.0 of hydroxide turns 2.0 of HA into A-, leaving a buffer at pH 4.56

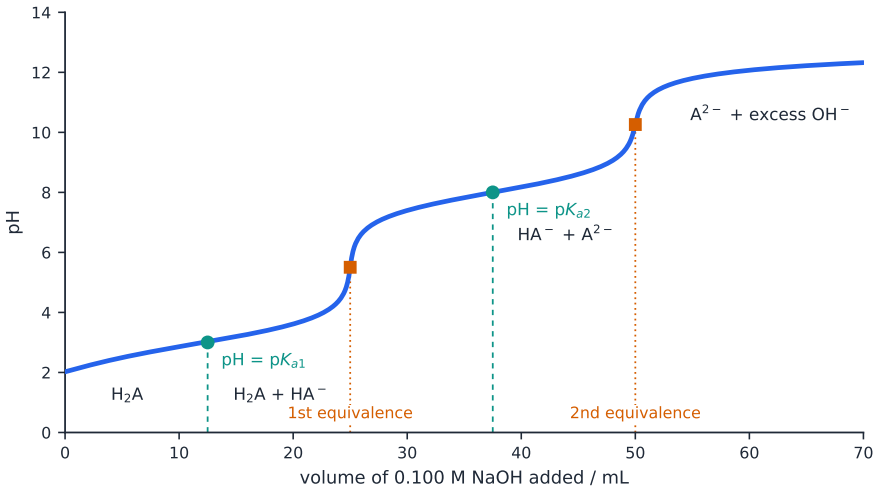
Acid-Base Titrations

A **titration curve** 滴定曲线 plots pH as base (or acid) is added. Key points: the **equivalence point** 等当点 (acid and base mixed in their balanced stoichiometric ratio; equal moles only for a 1:1 reaction), and, for a single weak-acid titration stage, the **half-equivalence point**, where $\text{pH} = pK_a$ (half the weak acid is converted, so a buffer is at its center).

An **acid-base indicator** 酸碱指示剂 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.

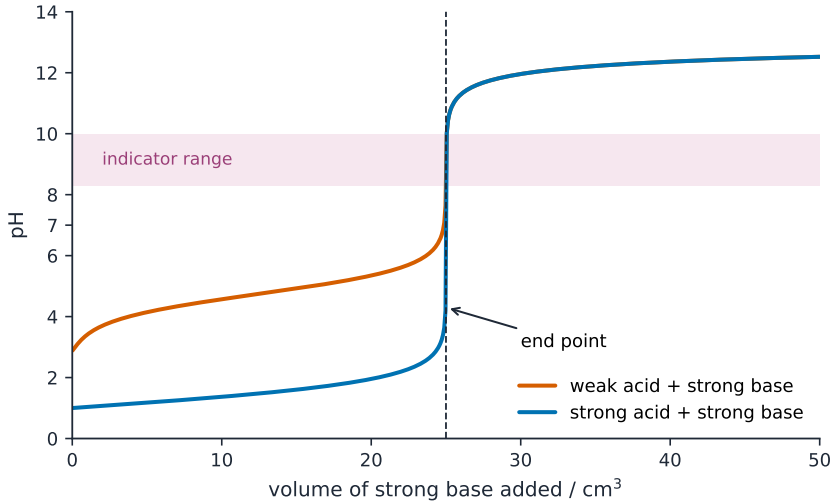
Why is the equivalence point of a weak acid titrated with NaOH basic? At that point all the HA has become A^-, and A^- is a weak base that reacts with water to make OH^-. For example, titrating 0.100 M acetic acid with an equal volume of 0.100 M NaOH gives an equivalence pH of about 8.7, so **phenolphthalein** (colour change near pH 9) is a good choice. For a weak base titrated with a strong acid, the equivalence pH is below 7, so choose an indicator such as methyl red that changes near pH 5. In general, choose an indicator whose pK_a is close to the equivalence-point pH.

A **polyprotic acid** 多元酸 has more than one acidic proton, and loses them one at a time. Separate jumps appear only when successive acid strengths are sufficiently different and the stages give clear pH changes; not every acidic proton gives a visible jump.



This diprotic-acid example has two resolved jumps; halfway through each neutralization stage, pH is approximately the corresponding pKa

Read the curve region by region. Before the first jump the main species are H_2A and HA^-; halfway there, pH = pK_{a1}. Between the jumps they are HA^- and A^{2-}; halfway between the two equivalence points, pH = pK_{a2}. After the second jump the solution holds A^{2-} and excess OH^-. The second equivalence volume is twice the first, because each proton needs the same amount of base.



A titration curve has a steep jump near the equivalence point

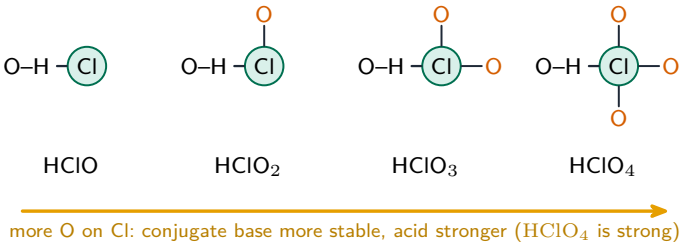
exercises.lol exercises.com.cn

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 with the same central element, more oxygen atoms generally mean a stronger acid.

Comparison	Stronger acid	Reason
$HClO$, $HClO_2$, $HClO_3$, $HClO_4$	$HClO_4$ (strong)	each extra O pulls electron density away and spreads the negative charge of the conjugate base
acetic acid (pK_a 4.76) vs chloroacetic acid (pK_a 2.87)	chloroacetic acid	the electronegative Cl pulls charge away from the COO^- (an inductive effect)
acetic acid vs ethanol (p$K_a \approx 16$)	acetic acid	the acetate ion's charge is shared over two O atoms by resonance

Carboxylic acids 羧酸, with the group –COOH, are the most common weak acids; only the H on the –COOH group is acidic, not the H atoms on carbon. Common weak bases contain a nitrogen atom with a lone pair, such as ammonia and amines, or are carboxylate ions such as acetate.



Each extra oxygen on chlorine pulls electron density away and spreads the conjugate base's charge, so acid strength rises up to HClO4

pH and pKa

p$K_a = -\log K_a$: 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.

Worked example (a drug in the body). Aspirin is a weak acid with $pK_a = 3.5$. In the stomach, at pH 1.5, the pH is 2 units **below** the pK_a, so $[A^-]/[HA] = 10^{1.5-3.5} = 10^{-2}$: about 99% is the neutral acid form HA. In the small intestine, at pH 7.5, the ratio is 10^4, and almost all of it is the ion A^-. The neutral form crosses cell membranes much more easily, so where a drug is absorbed depends on pH.

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.

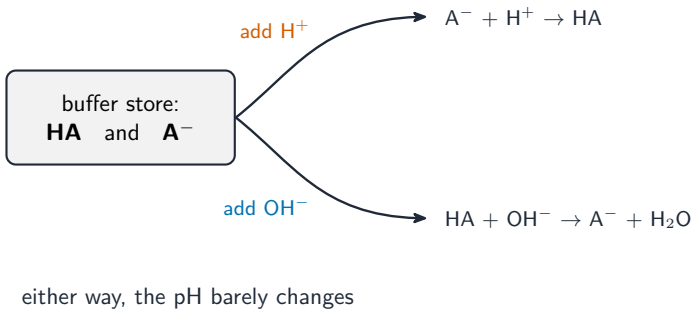
Worked example (adding acid to a buffer). 1.00 L of buffer holds 0.20 mol acetic acid and 0.30 mol acetate ($pK_a = 4.74$, pH 4.92). Then 0.050 mol HCl is added. (a) Write the net ionic equation. (b) Find the new pH.

(a) The added acid reacts with the conjugate base: $CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$. The reaction goes to completion, so write a single arrow.

(b) Do the stoichiometry first, in moles: acetate $0.30 - 0.050 = 0.25$ mol, acetic acid $0.20 + 0.050 = 0.25$ mol. Then use the ratio:

$$\text{pH} = 4.74 + \log\frac{0.25}{0.25} = 4.74.$$

The pH falls by only 0.18. The same 0.050 mol HCl in 1.00 L of pure water would give $[H_3O^+] = 0.050$ M, pH 1.30.



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:

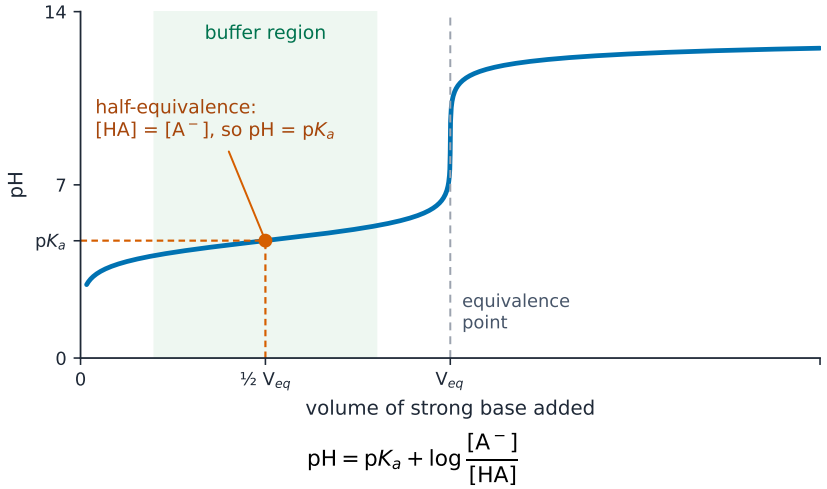
$$\text{pH} = pK_a + \log\frac{[A^-]}{[HA]}.$$

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

Worked example. A buffer holds 0.20 M acetic acid ($pK_a = 4.74$) 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 pK_a, as the equation predicts.



At half-equivalence [HA] = [A⁻], so the pH equals the pKa

Buffer Capacity

Buffer capacity 缓冲容量 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.

Capacity can also be lopsided. A buffer with more weak acid than conjugate base can absorb more added **base** than added acid, because there is more HA to react with OH^-. A buffer with more conjugate base can absorb more added **acid**. Blood

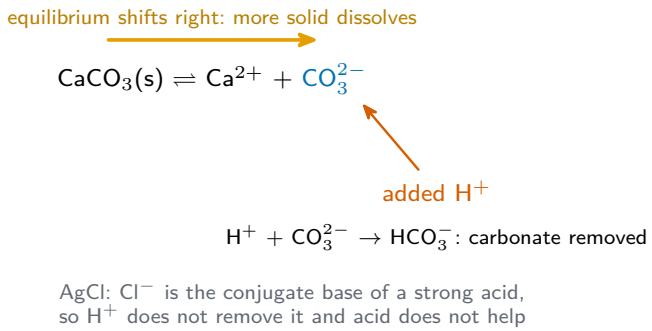
exercises.lol exercises.com.cn

has about twenty times more hydrogen carbonate than carbonic acid, which suits the body: metabolism mostly adds acid.

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.

This matters only when one of the ions is a weak base, a weak acid or hydroxide. Calcium carbonate dissolves in acid because CO_3^{2-} is a base; that is why acid rain eats away limestone statues and why vinegar removes the scale inside a kettle. $Mg(OH)_2$, the antacid "milk of magnesia", dissolves in stomach acid because acid removes its OH^-. By contrast, adding acid does not help AgCl dissolve: Cl^- is the conjugate base of a strong acid, so it does not react with H^+.



Acid dissolves a salt with a basic anion by removing that anion; chloride, from a strong acid, is not removed, so AgCl stays put

Common mistakes.

- Expecting every equivalence point to be at pH 7. Weak acid + strong base ends **above** 7 (the conjugate base is left); weak base + strong acid ends **below** 7.
- Reading pK_a at the equivalence point. pH = pK_a at the **half**-equivalence point, where $[HA] = [A^-]$.
- Turning the Henderson–Hasselbalch ratio upside down. It is $pH = pK_a + \log \frac{[A^-]}{[HA]}$: more base than acid gives a pH **above** pK_a.
- Using the strong-acid shortcut for a weak acid. For a weak acid, $[H_3O^+]$ is much smaller than the acid concentration; set up the K_a expression.

exercises.lol exercises.com.cn

- Saying a more concentrated buffer has a different pH. The pH depends on the **ratio** $[A^-]/[HA]$; a more concentrated buffer with the same ratio has the same pH but a larger **capacity**.
- Mixing up the direction of K_a and pK_a. A stronger acid has a **larger** K_a and a **smaller** pK_a.

Practice

Answer each before reading the answers below.

1. Find the pH of 0.010 M HCl and of 0.010 M NaOH at 25°C.
2. Find the pH of 0.10 M acetic acid, $K_a = 1.8 \times 10^{-5}$.
3. In $CH_3CH_2COOH + H_2O \rightleftharpoons CH_3CH_2COO^- + H_3O^+$, identify a conjugate acid-base pair and label the acid and the base.
4. A buffer has $[A^-] = 0.20$ M and $[HA] = 0.10$ M, with $pK_a = 4.74$. Find the pH.
5. A weak acid is titrated with NaOH. What is the pH at the half-equivalence point, and is the pH at the equivalence point above, below or equal to 7? Explain.
6. The equivalence point of a titration is at pH 8.7. Choose an indicator: methyl orange (range 3.1–4.4), bromothymol blue (6.0–7.6) or phenolphthalein (8.2–10).
7. Which is the stronger acid, CH_3COOH or $ClCH_2COOH$? Explain using structure.

Answers

1. pH = 2.00; pOH = 2.00, so pH = 12.00.
2. $[H^+] = \sqrt{(1.8 \times 10^{-5})(0.10)} = 1.3 \times 10^{-3}$ M; pH = 2.87.
3. CH_3CH_2COOH (acid) and $CH_3CH_2COO^-$ (its conjugate base); or H_3O^+ (acid) and H_2O (base).
4. $pH = 4.74 + \log \frac{0.20}{0.10} = 5.04$.
5. At half-equivalence $[HA] = [A^-]$, so pH = pK_a. At equivalence the solution contains A^-, a weak base, so the pH is above 7.
6. Phenolphthalein: its colour change range includes pH 8.7.
7. $ClCH_2COOH$. The electronegative Cl pulls electron density away from the O–H bond and stabilizes the conjugate base by spreading its negative charge.

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 $[H_3O^+]$.
- $pH = -\log[H^+]$ is **logarithmic** – each unit is a ten-fold change in $[H^+]$.

- For **strong** acids/bases use complete ionisation or dissociation with the balanced ion ratio; for **weak** species use the appropriate equilibrium constant.
- A **buffer** holds a weak acid **and** its conjugate base, which mop up added acid or base.
- On a titration curve the **equivalence point** is the steep jump; at **half-equivalence** $\mathrm{pH} = \mathrm{p}K_a$, and a smaller $\mathrm{p}K_a$ means a stronger acid.

exercises.lol exercises.com.cn

Thermodynamics and Electrochemistry

AP Chemistry

Introduction to Entropy

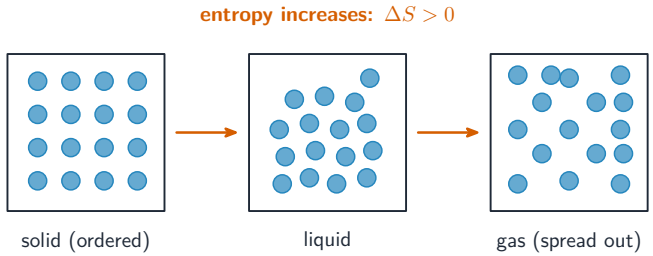
Put a glass of water in a freezer at −10 °C and it turns to ice. Leave ice on a table at +10 °C and it melts. It is the same change, run in opposite directions, and only the temperature decides which way it goes. Freezing gives out energy, which favours it; but it also locks the molecules into place, which works against it. This unit shows how to weigh those two effects against each other, and then how the same idea powers every battery.

Entropy 熵 S measures the **dispersal** 分散 of energy and matter – loosely, the number of ways to arrange a system. Entropy usually increases on melting or **vaporisation** 汽化 and when accessible gas states increase. Dissolving a solid can increase or decrease the system entropy because **solvation** 溶剂化 also affects particle arrangements. Compare the actual states and conditions.

Entropy also rises when **energy** spreads out. Heating a gas widens the range of speeds its molecules have, so the energy is shared out in more ways and the entropy increases. A gas expanding into a larger volume and two different gases mixing both increase entropy too, because each molecule has more places it could be.

> **Worked example (predict the sign).** Decide whether ΔS is positive or negative for each process.

- $\mathrm{H_2O}(s) \rightarrow \mathrm{H_2O}(l)$: **positive**; the molecules become free to move.
- $2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightarrow 2\mathrm{SO_3}(g)$: **negative**; 3 mol of gas become 2.
- $\mathrm{CaCO_3}(s) \rightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$: **positive**; a gas forms from a solid.
- $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \rightarrow \mathrm{AgCl}(s)$: **negative**; free ions lock into a solid.



Entropy rises from solid to liquid to gas

Absolute Entropy and Entropy Change

At temperatures above 0 K, substances have positive **absolute entropy** 绝对熵 S°. For a reaction,

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

Changes in gas moles often predict its **sign**: more gas usually raises entropy, but use the tabulated entropies when a definite value is needed.

Worked example (calculate ΔS°). For $N_2(g)+3H_2(g) \rightarrow 2NH_3(g)$, use S° values of 191.6 (N_2), 130.7 (H_2) and 192.5 (NH_3) J/(mol K):

$$\Delta S^\circ = 2(192.5) - [191.6 + 3(130.7)] = 385.0 - 583.7 = -198.7 \text{ J/K}.$$

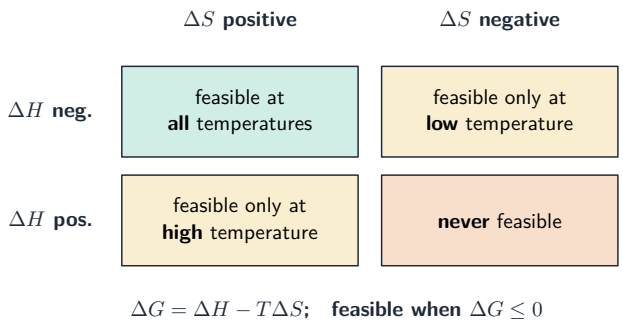
The sign agrees with the prediction: 4 mol of gas become 2. Unlike ΔH_f°, the S° of an element is **not** zero, so N_2 and H_2 must be included.

Gibbs Free Energy and Thermodynamic Favorability

Gibbs free energy 吉布斯自由能 combines enthalpy and entropy:

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

At constant temperature and pressure, a process is **thermodynamically favorable** 热力学有利 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.



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

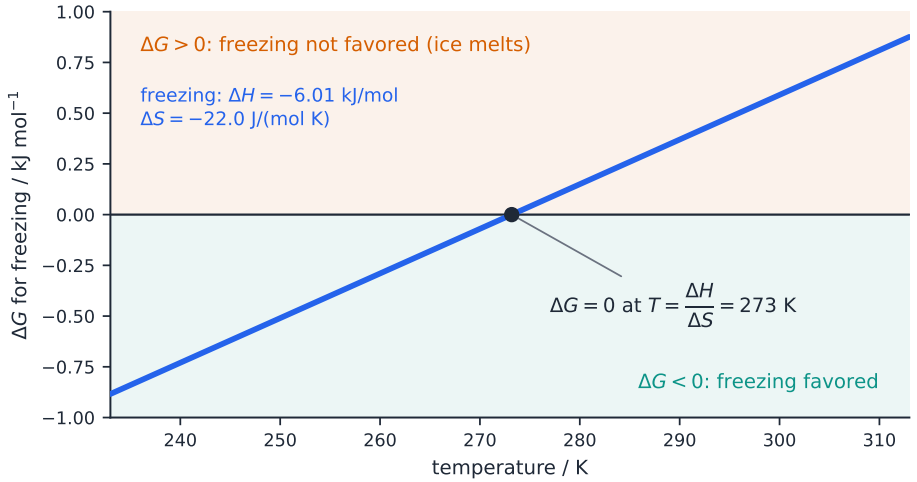
exercises.lol exercises.com.cn

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/(mol K)):

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

The signs of ΔH and ΔS give four cases:

ΔH	ΔS	**Favored ($\Delta G < 0$) at**	**Example**
−	+	all temperatures	burning graphite to $CO_2(g)$
+	−	no temperature	reversing graphite combustion
+	+	high temperature	melting, dissolving $NaNO_3$
−	−	low temperature	freezing, making NH_3



For freezing water both ΔH and ΔS are negative, so ΔG changes sign at 273 K: the line explains the opening question

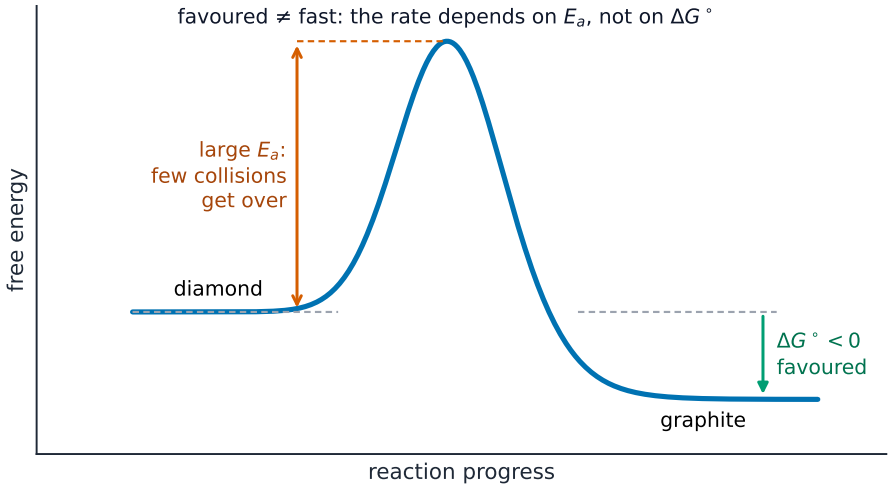
Worked example (the freezing point from thermodynamics). For freezing, $\Delta H = -6.01$ kJ/mol and $\Delta S = -22.0$ J/(mol K). Freezing is favored when $\Delta H - T\Delta S < 0$, which is when $T < \Delta H/\Delta S = 6010/22.0 = 273$ K. Thermodynamics predicts the freezing point of water, 0 °C.

ΔG° can also come from tables of **standard free energies of formation**, in exactly the same way as ΔH°: products minus reactants, each multiplied by its coefficient.

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** 活化能 (diamond → graphite). **Thermodynamics** 热力学 gives the direction; **kinetics** 动力学 gives the speed.

Your own body is an example. Glucose burning in oxygen has $\Delta G^\circ \approx -2900$ kJ/mol, yet sugar in a bowl does not catch fire. Its activation energy is too high at room temperature. In cells, enzymes lower that barrier, so the same reaction runs steadily at 37 °C. Such a reaction is said to be under **kinetic control** 动力学控制. A slow reaction is not an unfavorable one.



A reaction can be thermodynamically favoured yet slow when its activation energy is large

Free Energy and Equilibrium

Free energy links to the **equilibrium constant** 平衡常数:

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

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

The size of K depends on how ΔG° compares with RT, which is about 2.5 kJ/mol at 298 K. If ΔG° is close to zero, K is close to 1. If it is many times RT, K is huge or tiny.

exercises.lol exercises.com.cn

> **Worked example (K from ΔG°).** A reaction has $\Delta G^\circ = -10.0$ kJ/mol at 298 K. Then

$$K = e^{-\Delta G^\circ/RT} = e^{10000/(8.314\times298)} = e^{4.04} = 57.$$

A modest −10 kJ already gives products a clear advantage. For $\Delta G^\circ = -50$ kJ/mol, $K \approx 6 \times 10^8$: the reaction effectively goes to completion. Use $R = 8.314$ J/(mol K) and ΔG° in **joules**.

Free Energy of Dissolution

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

Three steps contribute. Breaking the solid's lattice costs energy. The water molecules must move apart and rearrange around each ion. Then the ions are attracted to the water (**hydration**), which releases energy. Sodium nitrate dissolves well even though dissolving it is endothermic ($\Delta H \approx +20$ kJ/mol): the large entropy gain makes ΔG negative at room temperature. Some salts with small, highly charged ions, such as $CaCO_3$, barely dissolve. Their lattice is very strong, and the water ordered around Ca^{2+} and CO_3^{2-} makes ΔS unfavorable too.

Coupled Reactions

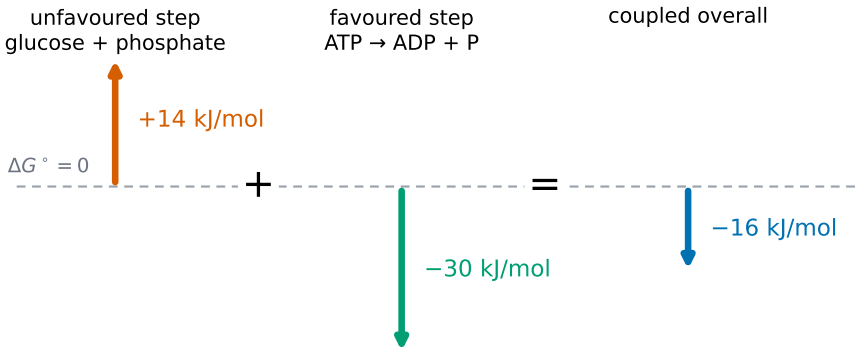
An unfavorable reaction ($\Delta G > 0$) can be driven by **coupling** 偶联 it to a favorable one ($\Delta G < 0$) that shares a common **intermediate** 中间体, as long as the **sum** has $\Delta G < 0$. This is how cells use ATP to power otherwise unfavorable processes.

> **Worked example (driving a reaction with ATP).** Cells make the amino acid glutamine from glutamate and ammonia. The following values are biochemical standard free energies at fixed pH 7, written $\Delta G^{\circ\prime}$:

$$\text{glutamate} + NH_3 \rightarrow \text{glutamine} + H_2O \qquad \Delta G^{\circ\prime} = +14.2 \text{ kJ}$$

$$ATP + H_2O \rightarrow ADP + P_i \qquad \Delta G^{\circ\prime} = -30.5 \text{ kJ}$$

The two are coupled through a shared intermediate, so the overall $\Delta G^{\circ\prime} = +14.2 - 30.5 = -16.3$ kJ is favorable. An unfavorable process can also be driven by an **outside source of energy**: electricity charges a phone battery, and sunlight drives photosynthesis, turning carbon dioxide and water into glucose.

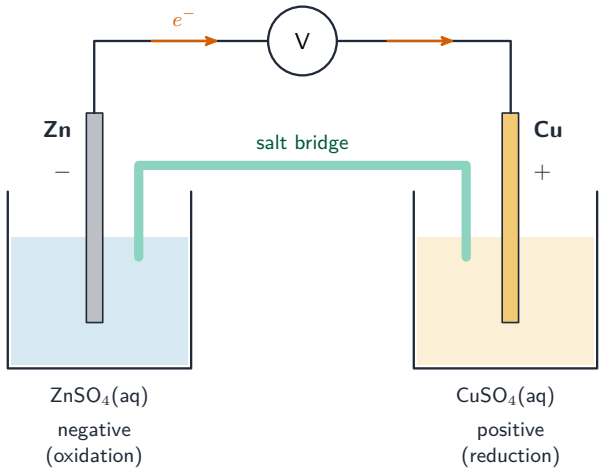


Coupling an unfavourable reaction to a favourable one makes the total $\Delta G°$ negative

Galvanic and Electrolytic Cells

Redox reactions 氧化还原反应 can move electrons through a wire:

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



A galvanic cell with a salt bridge and voltmeter

In both, **oxidation** 氧化 happens at the **anode** 阳极 and **reduction** 还原 at the **cathode** 阴极.

Each part of a cell has a job:

Part	Its job
Electrodes	conduct electrons; the anode may dissolve, the cathode may gain metal
Half-cell solutions	supply the ions that are reduced, or receive the ions that are formed
Wire	carries electrons from anode to cathode
Salt bridge 盐桥	lets ions move so each half-cell stays neutral; without it the current stops at once
Voltmeter	measures the cell potential

In the zinc–copper cell, zinc atoms lose electrons and enter the solution, so the zinc electrode loses mass. Copper ions gain electrons and plate out, so the copper electrode gains mass.

Exam skill (reading a cell diagram). Free-response questions often show a cell and ask four things. For a metal/metal-ion cell such as Zn/Cu, draw the electron arrow along the *wire*, from the anode to the cathode. In the salt bridge, anions move toward the anode, where positive ions are being made, and cations move toward the cathode, where they are being used up. The electrode that loses mass is the anode: its atoms have become ions *in the solution*, so the mass has not disappeared. Observations identify the electrodes: an electrode that gets lighter, or a solution that gains colour from new ions, marks oxidation; metal plating out or a colour fading marks reduction.



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

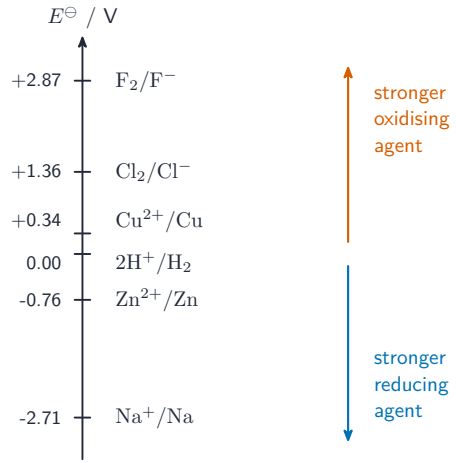
exercises.lol exercises.com.cn

Cell Potential and Free Energy

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

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

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



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** 自发的 and the cell (a Daniell cell) acts as a battery.

Two electrons move per zinc atom, so $n = 2$:

$$\Delta G^\circ = -nFE^\circ = -(2)(96485)(1.10) = -2.12 \times 10^5 \text{ J} = -212 \text{ kJ}.$$

The negative ΔG° agrees with the positive E°. Running the cell backwards, plating zinc and dissolving copper, has $E^\circ = -1.10$ V. Under these standard conditions, reversing it requires an outside power supply above 1.10 V (and additional voltage for real-cell losses): that is an electrolytic cell.

exercises.lol exercises.com.cn

Cell Potential Under Nonstandard Conditions

Away from standard conditions, the potential shifts with concentration – the **Nernst equation** 能斯特方程 (qualitatively): as reactants are consumed, Q rises and E_{cell} falls, reaching zero at equilibrium (a dead battery). The cell potential is a driving force toward equilibrium: the further the cell is from equilibrium, the larger $|E|$. Compare Q with K, using

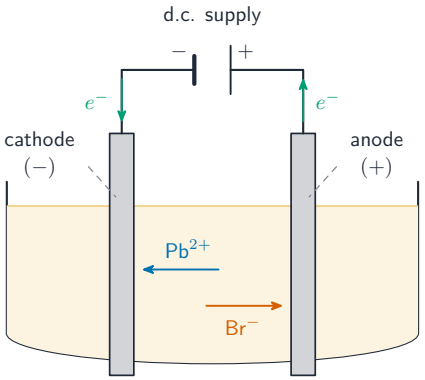
$$E = E^\circ - \frac{RT}{nF}\ln Q.$$

AP asks you to reason with this, not to plug numbers in. When $Q < 1$ (the reaction quotient is below its standard-state value), $\ln Q < 0$ and $E > E^\circ$. When $Q > 1$, $E < E^\circ$. When $Q = K$, $E = 0$. AP notes that **Le Chatelier's principle** 勒夏特列原理 should not be used here, because a working cell is not at equilibrium; argue from Q instead.

> **Worked example (a concentration change).** In the zinc–copper cell, $Q = [Zn^{2+}]/[Cu^{2+}]$. If $[Cu^{2+}]$ is raised to 2.0 M while $[Zn^{2+}]$ stays at 1.0 M, then $Q = 0.50 < 1$, and E_{cell} is slightly **greater** than 1.10 V. As the cell runs, $[Zn^{2+}]$ rises and $[Cu^{2+}]$ falls, so Q grows and E drops until it reaches zero.

Electrolysis and Faraday's Law

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



molten lead(II) bromide, $PbBr_2$

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

anode: $2Br^- \to Br_2 + 2e^-$ (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 ($Cu^{2+} + 2e^- \to Cu$). 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.

Worked example (silver plating, working backwards). A jeweller wants to plate 0.500 g of silver onto a ring with a current of 0.250 A. How long does it take? $Ag^+ + e^- \to Ag$ needs one electron per atom.

$$n(e^-) = n(\text{Ag}) = \frac{0.500}{107.9} = 4.63 \times 10^{-3}\ \text{mol}, \qquad q = nF = (4.63 \times 10^{-3})(96485) = 447\ \text{C}.$$

$$t = \frac{q}{I} = \frac{447}{0.250} = 1790\ \text{s} \approx 30\ \text{min}.$$

The same equations also find an ion's charge. If 0.0100 mol of electrons deposits 0.0050 mol of a metal, each ion needed 2 electrons, so the ion was M^{2+}.

Common mistakes.

- Mixing units in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. ΔS° is usually given in J/(mol K) and ΔH° in kJ/mol: convert one of them before you subtract.
- Saying a thermodynamically favorable reaction is fast. $\Delta G^\circ < 0$ says nothing about the rate; a high activation energy can keep it under **kinetic control**.

exercises.lol exercises.com.cn

- Multiplying a reduction potential by the coefficient in the balanced equation. E° is an intensive property, so it is **not** multiplied; only n in $\Delta G^\circ = -nFE^\circ$ changes.
- Thinking the anode is always negative. Oxidation **always** happens at the anode; it is negative in a galvanic cell but positive in an electrolytic cell.
- Sending electrons through the salt bridge. Electrons move only through the external wire; **ions** move through the salt bridge to keep each half-cell neutral.
- Using Le Chatelier's principle for a working cell. Compare Q with K (or with 1) instead.
- Getting the sign link between K and ΔG° wrong. $\Delta G^\circ = -RT\ln K$: $K > 1$ goes with $\Delta G^\circ < 0$ and $E^\circ_{\text{cell}} > 0$.

Practice

Answer each before reading the answers below.

1. Predict the sign of ΔS for $2H_2O(l) \to 2H_2(g) + O_2(g)$ and explain.
2. For $CaCO_3(s) \to CaO(s) + CO_2(g)$, $\Delta H^\circ = +178$ kJ/mol and $\Delta S^\circ = +161$ J/(mol·K). Is it favorable under standard conditions at 298 K? Above what temperature is it favorable under standard conditions, taking ΔH° and ΔS° as constant?
3. A reaction has $\Delta G^\circ = -10.0$ kJ/mol at 298 K. Find K.
4. For a Zn/Cu galvanic cell (E°: $Cu^{2+}/Cu = +0.34$ V, $Zn^{2+}/Zn = -0.76$ V), find E°_{cell} and ΔG°, name the anode, and say which way electrons flow in the wire.
5. In the Zn/Cu cell, $[Cu^{2+}]$ is decreased. Does the cell potential increase or decrease? Explain using Q.
6. A current of 2.00 A passes through $Cu^{2+}(aq)$ for 30.0 min. What mass of Cu is deposited?
7. The conversion of diamond to graphite has $\Delta G^\circ < 0$, yet diamonds last for ever. Explain.

Answers

1. Positive: a liquid becomes gases, and the number of moles of gas increases from 0 to 3.
2. $\Delta G^\circ = 178 - (298)(0.161) = +130$ kJ/mol: not favorable under standard conditions. Favorable under standard conditions when $T > \dfrac{178}{0.161} = 1.11 \times 10^3$ K.
3. $\ln K = \dfrac{10\,000}{(8.314)(298)} = 4.04$, so $K = 57$.
4. $E^\circ = 0.34 - (-0.76) = 1.10$ V. $\Delta G^\circ = -nFE^\circ = -(2)(96\,485)(1.10) = -212$ kJ/mol. Zn is the anode; electrons flow from Zn to Cu.

5. It decreases: $Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ increases, and by the Nernst equation a larger Q lowers E.
6. $q = (2.00)(1800) = 3600$ C; $3600 \div 96\,485 = 0.0373$ mol e^-; $\div 2 = 0.0187$ mol Cu; $\times 63.55 = 1.19$ g.
7. The reaction is thermodynamically favorable but has a very large activation energy, so its rate is negligible: it is under kinetic control.

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 usually 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).

exercises.lol exercises.com.cn