

# AP Chemistry

Atoms · Bonding · Mixtures · Reactions · Kinetics · Heat · Equilibrium · Acids and bases · Thermodynamics and cells

| The exam                     | Questions | Time    | Share of score | What it looks like                                                                                                                                                                                 |
|------------------------------|-----------|---------|----------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Section I<br>Multiple choice | 60        | 90 min  | 50%            | Some questions stand alone; others come in a set that shares one table, graph or diagram. You answer on screen in the Bluebook app. A wrong answer costs nothing, so never leave a question blank. |
| Section II<br>Free response  | 7         | 105 min | 50%            | Three long questions worth 10 points each and four short questions worth 4 points each, 46 points in all. You read the questions in Bluebook and write your answers by hand in a paper booklet.    |

## What each unit is worth

Share of the multiple-choice questions

|        |                                       |        |
|--------|---------------------------------------|--------|
| Unit 1 | Atomic Structure and Properties       | 7–9%   |
| Unit 2 | Compound Structure and Properties     | 7–9%   |
| Unit 3 | Properties of Substances and Mixtures | 18–22% |
| Unit 4 | Chemical Reactions                    | 7–9%   |
| Unit 5 | Kinetics                              | 7–9%   |
| Unit 6 | Thermochemistry                       | 7–9%   |
| Unit 7 | Equilibrium                           | 7–9%   |
| Unit 8 | Acids and Bases                       | 11–15% |
| Unit 9 | Thermodynamics and Electrochemistry   | 7–9%   |

Free-response questions are not tied to units; one titration question can need net ionic equations, stoichiometry, equilibrium and pH.

## Calculators

You can use a calculator on **both sections**. Bluebook has a scientific and a graphing Desmos calculator built in.

You may also bring up to **two handheld calculators**. Scientific and approved graphing calculators are allowed; four-function calculators are also permitted. You don't have to clear its memory.

Only the Desmos inside Bluebook is allowed, not the website or the phone app.

## How the free response is scored

Each point is for one specific thing, such as a number with its setup and units or a correct drawing. A right answer with no work shown can lose the point.

Some later parts accept an answer that is consistent with your own earlier mistake, but only when your work shows where the number came from.

An explanation earns the point only if it gives the cause. "Because of the periodic trend" or "Le Châtelier's principle" with no cause earns nothing.

## You have to know these yourself

- The names and charges of common ions, the strong acids and bases, and the one solubility rule: every sodium, potassium, ammonium and nitrate salt dissolves.
- A few formulas:  $M_1V_1 = M_2V_2$  for dilution; formal charge = valence  $e^-$  – nonbonding  $e^-$  –  $\frac{1}{2}$  bonding  $e^-$ ;  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ ; and  $\Delta H \approx \text{energy of bonds broken} - \text{energy of bonds formed}$ .

## Significant figures and units

When you multiply or divide, round to the fewest significant figures in your data. When you add or subtract, round to the fewest decimal places. Counted numbers and the coefficients of a balanced equation are exact, so they never limit an answer.

Carry extra digits through every step and round once, at the end. Put a unit on every number, including the answer.

## Given to you on exam day

A **periodic table** with each element's symbol, atomic number and average atomic mass, and the **equation sheet**, a booklet of equations and constants, on paper and in Bluebook. You can write on it, but nothing written there is scored. Electronegativities, specific heats, bond energies,  $K_a$ ,  $K_{sp}$  and reduction potentials are printed in the questions that use them. The sheet lists these:

### Constants and units

$h = 6.626 \times 10^{-34} \text{ J s}$ ,  $c = 2.998 \times 10^8 \text{ m/s}$ ,  
Avogadro's number  $6.022 \times 10^{23} \text{ mol}^{-1}$ ,  $R = 8.314 \text{ J/(mol}\cdot\text{K)}$  or  $0.08206 \text{ L}\cdot\text{atm/(mol}\cdot\text{K)}$ ,  
 $F = 96,485 \text{ C per mol } e^-$ . STP is  $273.15 \text{ K}$  and  $1.0 \text{ atm}$ , where an ideal gas fills  $22.4 \text{ L per mole}$ ; Kelvin temperature =  $^\circ\text{C} + 273.15$ ;  $1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$ ; metric prefixes.

### Atoms and light

Coulomb's law  $F \propto q_1q_2/r^2$ ,  $E = h\nu$ ,  $c = \lambda\nu$  ( $\nu$ , the Greek letter nu, is the frequency)

### Gases, liquids and solutions

$PV = nRT$ ,  $P_1V_1/T_1 = P_2V_2/T_2$ ,  
 $P_A = P_{\text{total}}X_A$ ,  $P_{\text{total}} = P_A + P_B + \dots$ ,  $n = m/M$ ,  
 $D = m/V$ ,  $KE = \frac{1}{2}mv^2$ , molarity  
 $= n_{\text{solute}}/V_{\text{solution}}$ ,  $A = \epsilon bc$

### Kinetics

The integrated rate laws for zero, first and second order, and  $t_{1/2} = 0.693/k$  (first order)

### Equilibrium and acids

$K_c$ ,  $K_p$ ,  $K_a$ ,  $K_b$  and  $K_w$  expressions; pH, pOH,  $pK_a$ ,  $pK_b$ ;  $K_w = K_aK_b$ ;  $\text{pH} + \text{pOH} = 14$  at  $25^\circ\text{C}$ ; Henderson–Hasselbalch

### Thermodynamics and cells

$q = mc\Delta T$ ; products minus reactants for  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ ;  
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K = -nFE^\circ$ ;  
 $I = q/t$ ; the Nernst equation

## Unit 1 Atomic Structure and Properties

This unit starts with counting atoms by weighing them and finding out what substances and mixtures are made of. It then arranges the electrons in an atom, and that arrangement explains the periodic table and its trends.

Unit 1 7–9%   Unit 2 7–9%   Unit 3 18–22%   Unit 4 7–9%   Unit 5 7–9%   Unit 6 7–9%   Unit 7 7–9%   Unit 8 11–15%   Unit 9 7–9%

Unit 1 is 7–9% of the multiple-choice section. In the free response it shows up inside larger questions, such as reading a mass spectrum, writing an electron configuration, or using Coulomb's law to explain why one atom is larger than another.

### 1.1 Moles and molar mass

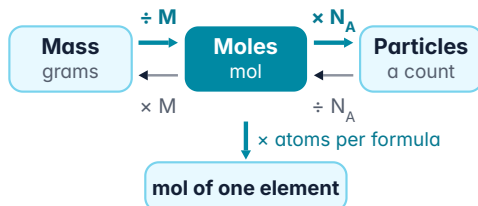
You can't count atoms, so you weigh them. A **mole** is  $6.022 \times 10^{23}$  particles, and the molar mass from the periodic table is the mass of one mole, in grams. Chlorine atoms average 35.45 amu each, so a mole of them weighs 35.45 g.

#### On the equation sheet

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

and Avogadro's number,  $6.022 \times 10^{23} \text{ mol}^{-1}$

M = molar mass (g/mol), from the periodic table



#### Worked example

How many grams of chlorine are in 1.25 mol of  $\text{AlCl}_3$ ?

- Use the formula's ratio:  $1.25 \times 3 = 3.75 \text{ mol Cl}$
- $3.75 \text{ mol} \times 35.45 \text{ g/mol} = 132.9 \text{ g}$

**133 g of Cl (three significant figures, as in 1.25 mol)**

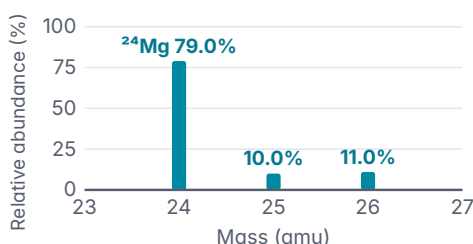
#### Common mistake

**Using the atom's molar mass when the substance is a molecule.** Iodine is  $\text{I}_2$ , so 1.021 g of it is  $1.021 \div 253.80 = 0.004023 \text{ mol}$ . Dividing by 126.90 g/mol, the molar mass of I atoms, doubles the answer. **Build the molar mass from the formula.**

### 1.2 Mass spectra of elements

A mass spectrometer sorts an element's atoms by mass. Each peak is one **isotope**: its position is the isotope's mass and its height is how common it is. Isotopes differ only in neutrons (mass number – atomic number). The average atomic mass, not on the equation sheet, is  $\Sigma (\text{mass} \times \text{fraction})$ .

### 1.2 Mass spectra of elements, continued



The mass spectrum of magnesium.

#### Worked example

Chlorine is 75.76%  $^{35}\text{Cl}$  (34.969 amu) and 24.24%  $^{37}\text{Cl}$  (36.966 amu). Find its average atomic mass.

- $0.7576(34.969) + 0.2424(36.966) = 26.49 + 8.961 = 35.45$

**35.45 amu, near 35 because  $^{35}\text{Cl}$  is about three times as common**

#### Common mistake

**Treating the average as the mass of a real atom.** No chlorine atom has a mass of 35.45 amu: every atom is  $^{35}\text{Cl}$  or  $^{37}\text{Cl}$ . The average is a weighted mean, for samples, not single atoms.

### 1.3 Elemental composition

A pure compound always has the same composition by mass: water is 11.19% hydrogen wherever it comes from. The **empirical formula** is the lowest whole-number ratio of atoms; the **molecular formula** is a whole-number multiple of it (glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , is six times its empirical formula,  $\text{CH}_2\text{O}$ ).

#### Not on the equation sheet, so learn it

$\% X = \text{mass of X in 1 mol} \div \text{molar mass} \times 100$ .

For an empirical formula, assume 100 g so each percent becomes grams, change each mass to moles, divide all by the smallest, and multiply to clear any fraction. For the molecular formula, divide the molar mass by the empirical-formula mass.

### 1.3 Elemental composition, continued

#### Worked example

An iron oxide is 69.94% Fe by mass. Find its empirical formula.

- In 100 g: Fe  $69.94 \div 55.85 = 1.252 \text{ mol}$ ; O  $30.06 \div 16.00 = 1.879 \text{ mol}$
- Divide by unrounded Fe moles: Fe 1, O 1.500; double to 2 : 3.

**$\text{Fe}_2\text{O}_3$**

#### Common mistake

**Rounding 1.5 up to 2** and writing  $\text{FeO}_2$ . 1.500 is 3/2, not a rounding error from 2. Round only values within about 0.1 of a whole number; otherwise multiply everything by 2 (for .5), 3 (for .33 or .67) or 4 (for .25 or .75).

### 1.4 Composition of mixtures

A **mixture** holds two or more substances in proportions that can vary. To find how pure a sample is, react it so the substance you want ends up in a product you can weigh, such as a precipitate. Turn that mass into moles, use the formula's ratio, change to grams of your substance and divide by the sample's mass.

#### Worked example

A 1.000 g mixture of NaCl and sand gives 2.200 g of dry  $\text{AgCl}$  with excess  $\text{AgNO}_3$ . What percent is NaCl?

- $2.200 \div 143.32 = 0.01535 \text{ mol AgCl} = \text{mol NaCl}$
- $0.01535 \times 58.44 = 0.8971 \text{ g NaCl}$

**$0.8971 \div 1.000 \times 100 = 89.71\% \text{ NaCl}$**

#### Common mistake

**Answering "human error" or just "too high."** Name one specific error and follow it through the math. Wet  $\text{AgCl}$  weighs too much, so the moles of  $\text{AgCl}$ , the mass of NaCl and the percent NaCl all come out too high. Drying to constant mass prevents it.

## 1.5 Atomic structure and electron configuration

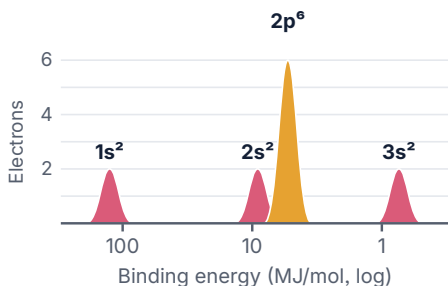
Electrons sit in shells ( $n = 1, 2, 3 \dots$ ) that split into subshells: **s, p, d and f hold 2, 6, 10 and 14 electrons**. Lower-energy subshells fill first, and the periodic table shows the order: the row gives the shell, the block gives the subshell, and the d block runs one shell behind (row 4 fills 3d). In main-group atoms, electrons in the outermost shell are valence electrons; the rest are core electrons. Quantum numbers and exceptions such as Cr are not tested.

|   |    |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    |          |
|---|----|----|----|----|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----------|
| 1 | H  |    |    |    |   |    |    |    |    |    |    |    |    |    |    |    |    | He | 1s       |
| 2 | Li | Be |    |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    | 2s 2p    |
| 3 | Na | Mg |    |    |   |    |    |    |    |    |    |    |    |    |    |    |    |    | 3s 3p    |
| 4 | K  | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | 4s 3d 4p |

The colors mark the blocks: s pink, p orange, d teal.

## 1.6 Photoelectron spectroscopy

Photoelectron spectroscopy (PES) uses high-energy light to knock electrons out of atoms and measures the energy each one needed, its **binding energy**. There is one peak per subshell. Peaks farther left (higher energy) belong to electrons closer to the nucleus; a peak's height is the number of electrons in that subshell.



The photoelectron spectrum of magnesium.

### Worked example

Peaks at 39.6, 2.45 and 1.40 MJ/mol have heights 2 : 2 : 3. Name the element.

- From highest to lowest binding energy:  $1s^2$ ,  $2s^2$ ,  $2p^3$

**2 + 2 + 3 = 7 electrons, so the element is nitrogen**

### How to earn the point

**Why is the 1s peak farthest to the left?**

The 1s electrons are closest to the nucleus, so they feel the strongest Coulombic attraction and need the most energy to remove.

### Common mistake

**Reading a peak as one electron.** Each peak is a whole subshell, and its height counts its electrons: silicon's 3p peak is 2 tall because Si has two 3p electrons.

## 1.7 Periodic trends

### On the equation sheet

$$F_{\text{Coulombic}} \propto \frac{q_1 q_2}{r^2}$$

**Across a period**, protons are added but the outer electrons stay in the same shell and shield each other poorly. The pull grows, so atoms shrink and hold their electrons tighter. **Down a group**, each step adds a shell: the outer electrons are farther out behind more core electrons, so the pull weakens and atoms grow.

|                   | Across → | Down ↓ |
|-------------------|----------|--------|
| Atomic radius     | smaller  | larger |
| Ionization energy | higher   | lower  |
| Electronegativity | higher   | lower  |

Across periods 2 and 3, first ionization energy rises with two exceptions. **B is lower than Be** (and Al lower than Mg) because its outer electron sits in a new, higher-energy p subshell. **O is lower than N** (and S lower than P) because its fourth p electron shares an orbital, and its partner repels it.

A cation is smaller than its atom because it has lost its outer electrons. An anion is larger because its added electrons repel each other while the nuclear charge stays the same. Ions with the same number of electrons shrink as protons are added:  $O^{2-}$  (140 pm) >  $F^-$  (133 pm) >  $Na^+$  (102 pm) >  $Mg^{2+}$  (72 pm).

### Common mistake

**Naming the trend instead of the reason.** "K is lower in the group" earns nothing. **Say which shell the outer electrons are in, compare the distance (or, in the same shell, the nuclear charge), then compare the pull.**

| Species (electrons) | Configuration              |
|---------------------|----------------------------|
| N (7)               | $1s^2 2s^2 2p^3$           |
| Fe (26)             | $[Ar] 4s^2 3d^6$           |
| $Cl^-$ (18)         | $[Ne] 3s^2 3p^6$ , like Ar |
| $Fe^{2+}$ (24)      | $[Ar] 3d^6$                |

### Common mistake

**Taking an ion's electrons from the last subshell filled.** A d-block metal in period 4 loses its 4s electrons before any 3d electrons, because 4s is its outermost shell ( $n = 4$ ), so  $Fe^{2+}$  is  $[Ar] 3d^6$ , not  $[Ar] 4s^2 3d^4$ . An ion has (atomic number – charge) electrons.

## 1.7 Periodic trends, continued

### How to earn the point

**Why does K have a lower first ionization energy than Na?**

K's valence electron is in  $n = 4$  and Na's is in  $n = 3$ , so K's is farther from the nucleus and shielded by more core electrons. It feels a weaker Coulombic attraction, so it is easier to remove.

## 1.8 Valence electrons and ionic compounds

Common ions of period-2 and period-3 main-group elements reach a noble gas's electron count by losing or gaining electrons:  $Na^+$  and  $Mg^{2+}$  match Ne,  $Cl^-$  matches Ar. The ions combine in the ratio that makes the total charge zero.

|           |           |           |    |           |           |           |          |
|-----------|-----------|-----------|----|-----------|-----------|-----------|----------|
| 1         | 2         | 13        | 14 | 15        | 16        | 17        | 18       |
| <b>+1</b> | <b>+2</b> | <b>+3</b> |    | <b>-3</b> | <b>-2</b> | <b>-1</b> | <b>0</b> |
| Li        | Be        | B         | C  | N         | O         | F         | Ne       |
| Na        | Mg        | Al        | Si | P         | S         | Cl        | Ar       |
| K         | Ca        | Ga        | Ge | As        | Se        | Br        | Kr       |

Usual ion charges by group. Group 14 elements and boron share electrons instead of forming ions.

### Worked example

Aluminum's first four ionization energies are 578; 1,817; 2,745; and 11,578 kJ/mol. What ion does it form, and what is its oxide's formula?

- The big jump comes after the third electron: the fourth would come from the core. So Al forms  $Al^{3+}$ .
- Two  $Al^{3+}$  and three  $O^{2-}$  make the total charge zero:  $2(+3) + 3(-2) = 0$ .

**$Al^{3+}$  and  $Al_2O_3$**

## Unit 2 Compound Structure and Properties

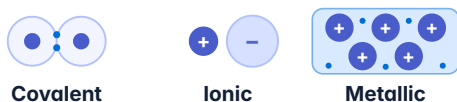
This unit is about how atoms hold together in molecules, ionic solids and metals, and how much energy it takes to pull them apart. Lewis diagrams then predict a molecule's shape and whether it is polar.

Unit 1 7–9%   Unit 2 7–9%   Unit 3 18–22%   Unit 4 7–9%   Unit 5 7–9%   Unit 6 7–9%   Unit 7 7–9%   Unit 8 11–15%   Unit 9 7–9%

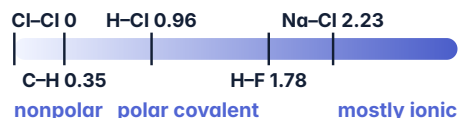
Unit 2 is 7–9% of the multiple-choice section. In the free response, a Lewis diagram to draw or complete has appeared every recent year, often with a question about shape, bond angle, hybridization or formal charge.

### 2.1 Types of chemical bonds

The kind of bond depends on where the valence electrons go. Two nonmetals **share** a pair (covalent). A metal hands electrons to a nonmetal and the ions attract (ionic). In a metal, every atom's valence electrons are shared through the whole piece (metallic).



In a shared pair, the more **electronegative** atom pulls the electrons closer and takes a partial negative charge, as in  $\delta^+ \delta^-$  H–Cl. The bigger the electronegativity difference, the more polar the bond; there is no sharp line between polar covalent and ionic.



Electronegativity difference between the two bonded atoms.

#### Not on the equation sheet, so learn it

Electronegativity rises across a period and falls down a group; fluorine is the highest. The periodic table you get prints no electronegativity values.

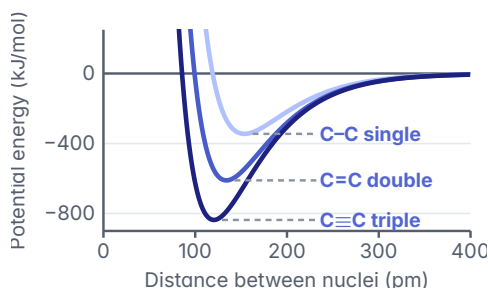
#### Common mistake

**Naming the most polar bond without the reason.** In  $\text{CBrClF}_2$  the C–F bond is the most polar, but the point needs the comparison: F is more electronegative than Cl or Br, so C–F has the biggest electronegativity difference.

### 2.2 Intramolecular force and potential energy

In a bond, each nucleus attracts electrons while nuclei repel nuclei and electrons repel electrons. The **bond length** is where these forces balance, at the bottom of the potential-energy well. The well's depth is the **bond energy**, the energy it takes to pull the atoms apart.

### 2.2 Intramolecular force and potential energy, continued



| Bond       | Length | Bond energy |
|------------|--------|-------------|
| C–C single | 154 pm | 345 kJ/mol  |
| C=C double | 134 pm | 611 kJ/mol  |
| C≡C triple | 120 pm | 837 kJ/mol  |

More shared pairs pull the nuclei closer and hold them harder. Bigger atoms make longer bonds: H–Br is longer than H–F because Br's bonding electrons sit two shells farther out.

#### Common mistake

**Reading the bond energy as a negative number, or the bond length where the curve crosses zero.** The C–C single-bond well bottoms out near  $-345$  kJ/mol, so breaking the bond takes  $+345$  kJ/mol; its length, 154 pm, is at the bottom.

For ions, Coulomb's law sets the strength: bigger charges and ion centers that sit closer together attract harder.

#### Worked example

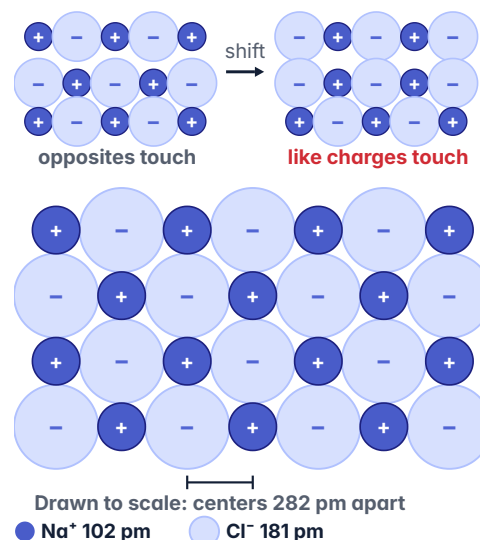
The lattice energy of  $\text{Na}_2\text{O}$  is 2481 kJ/mol and of  $\text{Rb}_2\text{O}$  2163 kJ/mol. Explain the difference.

- Same charges, so compare distance:  $\text{Rb}^+$  (152 pm) is larger than  $\text{Na}^+$  (102 pm), so the ion centers in  $\text{Rb}_2\text{O}$  are farther apart.

**The attraction in  $\text{Rb}_2\text{O}$  is weaker, so less energy is needed to separate its ions.**

### 2.3 Structure of ionic solids

An ionic solid is a single 3-D lattice of alternating cations and anions with no separate molecules. Every ion is surrounded by ions of the opposite charge. That makes ionic solids hard, with high melting points. They are also **brittle**: shift one layer by a single ion and like charges line up and push the crystal apart. They conduct only when melted or dissolved, once the ions can move.



#### How to earn the point

**Why does molten NaCl conduct electricity when solid NaCl doesn't?**

Solid NaCl doesn't conduct because its ions are locked in place. Melted or dissolved, the ions are free to move and carry charge.

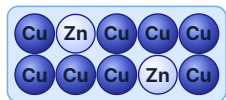
#### Common mistake

**Drawing NaCl as Na–Cl molecules joined by sticks, or with equal circles.**

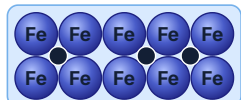
An ionic solid has no molecules and no bond between one particular pair of ions: each ion attracts all of its neighbors. Draw alternating ions with no sticks, and make  $\text{Cl}^-$  (181 pm) clearly larger than  $\text{Na}^+$  (102 pm).

## 2.4 Structure of metals and alloys

A metal is an array of positive ions in a sea of delocalized electrons. Its mobile electrons carry current, and its layers slide without breaking bonds, so it bends. Atoms of similar radius swap places in a **substitutional alloy**; much smaller atoms fill the gaps in an **interstitial alloy** and make the metal harder.

**Substitutional**

In brass, Zn (142 pm) replaces Cu (145 pm)

**Interstitial**

Small C (67 pm) fits between Fe (156 pm)

## How to earn the point

**Why is sterling silver, Ag with a little Cu, a substitutional alloy?**

Cu atoms (145 pm) are close in radius to Ag atoms (165 pm), so they take Ag atoms' places in the lattice.

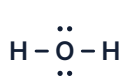
## Common mistake

**"Substitutional because the masses are similar."** An atom can take another's place only if it fits the same spot, which depends on its size, not its mass.

## 2.5 Lewis diagrams

A Lewis diagram shows every valence electron: shared pairs as lines, lone pairs as dots. These five steps work for most molecules and ions.

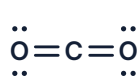
- Count valence electrons: add one per negative charge, subtract one per positive charge.
- Join atoms with single bonds, the least electronegative in the middle (never H).
- Give outer atoms full octets (H gets 2).
- Put any leftovers on the central atom.
- If the central atom has under 8, turn an outer lone pair into a multiple bond.



$\text{H}_2\text{O}$   
8 valence  $e^-$



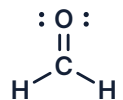
$\text{NH}_3$   
8 valence  $e^-$



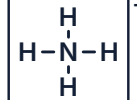
$\text{CO}_2$   
16 valence  $e^-$



$\text{HCN}$   
10 valence  $e^-$



$\text{CH}_2\text{O}$   
12 valence  $e^-$



$\text{NH}_4^+$   
8 valence  $e^-$

## 2.5 Lewis diagrams, continued

**Exceptions to the octet rule**

B and Al often keep only 6 electrons ( $\text{BF}_3$ ,  $\text{AlCl}_3$ ). A molecule with an odd number of valence electrons has one unpaired electron ( $\text{NO}$ ,  $\text{NO}_2$ ). Only atoms from period 3 down can hold more than 8:  $\text{SF}_6$  has 12 around S. C, N, O and F never do.

## Common mistake

**Adding an electron for a positive charge.** A cation has lost electrons, so  $\text{NO}_2^+$  has  $5 + 2(6) - 1 = 16$  valence electrons, not 18.

## 2.6 Resonance and formal charge

When equally good diagrams differ only in where electrons sit, the real species is a blend of all of them, all the time. Ozone's two O–O bonds are identical, each 128 pm long, between a single (148 pm) and a double bond (121 pm). The molecule never flips between the drawings.

Use **formal charge** to choose the best of several diagrams: the one whose formal charges are closest to zero, with any negative charge on the more electronegative atom.

## Not on the equation sheet, so learn it

formal charge = valence  $e^-$  – nonbonding  $e^-$  –  $\frac{1}{2}$  bonding  $e^-$

The formal charges add up to the charge on the whole species. Bond order = shared pairs ÷ the bonds they are shared across:  $\text{O}_3$  has 3 pairs over 2 O–O bonds, so  $1\frac{1}{2}$ .

## Worked example

Which is the better diagram for  $\text{CO}_2$ :  $\text{O}=\text{C}=\text{O}$  or  $\text{O}\equiv\text{C}-\text{O}$ ?

- $\text{O}=\text{C}=\text{O}$ : each O is  $6 - 4 - \frac{1}{2}(4) = 0$ ; C is  $4 - 0 - \frac{1}{2}(8) = 0$
- $\text{O}\equiv\text{C}-\text{O}$ : the triple-bonded O is  $6 - 2 - \frac{1}{2}(6) = +1$ ; the single-bonded O is  $6 - 6 - \frac{1}{2}(2) = -1$

**$\text{O}=\text{C}=\text{O}$  is better because every formal charge in it is zero.**

## Common mistake

**Giving one formal charge for the whole molecule.** "The formal charge is zero" earns nothing: give each atom's formal charge in every diagram you compare.

## 2.7 VSEPR and hybridization

Around a central atom, each bond (single, double or triple) and each lone pair is one **electron domain**, and domains spread as far apart as they can. The shape's name describes only where the atoms sit. Lone pairs push harder than bonds, because a lone pair is held by only one nucleus and spreads out more. They squeeze the angles:  $\text{CH}_4$  109.5°,  $\text{NH}_3$  106.7°,  $\text{H}_2\text{O}$  104.5°.

| Domains | Shape and angle (number of lone pairs)                                   |
|---------|--------------------------------------------------------------------------|
| 2       | linear, 180°                                                             |
| 3       | trigonal planar, 120°; bent (1)                                          |
| 4       | tetrahedral, 109.5°; trigonal pyramidal (1); bent (2)                    |
| 5       | trigonal bipyramidal, 90° and 120°; seesaw (1); T-shaped (2); linear (3) |
| 6       | octahedral, 90°; square pyramidal (1); square planar (2)                 |

Polar bonds cancel when identical outer atoms sit symmetrically:  $\text{CO}_2$ ,  $\text{BF}_3$  and  $\text{CCl}_4$  are nonpolar; bent  $\text{H}_2\text{O}$  and pyramidal  $\text{NH}_3$  are polar. Two, three and four domains mean  $sp$ ,  $sp^2$  and  $sp^3$  hybridization; d-orbital hybridization is not tested. A single bond is one  $\sigma$  bond; a double bond adds one  $\pi$  bond, a triple bond two.

## Worked example

Give the shape, O–S–O angle and hybridization of  $\text{SO}_2$ .

- $6 + 2(6) = 18$  electrons:  $\text{O}=\text{S}-\text{O}$  with a lone pair on S, so S has 3 domains

**Bent and  $sp^2$ , with an angle a little under 120° (measured 119.5°) because the lone pair squeezes it.**

## How to earn the point

**Why is  $\text{NO}_2$  bent but  $\text{NO}_2^+$  linear?**

Around N,  $\text{NO}_2$  has two bonds and an unpaired electron. The unpaired electron repels the bonds less than a lone pair would, so the molecule is bent with an O–N–O angle of about 134°.  $\text{NO}_2^+$  has only two domains, which point in opposite directions, so it is linear.

## Common mistake

**Counting shared pairs instead of domains.** C in  $\text{CH}_2\text{O}$  has four shared pairs, but both pairs of the double bond point the same way, so they fill one domain: 3 domains, so  $sp^2$ , not  $sp^3$ .

## Unit 3 Properties of Substances and Mixtures

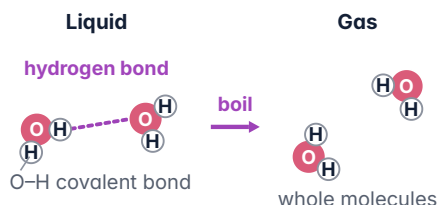
The attractions between particles set melting points, boiling points and what dissolves in what. The unit also covers gases, making and separating solutions, and how chemists use light to measure what a sample contains.

Unit 1 7–9%   Unit 2 7–9%   **Unit 3 18–22%**   Unit 4 7–9%   Unit 5 7–9%   Unit 6 7–9%   Unit 7 7–9%   Unit 8 11–15%   Unit 9 7–9%

**Unit 3 is 18–22% of the multiple-choice section.** It appears in the free response every year, for example explaining a boiling point or vapor pressure with intermolecular forces, a gas or molarity calculation, preparing a solution, or turning absorbance into concentration.

### 3.1 Intermolecular and interparticle forces

A covalent bond holds atoms together inside a molecule. **Intermolecular forces** are the far weaker pulls between neighboring molecules. Melting or boiling a molecular substance overcomes these forces; the molecules stay whole.



| Force             | Acts when                                                                   |
|-------------------|-----------------------------------------------------------------------------|
| London dispersion | always, between any two particles                                           |
| Dipole–dipole     | both molecules are polar                                                    |
| Hydrogen bond     | an H bonded to N, O or F meets a lone pair on N, O or F of another molecule |
| Ion–dipole        | an ion meets a polar molecule, such as water                                |

Dispersion forces grow with the number of electrons, because a bigger electron cloud is easier to distort. They also grow with contact: long chains attract each other more than compact balls do. Stronger attractions mean a higher boiling point, a larger enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ) and a lower vapor pressure at the same temperature.



The O–H hydrogen is drawn to a lone pair on O



C–H is not polar enough for a hydrogen bond

### 3.1 Intermolecular and interparticle forces, continued

| Molecule       | Forces between them                          | Boils at |
|----------------|----------------------------------------------|----------|
| propane        | dispersion                                   | 231 K    |
| dimethyl ether | dispersion and dipole–dipole                 | 248 K    |
| ethanol        | dispersion, dipole–dipole and hydrogen bonds | 352 K    |

#### How to earn the point

**Why does ethanol boil higher than dimethyl ether?**

Both have 26 electrons and dipole–dipole forces, but only ethanol's O–H lets its molecules hydrogen-bond. Its attractions are stronger, so separating its molecules takes more energy.

#### Common mistake

**Assuming the polar molecule always boils higher.** Nonpolar  $\text{CBr}_4$  boils at 463 K, far above polar  $\text{CBrClF}_2$  (269 K), because  $\text{CBr}_4$ 's much larger electron cloud gives stronger dispersion forces. **List every force in both, then compare.**

#### Common mistake

**"It boils higher because it's heavier."** Mass isn't the reason:  $\text{Br}_2$  (70 electrons) boils at 332 K and  $\text{Cl}_2$  (34) at 239 K because the bigger electron cloud of  $\text{Br}_2$  is easier to distort, so its dispersion forces are stronger.

### 3.2 Properties of solids

The kind of particle in a solid sets how it melts and conducts.

| Solid                    | Melts        | Conducts            |
|--------------------------|--------------|---------------------|
| Ionic ( $\text{NaCl}$ )  | high         | melted or dissolved |
| Network (diamond)        | usually high | no; graphite does   |
| Metallic ( $\text{Cu}$ ) | varies       | yes                 |
| Molecular (ice)          | low          | no                  |

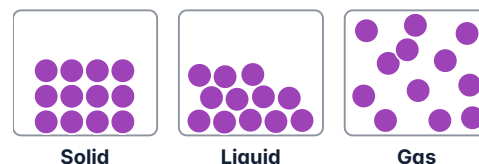
### 3.2 Properties of solids, continued

#### Common mistake

**Breaking covalent bonds to melt a molecular solid.** Melting ice or sugar only separates whole molecules. Only a network solid such as diamond must break covalent bonds to melt, which is why it melts so high.

### 3.3 Solids, liquids, and gases

The molecules are the same in every phase; only their spacing and motion change. In a solid they touch and vibrate in place. In a liquid they still touch but slide past each other. In a gas they are far apart, move fast and fill the whole container. A crystal is ordered; an amorphous solid such as glass is disordered, but its particles still stay in place.



#### Worked example

$\text{CH}_3\text{OH}$  melts at 176 K and boils at 338 K;  $\text{CH}_2\text{O}$  melts at 181 K and boils at 254 K. At what temperatures are both liquids?

- Above the higher melting point and below the lower boiling point

Between 181 K and 254 K

#### Common mistake

**Drawing a liquid's particles far apart, or a gas piled at the bottom.** Liquid particles touch; gas particles spread through the whole container. Keep every molecule whole: boiling water is still  $\text{H}_2\text{O}$  molecules, never separate H and O atoms.

## 3.4 Ideal gas law

Pressure, volume, moles and temperature describe any gas, and  $PV = nRT$  ties them together. Temperature must be in kelvins. In a mixture, each gas pushes on the walls as if it were alone, so its share of the pressure equals its share of the moles.

## On the equation sheet

$$PV = nRT \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_A = P_{\text{total}} \times X_A \quad P_{\text{total}} = P_A + P_B + \dots$$

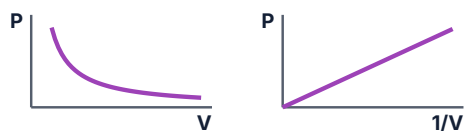
$$X_A = \text{moles of A} \div \text{total moles};$$

$$R = 0.08206 \text{ L}\cdot\text{atm}/(\text{mol}\cdot\text{K}) \text{ or } 8.314 \text{ J}/(\text{mol}\cdot\text{K});$$

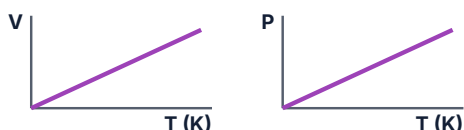
$$\text{STP is } 273.15 \text{ K and } 1.0 \text{ atm, where an ideal gas fills } 22.4 \text{ L per mole; } 1 \text{ atm} = 760 \text{ mm Hg.}$$

## Not on the equation sheet, so learn it

Use  $R = 0.08206$  with liters and atmospheres;  $8.314$  goes with energy in joules. Gas density gives molar mass:

$$\text{molar mass} = \frac{DRT}{P}$$


Halve V and P doubles



Double T (K), V doubles    Double T (K), P doubles

Top: with  $n$  and  $T$  fixed, halving  $V$  doubles  $1/V$  and doubles  $P$ . Bottom:  $n$  and  $P$  (left) or  $n$  and  $V$  (right) fixed.

## Worked example

$\text{H}_2$  is collected over water at  $25^\circ\text{C}$  in a  $0.250 \text{ L}$  container. The total pressure is  $752 \text{ mm Hg}$ , and water's vapor pressure at  $25^\circ\text{C}$  is  $24 \text{ mm Hg}$ . How many moles of  $\text{H}_2$ ?

- 1 Subtract the water vapor:  $752 - 24 = 728 \text{ mm Hg} = 0.958 \text{ atm}$
- 2  $n = \frac{PV}{RT} = \frac{(0.958)(0.250)}{(0.08206)(298)}$

$$9.79 \times 10^{-3} \text{ mol H}_2$$

## Common mistake

**Putting Celsius into the equation.** At  $198^\circ\text{C}$ ,  $T$  is  $471 \text{ K}$ ; using  $198$  makes  $n$  2.4 times too big. Gas laws need a scale that starts at absolute zero; at  $0^\circ\text{C}$  a gas still has plenty of kinetic energy. **Add 273.15 to every Celsius temperature first.**

## 3.4 Ideal gas law, continued

## Common mistake

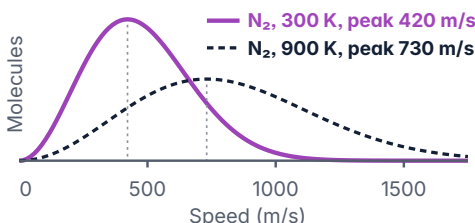
**Using 22.4 L/mol away from STP.** A mole of gas fills  $22.4 \text{ L}$  only at STP. At  $293 \text{ K}$  and  $1.25 \text{ atm}$ ,  $PV = nRT$  gives  $0.219 \text{ L}$  for  $0.0114 \text{ mol}$  of  $\text{CO}_2$ , not  $0.255 \text{ L}$ .

## 3.5 Kinetic molecular theory

A gas is mostly empty space. Its particles fly in straight lines, collide without losing energy overall and, in the ideal model, don't attract each other. Their **average kinetic energy is proportional to the Kelvin temperature**, so at one temperature every gas has the same average kinetic energy and lighter particles move faster.

## On the equation sheet

$$KE = \frac{1}{2}mv^2 \quad \text{one particle: } m \text{ in kg, } v \text{ in m/s}$$



Heating spreads the speeds out, but both curves hold the same number of molecules.

## How to earn the point

**Why does heating a sealed, rigid container of gas raise its pressure?**

At constant volume, a higher temperature makes the particles move faster, so they hit the walls more often and harder, which raises the pressure.

## Common mistake

**"Same temperature, same speed."** He and Ar at  $300 \text{ K}$  have the same average kinetic energy. Since  $KE = \frac{1}{2}mv^2$ , the lighter He atoms must move faster.

## 3.6 Deviation from ideal gas law

$PV = nRT$  assumes particles take up no room and never attract, but real particles do both. At low temperature, close to the point where the gas would condense, attractions pull particles back from the walls and the pressure is **lower** than ideal. At very high pressure, the particles' own volume crowds the container and the pressure is **higher**. Small nonpolar gases such as He behave most ideally, polar or large ones such as  $\text{SO}_2$  the least.

## 3.6 Deviation from ideal gas law, continued

## Worked example

A  $2.00 \text{ L}$  tank holds  $1.00 \text{ mol}$  of  $\text{CO}_2$  at  $300 \text{ K}$  and  $11.58 \text{ atm}$ . What pressure would an ideal gas have?

$$1 \quad P = \frac{nRT}{V} = \frac{(1.00)(0.08206)(300)}{2.00}$$

The ideal value is  $12.3 \text{ atm}$ ; the real gas is about 6% lower because its molecules attract.

## 3.7 Solutions and mixtures

A solution is a mixture that is the same all the way through. Its **molarity** counts moles of solute per liter of solution, not per liter of water. Diluting adds water but no solute, so the moles stay the same while the volume grows.

## On the equation sheet

$$M = \frac{n_{\text{solute}}}{\text{L of solution}} \quad \text{so } n = MV$$

## Not on the equation sheet, so learn it

For a dilution,  $M_1V_1 = M_2V_2$ , where  $V_2$  is the final total volume. For an ion, multiply by its count in the formula:  $0.100 \text{ M CaCl}_2$  is  $0.200 \text{ M in Cl}^-$ .

## Worked example

What mass of  $\text{NaCl}$  makes  $100.0 \text{ mL}$  of  $0.340 \text{ M NaCl}$ ?

$$1 \quad 0.1000 \text{ L} \times 0.340 \text{ mol/L} \times 58.44 \text{ g/mol}$$

$$1.99 \text{ g NaCl}$$



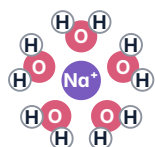
Making it in a  $100.0 \text{ mL}$  volumetric flask.

## Common mistake

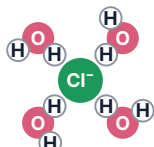
**"Dissolve 1.99 g in 100.0 mL of water."** The solution would no longer be  $100.0 \text{ mL}$ . **Dissolve the solid in some water in a  $100.0 \text{ mL}$  volumetric flask, then add water up to the mark.**

### 3.8 Representations of solutions

A particle drawing of a solution must show the right particles in the right ratio. A soluble ionic compound such as the strong base  $\text{Sr}(\text{OH})_2$  appears as separate ions, two  $\text{OH}^-$  for every  $\text{Sr}^{2+}$ ; a strong acid also splits fully into ions. Sugar molecules stay whole, and a weak acid is mostly intact molecules. Water's partly negative O faces cations; its partly positive H atoms face anions.



$\delta^- \text{O}$  toward  $\text{Na}^+$



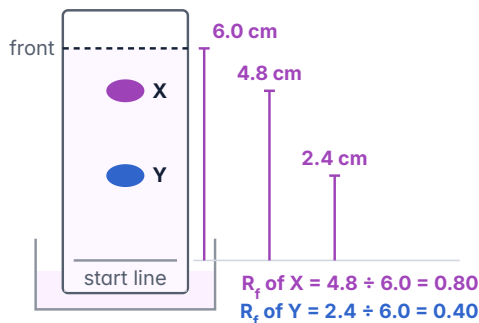
$\delta^+ \text{H}$  toward  $\text{Cl}^-$

#### Common mistake

**Pointing water's oxygen at  $\text{Cl}^-$ .** An anion attracts the partly positive H end of water, so H atoms face  $\text{Cl}^-$  and O atoms face  $\text{Na}^+$ . Draw several waters around each ion, all turned the right way.

### 3.9 Separation of solutions and mixtures

A filter catches undissolved solid; dissolved ions pass straight through. Distillation separates liquids by volatility: the vapor is richer in the more volatile component. In **chromatography** a solvent (the mobile phase) carries a mixture across paper or silica (the stationary phase); a component held more strongly by the stationary phase travels less far.



#### Not on the equation sheet, so learn it

$R_f$  = distance the spot moved  $\div$  distance the solvent front moved, both measured from the starting line. With a polar stationary phase and a relatively nonpolar solvent, the more polar component usually has the smaller  $R_f$ .

### 3.9 Separation of solutions and mixtures, continued

#### How to earn the point

**With polar paper and nonpolar solvent, why did X travel farther than Y?**

X is less polar than Y, so it is attracted less to the polar paper and spends more time dissolved in the moving solvent.

#### Common mistake

**"The more polar dye moves farther."**

With a nonpolar solvent, a more polar dye is held more tightly by polar paper or silica, so it travels less far.

### 3.10 Solubility

Dissolving breaks solute-solute and solvent-solvent attractions and forms new solute-solvent ones. It goes well when the new attractions are like the old: polar and hydrogen-bonding solutes in water, nonpolar solutes in nonpolar solvents.

Alcohols in water at 20 °C (g per 100 mL)

|            |                     |
|------------|---------------------|
| methanol   | mixes in any amount |
| ethanol    | mixes in any amount |
| 1-propanol | mixes in any amount |
| 1-butanol  | 7.7 g               |
| 1-pentanol | 2.2 g               |
| 1-hexanol  | 0.59 g              |

#### How to earn the point

**Why does ethanol mix with water when hexane doesn't?**

Ethanol-water hydrogen bonds replace the hydrogen bonds broken in each liquid. Hexane offers only dispersion forces, too weak to replace water's hydrogen bonds.

#### Common mistake

**"It has an -OH group, so it dissolves."**

One -OH can hydrogen-bond to water, but each extra  $\text{CH}_2$  offers only dispersion forces, so solubility drops from about four carbons on. Only 0.59 g of 1-hexanol dissolves in 100 mL.

### 3.11 Spectroscopy and the electromagnetic spectrum

A molecule absorbs a photon only when the photon's energy matches one of its energy gaps. **Microwaves** make molecules rotate, **infrared** makes bonds vibrate, and **ultraviolet or visible** light raises electrons to higher energy levels. A colored solution shows the light it lets through: a blue dye absorbs orange light.

### 3.11 Spectroscopy and the electromagnetic spectrum, continued

#### Common mistake

**"Infrared breaks bonds."** Infrared photons carry too little energy to break bonds; they only make bonds vibrate. Breaking bonds or exciting electrons takes UV or visible light.

### 3.12 Properties of photons

#### On the equation sheet

$$E = h\nu \quad c = \lambda\nu$$

$\nu$ , the Greek letter nu, is frequency in  $\text{s}^{-1}$ ;  
 $h = 6.626 \times 10^{-34} \text{ J s}$ ;  $c = 2.998 \times 10^8 \text{ m/s}$

#### Not on the equation sheet, so learn it

Combine the two:  $E = hc/\lambda$ , with  $\lambda$  in meters. Multiply by  $6.022 \times 10^{23}$  for a mole of photons.

#### Worked example

Find the energy of one 589 nm photon of sodium light, and of a mole of them.

$$\begin{aligned} 1 \quad E &= hc/\lambda \\ &= (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s}) \\ &\quad \div (5.89 \times 10^{-7} \text{ m}) = 3.37 \times 10^{-19} \text{ J} \\ 2 \quad (3.37 \times 10^{-19} \text{ J})(6.022 \times 10^{23}) \\ &= 2.03 \times 10^5 \text{ J/mol} \end{aligned}$$

**$3.37 \times 10^{-19} \text{ J}$  per photon; 203 kJ per mole**

### 3.13 Beer-Lambert law

#### On the equation sheet

$$A = \epsilon bc$$

absorbance = molar absorptivity  $\times$  path length (cm)  $\times$  concentration (M)

At one wavelength in one cuvette, absorbance is proportional to concentration. At the wavelength the sample absorbs most, measure solutions of known concentration, plot absorbance against concentration, and read the unknown off the line.

#### Worked example

A sample diluted from 3.00 mL to 25.0 mL reads  $A = 0.22$  on a line with slope  $4.0 \text{ M}^{-1}$ . Find the original concentration.

$$\begin{aligned} 1 \quad c &= 0.22 \div 4.0 = 0.055 \text{ M (diluted)} \\ 2 \quad &\text{That is the diluted value, so undo the dilution: } 0.055 \times 25.0 \div 3.00 \end{aligned}$$

**The original sample is 0.46 M.**

## Unit 4 Chemical Reactions

This unit shows how to tell that a reaction happened, write it as a balanced net ionic equation or a particle picture, and count moles with its coefficients. It ends with acid–base, redox and precipitation reactions.

Unit 1 7–9%   Unit 2 7–9%   Unit 3 18–22%   **Unit 4 7–9%**   Unit 5 7–9%   Unit 6 7–9%   Unit 7 7–9%   Unit 8 11–15%   Unit 9 7–9%

**Unit 4 is 7–9% of the multiple-choice section.** In the free response, its equations and mole arithmetic sit inside questions from every later unit, such as finding the acid left over after a reaction or a concentration from a titration.

### 4.1 Introduction for reactions

A physical change alters a substance's form but not what it is made of; a **chemical change** makes new substances. Four clues point to a reaction, but each can also come from a physical change.

| Clue           | From a reaction                                         | From a physical change                                      |
|----------------|---------------------------------------------------------|-------------------------------------------------------------|
| A gas          | Baking soda and vinegar make new CO <sub>2</sub>        | A soda goes flat: its CO <sub>2</sub> was already dissolved |
| A solid        | AgNO <sub>3</sub> and NaCl solutions make AgCl          | Sugar crystallizes out of syrup                             |
| A color change | Copper in AgNO <sub>3</sub> makes blue Cu <sup>2+</sup> | Food dye spreads through water                              |
| Heat or light  | Iron and sulfur glow as iron sulfide forms              | A bulb filament glows but stays tungsten                    |

#### ⚠ Common mistake

**Treating one clue as proof.** Each clue in the table can also come from a physical change. **Name the new substance that formed, or rule out the physical cause.**

### 4.2 Net ionic equations

Write only the particles that change. Split dissolved **strong electrolytes** into ions, keep everything else whole, and cancel the **spectator ions** that appear unchanged on both sides. Then check that atoms and total charge balance.

| Split into ions                                                                   | Keep whole                                                                                     |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| Soluble ionic compounds:<br>NaCl → Na <sup>+</sup> + Cl <sup>−</sup>              | Solids, liquids and gases:<br>CaCO <sub>3</sub> (s), H <sub>2</sub> O (l), CO <sub>2</sub> (g) |
| Strong acids:<br>HNO <sub>3</sub> → H <sup>+</sup> + NO <sub>3</sub> <sup>−</sup> | Weak acids such as HF and CH <sub>3</sub> COOH                                                 |
| Strong bases:<br>KOH → K <sup>+</sup> + OH <sup>−</sup>                           | Other molecules, such as NH <sub>3</sub> and sugar                                             |

### 4.2 Net ionic equations, continued

#### 📖 Not on the equation sheet, so learn it

**Always soluble:** every Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>−</sup> salt.

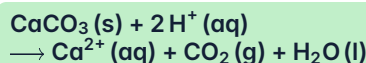
**Strong acids:** HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> (its first proton).

**Strong bases:** group 1 hydroxides and those of Ca, Sr and Ba.

#### 📊 Worked example

Write the net ionic equation for  
CaCO<sub>3</sub> (s) + 2 HCl (aq)  
→ CaCl<sub>2</sub> (aq) + CO<sub>2</sub> (g) + H<sub>2</sub>O (l)

- Split only HCl and CaCl<sub>2</sub>, then cancel Cl<sup>−</sup>, which is on both sides.
- Check: one Ca, one C, three O, two H and a +2 charge on each side.

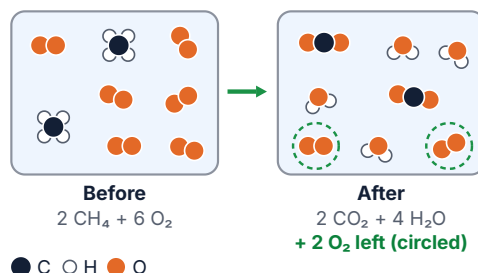


#### ⚠ Common mistake

**Splitting a solid or a weak acid into ions.** CaCO<sub>3</sub> (s) isn't dissolved, so writing Ca<sup>2+</sup> + CO<sub>3</sub><sup>2−</sup> on the left costs the point. Weak acids such as HF stay whole too: their ionization is incomplete.

### 4.3 Representations of reactions

A particle picture must obey the balanced equation atom for atom: leftover reactant stays in the box, and dissolved ions appear in the formula's ratio.



The number of molecules can change (in 2 H<sub>2</sub> + O<sub>2</sub> → 2 H<sub>2</sub>O three become two), but the number of each kind of atom can't: here 22 atoms go in and 22 come out.

### 4.3 Representations of reactions, continued

#### ⚠ Common mistake

**Drawing dissolved Sr(OH)<sub>2</sub> with equal numbers of each ion.** Each formula unit releases one Sr<sup>2+</sup> and two OH<sup>−</sup>, so the picture needs twice as many OH<sup>−</sup>. Saying only "the number is wrong" earns nothing: state the 1 : 2 ratio.

### 4.4 Physical and chemical changes

Sort a process by what breaks. If only the attractions between particles change, as when ice melts or sugar dissolves, the change is physical. If bonds break and new ones form, as when methane burns or HCl ionizes in water, it is chemical. Dissolving a salt breaks ionic bonds and forms ion–dipole attractions, so either label can earn credit if you name those interactions.

#### 🔗 How to earn the point

**Why is boiling water a physical change?**

Boiling breaks only the hydrogen bonds between H<sub>2</sub>O molecules; the O–H covalent bonds inside each molecule stay intact, so no new substance forms.

### 4.5 Stoichiometry

Coefficients count particles, so they compare **moles**, never grams. Turn what you're given into moles, use the coefficient ratio once, then turn moles into what is asked.

| Given      | Moles from it     | Moles back to it   |
|------------|-------------------|--------------------|
| Grams      | mass ÷ molar mass | moles × molar mass |
| A gas      | $n = PV \div RT$  | $V = nRT \div P$   |
| A solution | molarity × liters | moles ÷ molarity   |

To go from substance A to substance B in  $aA \rightarrow bB$ , multiply moles of A by  $b/a$ , the ratio of their coefficients.

## 4.5 Stoichiometry, continued

## On the equation sheet

$$n = \frac{m}{\text{molar mass}} \quad PV = nRT$$

$$M = \frac{n_{\text{solute}}}{L_{\text{solution}}} \text{ (molarity)}$$

An ideal gas at STP (273.15 K and 1.0 atm) fills 22.4 L/mol.

## Not on the equation sheet, so learn it

**Limiting reactant:** divide each reactant's moles by its coefficient; the smallest result runs out first and sets every product amount.

**Percent yield** = actual ÷ theoretical × 100.

With  $R = 0.08206 \text{ L}\cdot\text{atm}/(\text{mol}\cdot\text{K})$ , use liters, atmospheres and kelvins. Use 22.4 L/mol only at STP.

## Worked example

$2 \text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$ . 4.00 mol LiOH meets 3.00 mol  $\text{CO}_2$ . What is left when the reaction stops?

- $4.00 \div 2 = 2.00$  for LiOH is less than  $3.00 \div 1 = 3.00$  for  $\text{CO}_2$ , so LiOH runs out first, though there is more of it.
- 4.00 mol LiOH uses 2.00 mol  $\text{CO}_2$  and makes 2.00 mol of each product.

1.00 mol  $\text{CO}_2$  left, with 2.00 mol  $\text{Li}_2\text{CO}_3$  and 2.00 mol  $\text{H}_2\text{O}$

## Worked example

1.00 g of  $\text{CaCO}_3$  (100.09 g/mol) reacts with 50.0 mL of 1.00 M HCl, which is in excess:  
 $\text{CaCO}_3 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$ . Find the concentration of HCl, written [HCl], afterward; the volume stays 50.0 mL.

- $1.00 \div 100.09 = 0.00999$  mol of  $\text{CaCO}_3$  reacts, and it uses twice as much HCl: 0.0200 mol.
- The acid started with  $0.0500 \text{ L} \times 1.00 \text{ M} = 0.0500$  mol of HCl.
- $0.0500 - 0.0200 = 0.0300$  mol of HCl is left in 0.0500 L.

0.600 M HCl remains

## Common mistake

**Answering with the acid used when the question asks what is left.** 0.0200 mol ÷ 0.0500 L = 0.400 M is the HCl that reacted, not the HCl that is left. **Left = start – used, in moles, then divide by the volume.**

## 4.6 Introduction to titration

In a **titration**, a solution of known concentration (the titrant) is added from a buret to the substance being measured (the analyte). The moment it has used up all the analyte is the **equivalence point**. Choose an indicator whose color change, the endpoint, happens at or very near it.

## Not on the equation sheet, so learn it

At equivalence for  $aA + bB$ :  $\frac{n_A}{a} = \frac{n_B}{b}$ , so  
 $\frac{M_A V_A}{a} = \frac{M_B V_B}{b}$

## Worked example

An antacid's  $\text{Mg}(\text{OH})_2$  (58.3 g/mol) is titrated with 0.100 M  $\text{HNO}_3$ . The buret reads 2.17 mL at the start and 22.17 mL at the endpoint. What mass of  $\text{Mg}(\text{OH})_2$  was there?

- Volume added:  $22.17 - 2.17 = 20.00$  mL = 0.02000 L. Moles of  $\text{HNO}_3$ :  $0.02000 \text{ L} \times 0.100 \text{ M} = 0.00200$  mol.
- Each  $\text{Mg}(\text{OH})_2$  uses two  $\text{HNO}_3$ : 0.00100 mol
- $0.00100 \text{ mol} \times 58.3 \text{ g/mol}$

0.0583 g  $\text{Mg}(\text{OH})_2$

## Common mistake

**Using  $M_1V_1 = M_2V_2$  for every titration.** It works only for a 1 : 1 reaction; here it would ignore the 2 : 1 ratio and double the answer. **Use the balanced equation's mole ratio.**

## 4.7 Types of chemical reactions

In an **acid–base** reaction a proton ( $\text{H}^+$ ) passes between particles; in a **redox** reaction, such as burning, electrons pass and oxidation numbers change; in **precipitation**, two solutions make a solid.

## Not on the equation sheet, so learn it

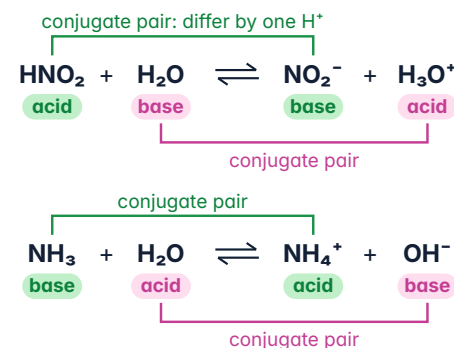
**Oxidation numbers:** a free element is 0; a monatomic ion equals its charge; they add up to the charge of the whole species. F is  $-1$ , O is usually  $-2$ , H is  $+1$  with nonmetals.

## Common mistake

**Calling a reaction redox because one ion turns into a different ion.** In  $2 \text{CrO}_4^{2-} + 2 \text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$ , Cr is  $+6$  on both sides:  $x + 4(-2) = -2$  and  $2x + 7(-2) = -2$ . No electrons moved; a proton did, so it is acid–base. **Check oxidation numbers first.**

## 4.8 Introduction to acid–base reactions

A Brønsted–Lowry **acid** donates a proton and a **base** accepts one. Each acid–base reaction has two **conjugate pairs**, whose formulas differ by exactly one  $\text{H}^+$ . Water can play either part: it takes a proton from  $\text{HNO}_2$  but gives one to  $\text{NH}_3$ .



## Common mistake

**Pairing the two reactants.**  $\text{HNO}_2$  and  $\text{H}_2\text{O}$  are not a conjugate pair;  $\text{HNO}_2$  and  $\text{NO}_2^-$  are: one species before and after it gives up a proton.

## 4.9 Oxidation–reduction (redox) reactions

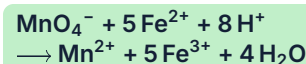
Split a redox reaction into two half-reactions. In the **oxidation** half, a species loses electrons, so they appear on the product side; in the **reduction** half, a species gains them. Electrons lost must equal electrons gained.

## Worked example

Balance in acid:



- Add  $\text{H}_2\text{O}$  for O,  $\text{H}^+$  for H, then electrons:  
 $\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$
- $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ , times 5 so the electrons cancel when you add. Check: charge  $+17$  on each side.



## Common mistake

**Electrons left in the overall equation.** Electrons only pass from one species to another, so none can be left over. Scale the halves until electrons lost equal electrons gained; then they cancel.

## Unit 5 Kinetics

Kinetics is about how fast reactions go and why. You measure a rate, find a rate law from data and follow concentrations over time, then explain the speed with collisions, energy profiles, mechanisms and catalysts.

Unit 1 7–9%

Unit 2 7–9%

Unit 3 18–22%

Unit 4 7–9%

Unit 5 7–9%

Unit 6 7–9%

Unit 7 7–9%

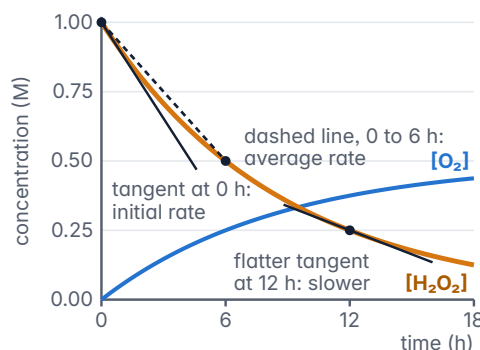
Unit 8 11–15%

Unit 9 7–9%

**Unit 5 is 7–9% of the multiple-choice section.** Rate data and rate laws appear in both long and short free-response questions, for example finding an order and  $k$  (with units) from trials or a graph, or judging a mechanism or a catalyst from its steps.

### 5.1 Reaction rates

A **rate** is how fast a concentration changes, in M/s. On a concentration–time graph it is the slope, with the minus sign dropped for a reactant. Higher concentration, more surface area or a higher temperature can speed a reaction up.



The reaction is  $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$ .

#### Not on the equation sheet, so learn it

For  $a\text{A} \rightarrow b\text{B}$ , divide each species' rate by its coefficient and the results are equal: rate of  $\text{A} \div a = \text{rate of B} \div b$ .

#### Worked example

In  $2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2$ ,  $\text{NO}_2$  is used up at  $6.52 \times 10^{-7} \text{ M/s}$ . How fast does  $\text{O}_2$  form?

$$1 \quad 6.52 \times 10^{-7} \times \frac{1 \text{ mol O}_2}{2 \text{ mol NO}_2}$$

$$3.26 \times 10^{-7} \text{ M/s}$$

#### Common mistake

##### Writing the $\text{O}_2$ rate as

$2 \times 6.52 \times 10^{-7} \text{ M/s}$ . The coefficient of  $\text{O}_2$  is half that of  $\text{NO}_2$ , so  $\text{O}_2$  forms half as fast: divide by 2.

#### How to earn the point

Why does powdered  $\text{CaCO}_3$  react with  $\text{HCl}$  faster than a lump?

The powder has more surface area, so more acid particles hit the solid each second, and more collisions per second make the reaction faster.

### 5.2 Introduction to rate law

The **rate law**,  $\text{rate} = k[\text{A}]^m[\text{B}]^n$ , can only be found by experiment. Here  $k$  is the rate constant: it changes with temperature, not with concentration. The exponents are the orders, and their sum is the overall order. Change a concentration by some factor and the rate changes by that factor raised to the order.



Doubling  $[\text{A}]$  leaves a zero-order rate unchanged, doubles a first-order rate and quadruples a second-order rate.

#### Worked example

Find the rate law and  $k$  for ascorbic acid (vitamin C), written  $\text{HAsc}$ , reacting with  $\text{I}_3^-$ .

| Trial | $[\text{HAsc}]$<br>(M) | $[\text{I}_3^-]$<br>(M) | Rate (M/s)             |
|-------|------------------------|-------------------------|------------------------|
| 1     | 0.450                  | 1.200                   | $2.457 \times 10^{-4}$ |
| 2     | 0.450                  | 0.600                   | $1.229 \times 10^{-4}$ |
| 3     | 0.900                  | 1.200                   | $4.914 \times 10^{-4}$ |

- From trial 1 to 3, only  $[\text{HAsc}]$  changes. It doubles and the rate doubles, so the reaction is first order in  $\text{HAsc}$ .
- From trial 1 to 2, only  $[\text{I}_3^-]$  changes. It halves and the rate halves, so it is first order in  $\text{I}_3^-$  too.
- $k = \frac{2.457 \times 10^{-4} \text{ M/s}}{(0.450 \text{ M})(1.200 \text{ M})}$ ; units: (M/s)  $\div (\text{M} \cdot \text{M}) = \text{M}^{-1} \text{ s}^{-1}$ .

$$\text{rate} = k[\text{HAsc}][\text{I}_3^-], \text{ with } k = 4.55 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

#### Common mistake

##### Taking orders from the balanced equation.

$2 \text{NO} + 2 \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$  has rate  $= k[\text{NO}]^2[\text{H}_2]$ : the coefficient of  $\text{H}_2$  is 2, but its order is 1.

### 5.3 Concentration changes over time

Plot the data three ways: whichever plot is a straight line tells you the order, and its slope gives  $k$ . Only first order has a constant half-life.

#### On the equation sheet

$$[\text{A}]_t - [\text{A}]_0 = -kt \quad \ln[\text{A}]_t - \ln[\text{A}]_0 = -kt$$

$$\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} = kt \quad t_{1/2} = \frac{0.693}{k}$$

| Order  | Straight plot                | Slope |
|--------|------------------------------|-------|
| zero   | $[\text{A}]$ against time    | $-k$  |
| first  | $\ln[\text{A}]$ against time | $-k$  |
| second | $1/[\text{A}]$ against time  | $+k$  |

#### Worked example

$[\text{N}_2\text{O}_5]$  is 0.160, 0.0800, 0.0400 and 0.0200 M at 0, 1.67, 3.34 and 5.01 h. Find the order and  $k$ .

- It halves every 1.67 h, a constant half-life, so it is first order:  $k = 0.693 \div 1.67 \text{ h}$ .

$$\text{First order, } k = 0.415 \text{ h}^{-1}$$

#### How to earn the point

How do you show from graphs that a reaction is second order in  $\text{NO}_2$ ?

Name the plot that is straight, because that is the evidence: "The plot of  $1/[\text{NO}_2]$  against time is linear, so the reaction is second order in  $\text{NO}_2$ ." "The graph on the right is linear" earns nothing.

#### Common mistake

**Reporting a negative  $k$ .**  $k$  is always positive; the minus sign only shows that the reactant is used up. For zero and first order the slope is  $-k$ , so a slope of  $-0.035 \text{ min}^{-1}$  means  $k = 0.035 \text{ min}^{-1}$ .

## 5.4 Elementary reactions

An **elementary step** happens in one event, exactly as written. Its rate law comes straight from its coefficients:  $2A \rightarrow \text{products}$  has rate =  $k[A]^2$ . Steps with three particles are rare, because three seldom collide at once.

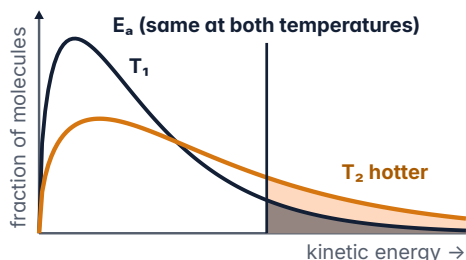
### ⚠ Common mistake

#### Reading exponents off an overall equation.

The overall equation is often several steps added together, so its coefficients need not match the rate law. Use data or the slow step instead.

## 5.5 Collision model

Most collisions do nothing. A collision makes products only if it has at least the **activation energy**,  $E_a$ , and the right orientation: to make A-B from A and B-C, A has to hit the B end. Heating raises the fraction of collisions with enough energy, which matters far more than the small rise in collisions per second.



The shaded area past  $E_a$  is the fraction that can react: navy at  $T_1$ , navy plus orange at the hotter  $T_2$ .

### 🔗 How to earn the point

#### Why is a reaction faster at a higher temperature?

A greater fraction of collisions have energy equal to or greater than the activation energy, so more collisions per second succeed.

### ⚠ Common mistake

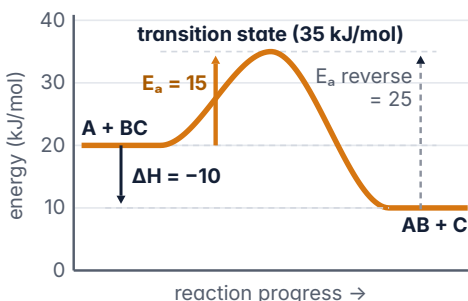
#### Writing only "the molecules move faster."

Add what that does: more collisions now have at least  $E_a$ . Heating doesn't lower  $E_a$ .

## 5.6 Reaction energy profile

An energy profile follows one collision: the reactants climb to the **transition state**, where bonds are partly broken and partly formed, then fall to the products.  $E_a$  is the climb from reactants to peak.

## 5.6 Reaction energy profile, continued



### ⚠ Common mistake

**Measuring  $E_a$  from zero.** Measure up from the reactants: here  $E_a$  is  $35 - 20 = 15$  kJ/mol, not 35.

### ⚠ Common mistake

#### Calling a reaction fast because it is exothermic.

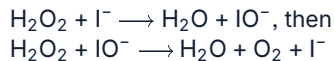
$\Delta H$  alone does not determine speed. Rate also depends on  $E_a$ , temperature, concentrations and collision orientation; a very exothermic reaction can still be slow.

## 5.7 Introduction to reaction mechanisms

A **mechanism** is the list of elementary steps a reaction takes; added together, they give the overall equation. An **intermediate** is made in one step and used in a later one; a **catalyst** is used in one step and given back later.

### 🔗 Worked example

Iodide speeds up the breakdown of  $\text{H}_2\text{O}_2$ . Name the catalyst and the intermediate.



**$\text{I}^-$  is the catalyst (used, then given back) and  $\text{IO}^-$  the intermediate (made, then used).**

## 5.8 Reaction mechanism and rate law

A reaction goes no faster than its slowest step. When the first step is slow, its rate law, read from its coefficients, is the whole reaction's rate law. For example,  $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$  can go through  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$  (slow), then  $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$  (fast).

## 5.8 Mechanism and rate law, continued

### 🔗 How to earn the point

#### Is that mechanism consistent with the measured rate law, rate = $k[\text{NO}_2]^2$ ?

The steps add up to the overall reaction, and the slow step's rate law, rate =  $k[\text{NO}_2]^2$ , matches, so it is consistent with the data.  $[\text{CO}]$  is absent because CO reacts only in the fast step. Never say the data "prove" a mechanism: another one might fit too.

## 5.9 Pre-equilibrium approximation

When a fast, reversible step comes first, the slow step's rate law holds an intermediate you can't measure. Replace it using the fast equilibrium.

### 🔗 Worked example

$\text{NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$  (fast), then  $\text{NOBr}_2 + \text{NO} \rightarrow 2\text{NOBr}$  (slow). Find the rate law.

1 Slow step: rate =  $k_2[\text{NOBr}_2][\text{NO}]$

2 Fast step:  $K_1 = [\text{NOBr}_2]/([\text{NO}][\text{Br}_2])$ , so  $[\text{NOBr}_2] = K_1[\text{NO}][\text{Br}_2]$ . Substitute: rate =  $k_2K_1[\text{NO}]^2[\text{Br}_2]$ .

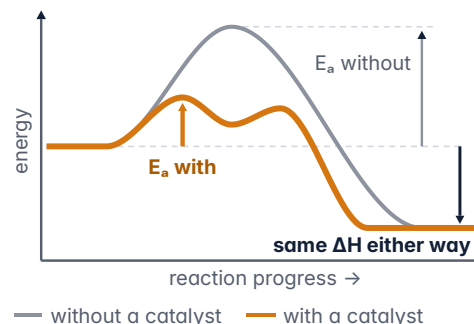
**rate =  $k[\text{NO}]^2[\text{Br}_2]$ , where  $k = k_2K_1$**

## 5.10 Multistep reaction energy profile

Each step has its own hump, with an intermediate in each valley between humps. Measure a step's  $E_a$  from the valley where it starts; the largest climb is usually the slow step.

## 5.11 Catalysis

A **catalyst** gives a new route with a lower activation energy. It speeds both directions alike, so  $K$  stays the same; so does  $\Delta H$ , since the reactants and products don't change. The catalyzed route below has two steps and an intermediate in the dip.



## Unit 6 Thermochemistry

Reactions, dissolving and phase changes all take in or give off heat. In this unit you find a reaction's enthalpy change from a temperature change in a calorimeter, from bond energies, from formation data, or by combining other reactions.

Unit 1 7–9%   Unit 2 7–9%   Unit 3 18–22%   Unit 4 7–9%   Unit 5 7–9%   Unit 6 7–9%   Unit 7 7–9%   Unit 8 11–15%   Unit 9 7–9%

Unit 6 is 7–9% of the multiple-choice section. A thermochemistry part has appeared in the free response every recent year, most often calorimetry, then Hess's law and the energy of phase changes.

### 6.1 Endothermic and exothermic processes

First name the **system**, the reaction or process you're studying. If it releases energy to its surroundings, it is **exothermic** ( $q < 0$ ,  $\Delta H < 0$ ) and the water around it warms, as with burning fuel or a  $\text{CaCl}_2$  hot pack. If it absorbs energy, it is **endothermic** ( $q > 0$ ,  $\Delta H > 0$ ) and the water cools, as with melting ice or an  $\text{NH}_4\text{NO}_3$  cold pack.

Dissolving can go either way: pulling the ions apart, and the water molecules apart, costs energy, and forming ion–water attractions releases energy. The larger one sets the sign.

#### How to earn the point

##### Why is dissolving $\text{CaCl}_2$ exothermic?

Forming ion–water attractions releases more energy than separating the ions and pulling the water molecules apart costs, so the dissolving releases energy ( $q < 0$ ).

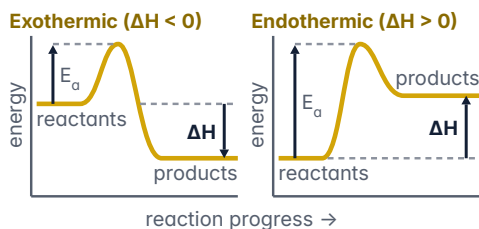
#### Common mistake

##### Saying a cold pack "releases cold."

Cold doesn't flow; energy flows out of the water into the dissolving  $\text{NH}_4\text{NO}_3$ , so  $q$  for the dissolving is positive and it is endothermic. **Name the system, then its sign.**

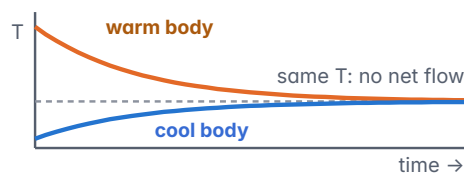
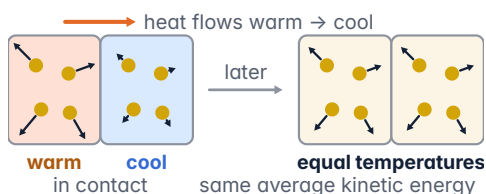
### 6.2 Energy diagrams

An energy diagram shows  $\Delta H = H_{\text{products}} - H_{\text{reactants}}$  as an arrow from the reactants' level to the products' level, which sits lower for an exothermic reaction. Two levels are enough when only  $\Delta H$  is asked; draw the hump when a question mentions activation energy, rate or a catalyst.



### 6.3 Heat transfer and thermal equilibrium

Temperature tracks the **average kinetic energy** of the particles. When a warm body touches a cool one, collisions pass energy from faster particles to slower ones until the temperatures match. At this **thermal equilibrium** the collisions go on, but the net flow of energy stops.



#### Common mistake

##### Treating equal temperature as equal energy.

A bathtub and a cup at  $40^\circ\text{C}$  have the same average kinetic energy per molecule, but the bathtub, with far more molecules, holds far more thermal energy.

#### How to earn the point

##### How do you draw the same water at a higher temperature?

Keep the same number and size of molecules, and make the motion arrows longer on average, because hotter molecules move faster on average.

### 6.4 Heat capacity and calorimetry

A calorimeter turns a temperature change you can read into heat you can't see. The reaction is the system; the solution around it is the surroundings, and the thermometer measures the solution. Whatever heat the reaction releases, the solution gains.

### 6.4 Heat capacity and calorimetry, continued

#### On the equation sheet

$$q = mc\Delta T$$

$m$  = mass of whatever changes temperature;

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

#### Not on the equation sheet, so learn it

Ignoring heat absorbed by the cup or room, the reaction's heat is the solution's with the sign flipped,  $q_{\text{rxn}} = -q_{\text{soln}}$ . Then  $\Delta H = q_{\text{rxn}} \div n_{\text{rxn}}$ , where the moles of reaction,  $n_{\text{rxn}}$ , are the moles of a reactant divided by its coefficient. For hot metal dropped into cool water,  $q_{\text{metal}} + q_{\text{water}} = 0$ .

#### Worked example

6.80 g of KCl (0.0912 mol) dissolves in 97.5 g of water. The solution ( $c = 3.95 \text{ J/(g}\cdot^\circ\text{C)}$ ) cools from  $24.5^\circ\text{C}$  to  $21.1^\circ\text{C}$ . Find  $\Delta H$  of dissolving.

- Whole solution:  $97.5 + 6.80 = 104.3 \text{ g}$ ;  
 $\Delta T = -3.4^\circ\text{C}$ , two significant figures
- $q_{\text{soln}} = (104.3)(3.95)(-3.4) = -1.4 \times 10^3 \text{ J}$
- The dissolving gained that heat:  
 $+1.4 \text{ kJ} \div 0.0912 \text{ mol}$

$\Delta H = +15 \text{ kJ/mol}$ , so dissolving KCl is endothermic.

#### Common mistake

##### Using only the solid's mass, or dropping the sign.

The thermometer reads the whole solution, so  $m$  is 104.3 g, not 6.80 g. And a solution that warms means a negative  $\Delta H$  for the reaction, so write the sign every time.

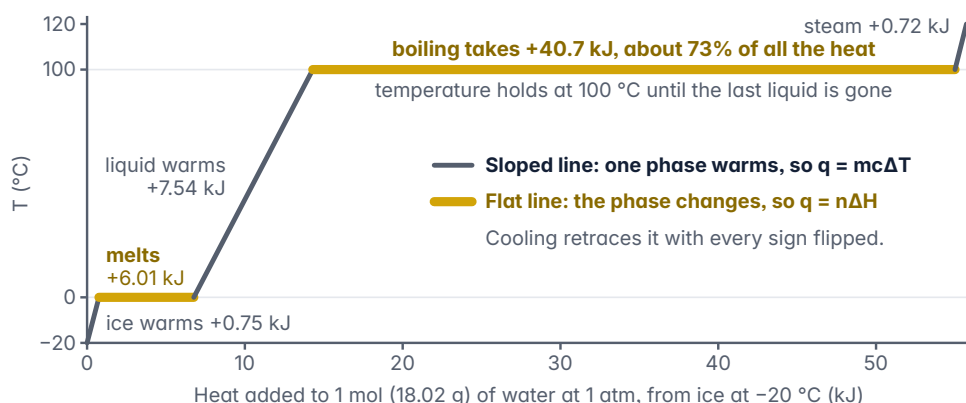
#### How to earn the point

##### How does heat exchanged with the room affect the calculated $\Delta H$ ?

If the solution starts at room temperature, heat exchanged with the air shrinks the measured temperature change, whether the cup warms or cools, so the calculated  $q$  and  $\Delta H$  come out smaller in size than the true values.

## 6.5 Energy of phase changes

A pure substance changes phase at fixed pressure and temperature while energy flows, because the energy pulls the particles apart (or comes out as they lock together) instead of speeding them up. The molecules stay whole, so boiling water breaks no O–H bonds.



**Not on the equation sheet, so learn it**  
 $q = n\Delta H$ . Melting and vaporizing absorb energy (+); freezing and condensing release the same amount (-).

### Worked example

How much heat vaporizes 6.85 g of HF? ( $\Delta H_{\text{vap}} = 25.2 \text{ kJ/mol}$ )

$$1 \quad (6.85 \div 20.01) \text{ mol} \times 25.2 \text{ kJ/mol}$$

**+8.63 kJ absorbed**

### Common mistake

**Using  $mc\Delta T$  across a flat stretch.**  $\Delta T$  is zero there but heat still flows, so use  $q = n\Delta H$ , plus  $mc\Delta T$  for each stretch where the temperature changes.

## 6.6 Enthalpy of reaction

$\Delta H$  is the heat released (-) or absorbed (+) at constant pressure by **one mole of reaction**, one run of the equation as written ( $\text{kJ/mol}_{\text{rxn}}$ ). For  $4 \text{ Na} + \text{O}_2 \rightarrow 2 \text{ Na}_2\text{O}$ ,  $\Delta H^\circ = -828 \text{ kJ/mol}_{\text{rxn}}$ , so 4 mol of Na and 1 mol of  $\text{O}_2$  release 828 kJ.

**Not on the equation sheet, so learn it**  
 $q = n_{\text{rxn}} \Delta H$ , where  $n_{\text{rxn}}$  = moles of a reactant  $\div$  its coefficient, using the limiting reactant.

### Worked example

18.4 g of Na reacts with 12.8 g of  $\text{O}_2$ . How much heat is released?

- Na:  $18.4 \div 22.99 \div 4 = 0.200 \text{ mol}_{\text{rxn}}$
- $\text{O}_2$ :  $12.8 \div 32.00 \div 1 = 0.400 \text{ mol}_{\text{rxn}}$
- Na gives fewer moles of reaction, so it runs out first;  $0.200 \times 828 = 166 \text{ kJ}$

**166 kJ is released ( $q = -166 \text{ kJ}$ ).**

### Common mistake

**Doubling  $\Delta H$  for twice the fuel.**  $\Delta H$  belongs to the equation as written: twice the fuel doubles  $q$ , the heat, but not  $\Delta H$ .

## 6.7 Bond enthalpies

Breaking a bond always takes energy in, and forming one releases it. Bonds broken minus bonds formed, using average bond energies, estimates  $\Delta H$ .

**Not on the equation sheet, so learn it**  
 $\Delta H \approx \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$

## 6.7 Bond enthalpies, continued

### Worked example

Estimate  $\Delta H$  for  $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{ HCl}$  using H–H 436, Cl–Cl 243 and H–Cl 431 kJ/mol.

- Broken  $436 + 243 = 679 \text{ kJ}$ ; formed  $2(431) = 862 \text{ kJ}$

$\Delta H = 679 - 862 = -183 \text{ kJ/mol}_{\text{rxn}}$ , exothermic because the new bonds release more energy than breaking the old ones takes.

### Common mistake

**Subtracting formed minus broken.** Breaking bonds costs energy (+) and forming them releases it (-), so  $\Delta H = \text{broken} - \text{formed}$ , counting every bond times its coefficient.

## 6.8 Enthalpy of formation

$\Delta H_f^\circ$  is the enthalpy change for making **one mole** of a compound from its elements in their standard states, whose own  $\Delta H_f^\circ$  is 0. Water vapor is  $-241.8 \text{ kJ/mol}$  against liquid water's  $-285.8$ , because the vapor still holds the energy it took to vaporize.

### On the equation sheet

$$\Delta H_{\text{reaction}}^\circ = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants})$$

### Worked example

Thermite:  $\text{Fe}_2\text{O}_3 + 2 \text{ Al} \rightarrow \text{Al}_2\text{O}_3 + 2 \text{ Fe}$ , with  $\Delta H_f^\circ = -825.5 \text{ (Fe}_2\text{O}_3)$  and  $-1675.7 \text{ kJ/mol (Al}_2\text{O}_3)$ . Find  $\Delta H^\circ$ .

$$\Delta H^\circ = -1675.7 - (-825.5) = -850.2 \text{ kJ}$$

## 6.8 Enthalpy of formation, continued

### Common mistake

**Computing reactants minus products.** That gives  $+850.2 \text{ kJ}$  for thermite, the wrong sign. Formation enthalpies go products minus reactants, each times its coefficient; bond energies go the other way (broken – formed).

## 6.9 Hess's law

$\Delta H$  depends only on the starting and ending substances, so it is the same in one step or several, and you can build a target equation from equations you know.

### Not on the equation sheet, so learn it

Reversing an equation changes the sign of its  $\Delta H$ , multiplying it by a number multiplies  $\Delta H$  by that number, and adding equations adds their  $\Delta H$  values.

### Worked example

$\text{P}_4 + 6 \text{ Cl}_2 \rightarrow 4 \text{ PCl}_3$ ,  $-1148 \text{ kJ}$ ;  
 $\text{PCl}_3 + \text{Cl}_2 \rightarrow \text{PCl}_5$ ,  $-88 \text{ kJ}$ . Find  $\Delta H_f^\circ$  of  $\text{PCl}_5(\text{g})$ .

- Target:  $\frac{1}{4} \text{ P}_4(\text{s}) + \frac{5}{2} \text{ Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{g})$
- Divide the first by 4 ( $-287 \text{ kJ}$ ) and add the second ( $-88 \text{ kJ}$ );  $\text{PCl}_3$  cancels

$$\Delta H_f^\circ = -375 \text{ kJ/mol}$$

### Common mistake

**Adding the given  $\Delta H$  values as printed.** That gives  $\Delta H$  for a different reaction. Flip or scale each equation, and its  $\Delta H$ , to match the target, then add.

## Unit 7 Equilibrium

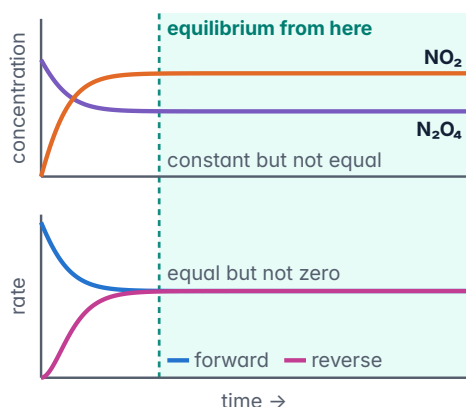
Reactions that run both ways settle where the forward and reverse rates are equal. This unit uses the equilibrium constant  $K$  to describe that mixture and the reaction quotient  $Q$  to predict which way a mixture shifts after a change.

Unit 1 7–9%   Unit 2 7–9%   Unit 3 18–22%   Unit 4 7–9%   Unit 5 7–9%   Unit 6 7–9%   Unit 7 7–9%   Unit 8 11–15%   Unit 9 7–9%

Unit 7 is 7–9% of the multiple-choice section.  $K$  expressions, solubility and explanations of a shift turn up in the free response almost every year, and the acid–base questions of Unit 8 use the same ideas.

### 7.1 Introduction to equilibrium

At equilibrium the forward and reverse reactions keep running at the **same rate**, so every concentration and pressure stays constant. Nothing visible changes, but the particles never stop reacting, which is why equilibrium is called dynamic.



$\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2$ , starting from pure  $\text{N}_2\text{O}_4$ .

#### Common mistake

**"At equilibrium the amounts are equal."**

They are constant, not equal:  $[\text{NO}_2]$  and  $[\text{N}_2\text{O}_4]$  can sit far apart forever. Equilibrium starts where the curves go flat, not where they cross.

### 7.2 Direction of reversible reactions

The net direction depends only on which rate is bigger right now. If the forward rate is larger, the mixture makes products; if the reverse rate is larger, it makes reactants; when they match, nothing changes overall.

A catalyst speeds both directions equally, so equilibrium comes sooner, with the same composition and the same  $K$ .

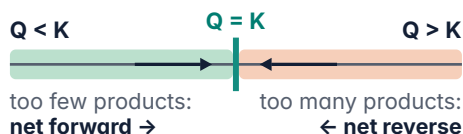
#### How to earn the point

**Why do the concentrations at equilibrium stay constant?**

The forward and reverse reactions run at the same rate, so each substance is made exactly as fast as it is used up.

### 7.3 Reaction quotient and equilibrium constant

$Q$  is built from the concentrations or partial pressures present right now;  $K$  is the value  $Q$  has at equilibrium. A mixture reacts in the direction that brings  $Q$  closer to  $K$ , and stops changing when  $Q = K$ .



#### On the equation sheet

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \text{ for } a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D};$$

$K_p$  has the same form with partial pressures

#### Not on the equation sheet, so learn it

Leave out solids and pure liquids, including solvent water. Use brackets (mol/L) for  $K_c$  and pressures for  $K_p$ .  $K$  has no units, and its value depends on temperature. So  $\text{Mg}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Mg}^{2+} + 2 \text{OH}^-$  gives  $K = [\text{Mg}^{2+}][\text{OH}^-]^2$ .

#### Common mistake

**Writing  $[2\text{OH}^-]$ , or putting  $[\text{Mg}(\text{OH})_2]$  on the bottom.** The coefficient becomes an exponent, so write  $[\text{OH}^-]^2$ ; a solid's concentration never changes, so it is left out.

### 7.4 Calculating the equilibrium constant

$K$  uses equilibrium values only. Given the starting amounts and one equilibrium amount, an **ICE table** (initial, change, equilibrium) and the balanced equation give the rest.

#### How to earn the point

**What must a  $K$  calculation show?**

The  $K$  expression with the equilibrium values put into it; an answer with no setup usually earns no credit.

### 7.4 Calculating the equilibrium constant, continued

#### Worked example

$\text{P}_4(\text{g}) \rightleftharpoons 2 \text{P}_2(\text{g})$  starts with 0.470 atm of  $\text{P}_4$  and no  $\text{P}_2$ . At equilibrium  $P_{\text{P}_2} = 0.630$  atm. Find  $K_p$ .

1  $P_{\text{P}_4}$  drops by  $x$  while  $P_{\text{P}_2}$  rises by  $2x = 0.630$  atm, so  $x = 0.315$  and  $P_{\text{P}_4} = 0.155$  atm

$$K_p = (0.630)^2 / 0.155 = 2.56$$

#### Common mistake

**Putting moles into  $K_c$ .** Divide each amount by the volume first. For  $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$  with 0.0320 mol  $\text{NO}_2$  and 0.0840 mol  $\text{N}_2\text{O}_4$  in 2.00 L,  $K_c = 0.0420 / (0.0160)^2 = 164$ ; raw moles give 82.0.

### 7.5 Magnitude of the equilibrium constant

At equilibrium,  $K \gg 1$  means mostly products (treat the reaction as complete),  $K \ll 1$  mostly reactants, and  $K$  near 1 measurable amounts of both.

#### Common mistake

**"A huge  $K$  means a fast reaction."**  $\text{H}_2$  and  $\text{O}_2$  can sit mixed for years though  $K$  for making water is huge;  $K$  tells how far, not how fast.

### 7.6 Properties of the equilibrium constant

**Reverse an equation** and  $K$  becomes  $1/K$ ; **multiply its coefficients by  $n$**  and  $K$  becomes  $K^n$ ; **add equations** and the  $K$  values multiply.

#### Worked example

$\text{A} \rightleftharpoons \text{B}$  has  $K_1 = 4.0$ ;  $\text{B} \rightleftharpoons \text{C}$  has  $K_2 = 25$ . Find  $K$  for  $\text{C} \rightleftharpoons \text{A}$ .

1  $\text{A} \rightleftharpoons \text{C}$  has  $K = 4.0 \times 25 = 100$

$$\text{Reversed, } K = 1/100 = 0.010$$

## 7.7 Calculating equilibrium concentrations

Given  $K$  and the starting amounts, a table of **initial, change and equilibrium** values (an ICE table) finds every equilibrium amount. Compare  $Q$  with  $K$  first to know which side gets  $-x$  and which gets  $+x$ .

### Not on the equation sheet, so learn it

In the change row, multiply  $x$  by each coefficient, negative on the side being used up. Only equilibrium values go into  $K$ . If  $K$  is very small, treat a term like  $0.100 - x$  as  $0.100$ , then check that  $x$  is less than 5% of  $0.100$ .

### Worked example

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ ,  $K_c = 50.4$ .  
Start:  $0.0100 \text{ M H}_2$ ,  $0.0100 \text{ M I}_2$ , no  $\text{HI}$ .  
Find  $[\text{HI}]$ .

- $[\text{H}_2] = [\text{I}_2] = 0.0100 - x$ ,  $[\text{HI}] = 2x$
- $50.4 = (2x)^2 / (0.0100 - x)^2$
- Square root:  $7.10 = 2x / (0.0100 - x)$ ,  
 $x = 0.00780$

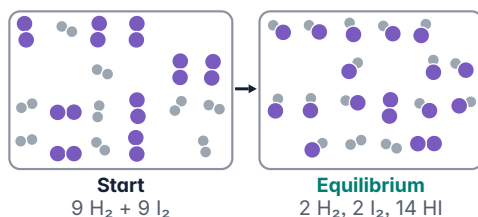
$[\text{HI}] = 0.0156 \text{ M}$ ;  $[\text{H}_2] = [\text{I}_2] = 0.0100 - 0.0078 = 0.0022 \text{ M}$ , two significant figures because subtraction keeps decimal places.

### Common mistake

**Reporting  $x$  as the answer.**  $x$  is how far the reaction went; the answer is in the equilibrium row, such as  $[\text{HI}] = 2x$ .

## 7.8 Representations of equilibrium

A particle drawing of an equilibrium mixture shows reactants and products together, in numbers that make  $Q = K$ , with every atom from the start still there.



Grey dots are H atoms and purple dots I atoms, 18 of each in both boxes. With 2 moles of gas on each side the volume cancels, so the counts give  $Q = 14^2 / (2 \times 2) = 49$ , close to  $K = 50.4$ .

### Common mistake

**Drawing the reaction run to completion.** At equilibrium some of every reactant is left, so choose the counts with the  $K$  expression, not the limiting reactant.

## 7.9 Introduction to Le Châtelier's principle

Disturb an equilibrium and it shifts to partly undo the disturbance:  $\text{N}_2$  added to  $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$  is partly used up, never all of it.

| Disturbance                                                  | Shifts toward    |
|--------------------------------------------------------------|------------------|
| Increase [reactant] or decrease [product]                    | products         |
| Increase [product] or decrease [reactant]                    | reactants        |
| Compress gases (no shift if both sides have equal gas moles) | fewer gas moles  |
| Raise the temperature                                        | endothermic side |
| Catalyst, inert gas at fixed volume, more solid              | no shift         |

## 7.10 Reaction quotient and Le Châtelier's principle

Changing concentrations or partial pressures can change  $Q$  while  $K$  stays the same. Changing the temperature is the only thing that changes  $K$ . "Le Châtelier's principle" alone earns nothing: name the change, its effect on  $Q$  or  $K$ , and the direction.

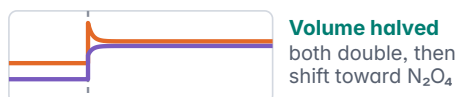
### How to earn the point

How does  $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$ , an exothermic reaction, respond to added  $\text{N}_2$  and to heating?

$\text{N}_2$  is in the denominator of  $Q$ , so adding  $\text{N}_2$  lowers  $Q$  below  $K$ , and the reaction proceeds forward until  $Q = K$ .

The forward reaction is exothermic, so raising the temperature decreases  $K$ . Now  $Q > K$ , so the reaction proceeds in reverse.

Concentration against time for  $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$  (exothermic forward), disturbed at the dashed line. Orange is  $\text{NO}_2$ ; violet is  $\text{N}_2\text{O}_4$ .



## 7.11 Introduction to solubility equilibria

A saturated solution with solid at the bottom is an equilibrium: ions leave the crystal and land back on it at equal rates. Its  $K$  is the **solubility product**,  $K_{sp}$ , with the solid left out. The **molar solubility**  $s$  is the moles of solid that dissolve per liter.

### Not on the equation sheet, so learn it

In pure water, a 1 : 1 salt ( $\text{AgCl}$ ) has  $K_{sp} = s^2$ , and a 1 : 2 or 2 : 1 salt ( $\text{CaF}_2$ ,  $\text{Ag}_2\text{CrO}_4$ ) has  $K_{sp} = 4s^3$ . A solid forms when  $Q > K_{sp}$ ; after mixing two solutions, use each ion's moles  $\div$  the total volume.

### Worked example

$0.0167 \text{ g of CaF}_2$  ( $78.08 \text{ g/mol}$ ) dissolves per liter. Find  $K_{sp}$ .

- $s = 0.0167 \div 78.08 = 2.14 \times 10^{-4} \text{ M}$ ;  
 $[\text{F}^-] = 2s$
- $K_{sp} = s(2s)^2 = 4s^3$

$$K_{sp} = 3.91 \times 10^{-11}$$

### Common mistake

**Ranking solubility by  $K_{sp}$  when the ion ratios differ.**  $\text{CaF}_2$  has the smaller  $K_{sp}$  ( $3.91 \times 10^{-11}$  against  $1.8 \times 10^{-10}$  for  $\text{AgCl}$ ), yet it dissolves about 16 times more ( $2.14 \times 10^{-4} \text{ M}$  against  $1.3 \times 10^{-5} \text{ M}$ ), because its  $K_{sp}$  is  $4s^3$ , not  $s^2$ . Work out  $s$  for each salt and compare those.

## 7.12 Common-ion effect

A salt dissolves less in water that already holds one of its ions, because  $Q$  reaches  $K_{sp}$  sooner.  $K_{sp}$  itself doesn't change; only temperature changes it.

### Worked example

What is the molar solubility of  $\text{CaF}_2$  ( $K_{sp} = 3.91 \times 10^{-11}$ ) in  $0.0100 \text{ M NaF}$ ?

- $s = [\text{Ca}^{2+}]$ ;  $[\text{F}^-] \approx 0.0100 \text{ M}$ , because the  $2s$  from  $\text{CaF}_2$  is tiny next to  $0.0100$
- $s = 3.91 \times 10^{-11} \div (0.0100)^2$

$s = 3.91 \times 10^{-7} \text{ M}$ , about 1/550 of its solubility in pure water ( $2.14 \times 10^{-4} \text{ M}$ )

### Common mistake

**"The common ion lowers  $K_{sp}$ ."** It lowers the solubility,  $s$ .  $K_{sp}$  stays the same at a given temperature.

## Unit 8 Acids and Bases

Acids give up protons and bases take them. This unit covers pH, how strong and weak acids and bases behave in water, what happens when they react and during a titration, why some acids are stronger than others, and how a buffer holds its pH steady.

Unit 1 7–9%   Unit 2 7–9%   Unit 3 18–22%   Unit 4 7–9%   Unit 5 7–9%   Unit 6 7–9%   Unit 7 7–9%   Unit 8 11–15%   Unit 9 7–9%

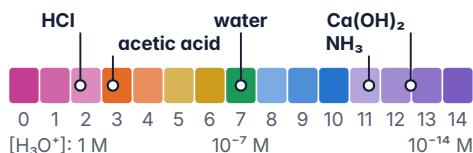
**Unit 8 is 11–15% of the multiple-choice section.** Acid–base questions have appeared in the free response every recent year, for example reading a titration curve, calculating a pH or a  $K_a$ , or explaining how a buffer works.

### 8.1 Introduction to acids and bases

Water passes protons between its own molecules, so even pure water holds a little  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , in equal amounts.  $\text{pH} = -\log[\text{H}_3\text{O}^+]$ , so one pH unit lower means ten times more  $\text{H}_3\text{O}^+$ . A solution is acidic when  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ , basic when  $[\text{OH}^-] > [\text{H}_3\text{O}^+]$ , and neutral when they are equal.

#### On the equation sheet

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$  at 25 °C  
 $\text{pH} = -\log[\text{H}_3\text{O}^+]$ ,  $\text{pOH} = -\log[\text{OH}^-]$   
 $\text{pH} + \text{pOH} = 14$  at 25 °C



← more acidic                      more basic →  
 0.0150 M HCl, 0.100 M acetic acid, pure water, 0.100 M  $\text{NH}_3$  and 0.0150 M  $\text{Ca}(\text{OH})_2$  on the pH scale. The acetic acid is more concentrated than the HCl yet less acidic, because it is weak.

#### Worked example

At 25 °C,  $[\text{OH}^-] = 2.0 \times 10^{-5}$  M. Find  $[\text{H}_3\text{O}^+]$  and the pH.

- $[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-5}} = 5.0 \times 10^{-10}$  M
- $\text{pH} = -\log(5.0 \times 10^{-10})$

**pH 9.30, so it is basic; two significant figures give two decimals**

#### Common mistake

**Assuming pH 7 is neutral at every temperature.** That holds only at 25 °C. Splitting water absorbs energy, so warming it raises  $K_w$ : pure water at 50 °C has pH 6.63 and is still neutral, because  $[\text{H}_3\text{O}^+]$  still equals  $[\text{OH}^-]$ .

#### Not on the equation sheet, so learn it

Going back from a pH:  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$ , and  $[\text{OH}^-] = 10^{-\text{pOH}}$ . For pH, use the log and  $10^x$  keys, not ln and  $e^x$ .

### 8.2 pH and pOH of strong acids and bases

A **strong** acid or base ionizes completely, so the ion concentration comes straight from the formula: 0.010 M HCl holds 0.010 M  $\text{H}_3\text{O}^+$ . Strength describes the tendency to ionize; concentration is how much is dissolved, so 0.0010 M HCl is strong but dilute.

#### Not on the equation sheet, so learn it

**Strong acids:** HCl, HBr, HI,  $\text{HClO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (its first proton). HF and acetic acid are weak; use supplied data for other acids.

**Strong bases:** the group 1 hydroxides, and  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$ , which each release two  $\text{OH}^-$ .

#### Worked example

0.20 g of NaOH dissolves to make 500.0 mL of solution at 25 °C. Find the pH.

- $0.20 \div 40.00 = 0.0050$  mol  $\text{OH}^-$ .  
Divide by 0.5000 L:  $[\text{OH}^-] = 0.010$  M.
- $\text{pOH} = -\log(0.010) = 2.00$ , so  $\text{pH} = 14.00 - 2.00$

**pH = 12.00 (2.00 is the pOH)**

#### Common mistake

**Forgetting that a group 2 hydroxide gives two  $\text{OH}^-$ .** 0.0050 M  $\text{Ba}(\text{OH})_2$  is 0.010 M  $\text{OH}^-$ , so the pOH is 2.00 and the pH is 12.00, not 11.70.

**Averaging pH values.** Mixing equal volumes of pH 2.00 and 4.00 HCl averages the concentrations,  $(0.010 + 0.00010) \div 2 = 0.00505$  M, so the pH is 2.30, not 3.00.

**Calling  $1.0 \times 10^{-8}$  M HCl "pH 8."** An acid can't make water basic. The acid adds less  $\text{H}_3\text{O}^+$  than water already holds, so the pH is just under 7 (6.98).

### 8.3 Weak acid and base equilibria

A **weak acid** gives its proton to water only partly, so HA and its ions coexist in solution.  $K_a$  measures how far it goes: the larger  $K_a$  (the smaller  $\text{p}K_a$ ), the stronger the acid. A **weak base** takes a proton from water and makes  $\text{OH}^-$ , and  $K_b$  measures how far that goes.

#### On the equation sheet

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$K_b = \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]}$$

$$\text{p}K_a = -\log K_a, K_w = K_a \times K_b$$

#### Not on the equation sheet, so learn it

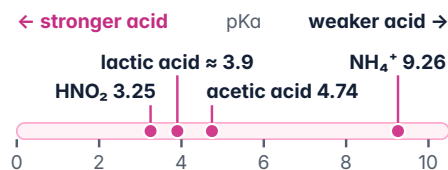
For a weak acid alone with starting concentration C,  $[\text{H}_3\text{O}^+] = x \approx \sqrt{K_a C}$ . Afterward, check that x is under about 5% of C. Percent ionized =  $x \div C \times 100$ .

#### Worked example

Find the pH of 0.100 M acetic acid,  $K_a = 1.8 \times 10^{-5}$ .

- $x = \sqrt{(1.8 \times 10^{-5})(0.100)} = 1.34 \times 10^{-3}$  M, which is 1.3% of 0.100, so the shortcut is fair
- $\text{pH} = -\log(1.34 \times 10^{-3})$

**pH 2.87, with only 1.3% of the acid ionized**



#### Common mistake

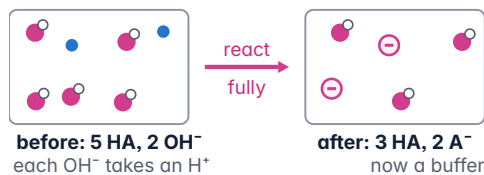
**Taking  $-\log$  of a weak base's x and calling it the pH.** For a base, x is  $[\text{OH}^-]$ . In 0.100 M  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ),  $[\text{OH}^-] = 1.34 \times 10^{-3}$  M, so the pOH is 2.87 and the pH is 11.13.

**Writing  $K_a = 1/K_b$ .** For a conjugate pair the link is  $K_a \times K_b = K_w$ , so  $K_a = K_w \div K_b$ .

### 8.4 Acid-base reactions and buffers

When a strong acid meets a base, or a strong base meets an acid, it reacts essentially completely before anything else happens. So work in moles first: let the strong one react, then look at what is left. What is left tells you how to find the pH.

| Left after the reaction       | How to get the pH                           |
|-------------------------------|---------------------------------------------|
| extra strong acid or base     | extra moles $\div$ total volume             |
| a weak acid (or base) alone   | $K_a$ (or $K_b$ ) and $x \approx \sqrt{KC}$ |
| only $A^-$ , a weak base      | $K_b = K_w \div K_a$ ; $x$ is $[OH^-]$      |
| only $HB^+$ , a weak acid     | $K_a = K_w \div K_b$ ; $x$ is $[H_3O^+]$    |
| HA and $A^-$ , both sizable   | a buffer: Henderson-Hasselbalch (8.9)       |
| only water and spectator ions | pH 7.00 at 25 °C                            |



Pink balls with a white H are HA, circled minus signs are  $A^-$  and blue dots are  $OH^-$ .

#### Worked example

10.00 mL of 0.100 M NaOH is added to 25.00 mL of 0.100 M acetic acid ( $K_a = 1.8 \times 10^{-5}$ ). Find the pH.

- Moles: 2.500 mmol HA and 1.000 mmol  $OH^-$ . The  $OH^-$  is used up, leaving 1.500 mmol HA and 1.000 mmol  $A^-$ .
- Both are left, so it's a buffer:  $pH = 4.745 + \log \frac{1.000}{1.500}$

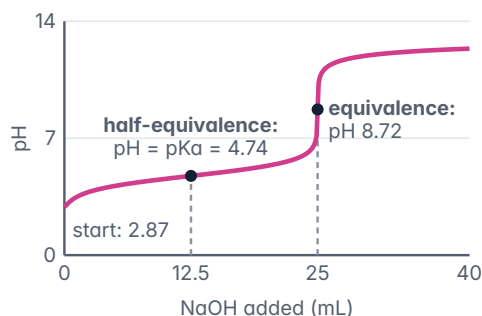
**pH 4.57**

#### Common mistake

**Putting the starting concentrations into  $K_a$  before the base has reacted.** The NaOH changes what is in the flask. Neutralize first, in moles; only then choose the equation.

### 8.5 Acid-base titrations

A titration adds a solution of known concentration until it exactly uses up the unknown. At the **equivalence point**, the middle of the steep jump, the moles of base added equal the moles of a monoprotic acid. Halfway there, at **half-equivalence**,  $[HA] = [A^-]$ , so  $pH = pK_a$ . An acid with two acidic protons can show two distinct jumps if its two  $K_a$  values are far enough apart. For such an acid, the exam asks you to name the main species in each region, not to calculate their amounts.



25.00 mL of 0.100 M acetic acid titrated with 0.100 M NaOH.

| NaOH  | In the flask             | pH    |
|-------|--------------------------|-------|
| 0 mL  | HA alone: $\sqrt{K_a C}$ | 2.87  |
| 10.00 | HA and $A^-$ : a buffer  | 4.57  |
| 12.50 | equal HA and $A^-$       | 4.74  |
| 25.00 | only $A^-$ , a weak base | 8.72  |
| 30.00 | extra $OH^-$             | 11.96 |

#### Worked example

10.0 mL of a weak acid HA needs 16.0 mL of 0.0550 M NaOH to reach equivalence. At 8.0 mL, the pH is 4.1. Find  $[HA]$  and the  $pK_a$ .

- $0.0160 \text{ L} \times 0.0550 \text{ M} = 8.80 \times 10^{-4}$  mol of base, so also  $8.80 \times 10^{-4}$  mol of HA. Divide by 0.0100 L.
- 8.0 mL is half of 16.0 mL, so  $pK_a = pH$  there

**$[HA] = 0.0880 \text{ M}$ ;  $pK_a \approx 4.1$**

#### Common mistake

**Reading the  $pK_a$  at the equivalence point.** There the flask holds only  $A^-$ , and the pH (8.72 above) is not equal to the  $pK_a$ . Go to half the equivalence volume.

**Expecting pH 7 at every equivalence point.** At 25 °C, a strong acid with a strong base gives 7.00. A weak acid titrated with a strong base has its equivalence point above 7; a weak base titrated with a strong acid has it below 7.

### 8.6 Molecular structure of acids and bases

The more stable the ion an acid leaves behind, the more readily the acid gives up its proton. **Resonance** stabilizes the conjugate base by spreading its charge over several atoms, and nearby **electronegative atoms** stabilize it by pulling electron density toward themselves. Down a group, the **H-X bond gets longer and weaker**, so  $H^+$  leaves more easily.

$pK_a$  as Cl atoms are added (smaller = stronger)

**$CH_3COOH$**  **4.74**

**$ClCH_2COOH$**   **$\approx 2.9$**

**$Cl_3CCOOH$**   **$\approx 0.7$**

#### How to earn the point

**Why is  $CH_3COOH$  stronger than ethanol?**

Acetic acid is the stronger acid because its conjugate base, acetate, is more stable: resonance spreads the negative charge over two O atoms, while in ethoxide (ethanol's conjugate base) it sits on one.

#### Common mistake

**"HF is the strongest of HF, HCl, HBr and HI because F is the most electronegative."** Down a group, bond length matters more. The H-F bond is short and strong (92 pm) and the H-I bond long and weak (161 pm), so HF is the weakest and HI the strongest.

### 8.7 pH and $pK_a$

Compare the pH with the acid's  $pK_a$ : below the  $pK_a$  there is more HA, above it more  $A^-$ , and at  $pH = pK_a$  they are equal.

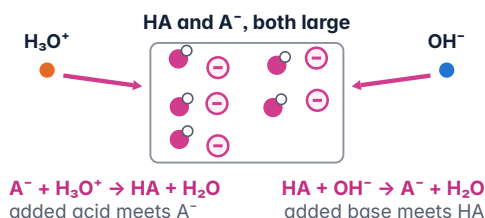
| $pH - pK_a$ | $[A^-] : [HA]$ | percent as $A^-$ |
|-------------|----------------|------------------|
| -1          | 1 : 10         | 9%               |
| 0           | 1 : 1          | 50%              |
| +1          | 10 : 1         | 91%              |

#### Not on the equation sheet, so learn it

$\frac{[A^-]}{[HA]} = 10^{pH - pK_a}$ , which is Henderson-Hasselbalch rearranged. An indicator is a weak acid whose two forms have different colors; it changes color across about  $pK_a \pm 1$ . Pick one whose range contains the equivalence pH: phenolphthalein (8.2–10) suits a weak acid with a strong base.

## 8.8 Properties of buffers

A **buffer** holds large amounts of both members of a conjugate pair: a weak acid and its conjugate base, or a weak base and its conjugate acid. HA uses up added  $\text{OH}^-$  and  $\text{A}^-$  uses up added  $\text{H}_3\text{O}^+$ , so a little added acid or base barely changes the pH.



| Mixture                                            | Buffer?                                                           |
|----------------------------------------------------|-------------------------------------------------------------------|
| $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ | yes                                                               |
| 1.0 mol HA + 0.5 mol NaOH                          | yes: 0.5 mol of each is left                                      |
| 1.0 mol HA + 1.0 mol NaOH                          | no: only $\text{A}^-$ is left                                     |
| $\text{HCl} + \text{NaCl}$                         | no: $\text{Cl}^-$ is too weak a base to take back an $\text{H}^+$ |

## Worked example

0.20 mol  $\text{NH}_3$  is mixed with 0.10 mol  $\text{HCl}$ . Is the result a buffer, and what is its pH? ( $\text{p}K_a$  of  $\text{NH}_4^+ = 9.26$ )

- $\text{HCl}$  reacts completely: 0.10 mol  $\text{NH}_3$  becomes  $\text{NH}_4^+$ , leaving 0.10 mol of each.

**Yes. Half the  $\text{NH}_3$  is neutralized, so  $[\text{NH}_3] = [\text{NH}_4^+]$  and  $\text{pH} = \text{p}K_a = 9.26$**

## How to earn the point

**Why does a buffer's pH barely change when a little acid is added?**

The added  $\text{H}_3\text{O}^+$  reacts with  $\text{A}^-$ :  $\text{A}^- + \text{H}_3\text{O}^+ \rightarrow \text{HA} + \text{H}_2\text{O}$ . The added  $\text{H}_3\text{O}^+$  is used up, so the ratio  $[\text{A}^-]/[\text{HA}]$ , and with it the pH, changes only slightly.

## Common mistake

**"A buffer keeps the pH at 7," or "keeps it constant."** A buffer sits near its own  $\text{p}K_a$ : acetate buffers near pH 4.7, ammonia buffers near 9.3. It resists change only until one partner runs out; after that the pH swings like any other solution's.

## 8.9 Henderson-Hasselbalch equation

In a buffer, the pH is the  $\text{p}K_a$  adjusted by the ratio of base to acid. Both partners share one volume, so moles work in the ratio. A useful buffer has a  $\text{p}K_a$  within 1 of the pH you want.

## On the equation sheet

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

## Worked example

1.00 L holds 0.150 mol acetic acid and 0.250 mol sodium acetate ( $K_a = 1.8 \times 10^{-5}$ ). Find the pH.

- $\text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.745$
- $\text{pH} = 4.745 + \log \frac{0.250}{0.150} = 4.97$

**pH 4.97, above the  $\text{p}K_a$  because there is more  $\text{A}^-$  than HA**

## Worked example

Equal moles of methylamine,  $\text{CH}_3\text{NH}_2$  ( $K_b = 4.4 \times 10^{-4}$ ), and  $\text{CH}_3\text{NH}_3\text{Cl}$  make a buffer. Find its pH.

- $\text{p}K_b = 3.36$ , so the conjugate acid's  $\text{p}K_a$  is 10.64
- The ratio is 1 : 1, so  $\text{pH} = \text{p}K_a$

**pH 10.64, and halving both amounts keeps the 1 : 1 ratio and the pH**

## Worked example

A particle drawing from a weak-acid titration ( $\text{p}K_a$  3.9) shows 4 HA and 2  $\text{A}^-$ . Where on the curve is it?

- $\text{pH} = 3.9 + \log \frac{2}{4} = 3.6$ , below the  $\text{p}K_a$

**More HA than  $\text{A}^-$  means less than half the acid has been neutralized, so the point comes before half-equivalence.**

## Common mistake

**Using Henderson-Hasselbalch where one partner is missing.** At the start or equivalence, one partner is present only through ionization or hydrolysis. You cannot use the initial mole ratio as the equilibrium ratio; solve with  $K_a$  or  $K_b$  first.

## 8.10 Buffer capacity

The ratio sets a buffer's pH; the amounts set its **capacity**, how much acid or base it can absorb before the pH changes a lot. Capacity runs out when one partner is used up, so more HA protects against added base and more  $\text{A}^-$  against added acid. Diluting a buffer keeps its ratio, so its pH barely moves, but each liter then holds less HA and  $\text{A}^-$ , so capacity per liter drops. The exam asks about capacity in words; it won't ask you to calculate how a buffer's pH changes when acid or base is added.



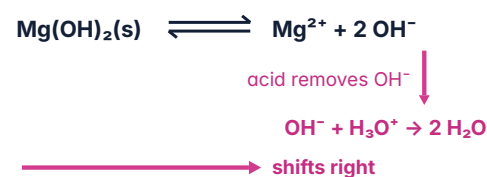
Same 1 : 1 ratio, so the same pH; B can absorb three times as much acid or base.

## Common mistake

**"The more concentrated buffer has the lower pH."** 1.0 L of 0.10 M HA and 0.10 M  $\text{A}^-$  and 1.0 L of 0.50 M of each both have  $\text{pH} = \text{p}K_a$ . The second exhausts its base at 0.50 mol acid, not 0.10 mol.

## 8.11 pH and solubility

A salt dissolves more in acid when its anion is a base:  $\text{OH}^-$  itself, or the conjugate base of a weak acid such as  $\text{CO}_3^{2-}$  or  $\text{F}^-$ . The acid removes that ion,  $Q$  drops below  $K_{sp}$ , and more solid dissolves.  $\text{AgCl}$ 's anion barely reacts with acid;  $\text{HCl}$  lowers solubility by adding  $\text{Cl}^-$ .



less  $\text{OH}^-$  lowers  $Q$ , so more  $\text{Mg(OH)}_2$  dissolves until equilibrium returns

## How to earn the point

**Why does adding  $\text{HNO}_3$  to saturated  $\text{Mg(OH)}_2$  dissolve more solid?**

The  $\text{H}_3\text{O}^+$  from  $\text{HNO}_3$  reacts with  $\text{OH}^-$ , lowering  $[\text{OH}^-]$ . Now  $Q < K_{sp}$ , so more  $\text{Mg(OH)}_2$  dissolves until equilibrium is reestablished.

## Common mistake

**"The acid changes  $K_{sp}$ ."** Only temperature does. The acid removes a dissolved ion and the equilibrium shifts to replace it, so the solubility changes while  $K_{sp}$  stays the same.

## Unit 9 Thermodynamics and Electrochemistry

Entropy measures how spread out matter and energy are.  $\Delta G^\circ$  combines it with  $\Delta H^\circ$  to tell whether a reaction is favored, and it ties that result to  $K$  and to the voltage of a cell.

Unit 1 7–9%   Unit 2 7–9%   Unit 3 18–22%   Unit 4 7–9%   Unit 5 7–9%   Unit 6 7–9%   Unit 7 7–9%   Unit 8 11–15%   Unit 9 7–9%

Unit 9 is 7–9% of the multiple-choice section. Entropy, favorability and electrochemical cells turn up in the free response almost every year, for example explaining the sign of  $\Delta S^\circ$ , finding the temperatures at which a reaction is favored, or working with a galvanic or electrolytic cell.

### 9.1 Introduction to entropy

**Entropy**,  $S$ , measures how spread out matter and energy are: the more ways the particles and their energy can be arranged, the higher the entropy. For one substance, gas has far more entropy than liquid, and liquid more than solid.

| Process, and why                                                                                                  | $\Delta S$ |
|-------------------------------------------------------------------------------------------------------------------|------------|
| Ice melts: the molecules start to slide past each other                                                           | +          |
| $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ : 0 $\rightarrow$ 1 mol of gas | +          |
| $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ : 3 $\rightarrow$ 2 mol of gas | –          |
| A gas spreads into a bigger flask: more room at the same temperature                                              | +          |
| A substance is heated: its particle energies spread wider                                                         | +          |

#### How to earn the point

Why is  $\Delta S^\circ$  negative for  $\text{P}_4(\text{s}) + 5\text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$ ?

Five moles of gaseous  $\text{O}_2$  end up in a solid. Gas particles are far more dispersed than the particles of a solid, so the products have fewer possible arrangements.

#### Common mistake

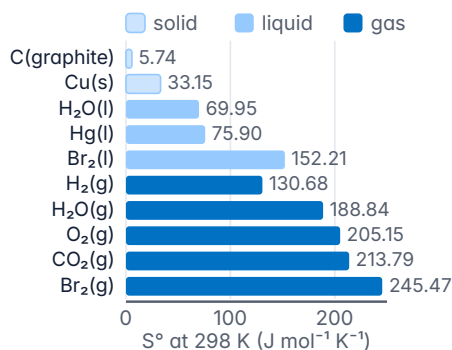
Writing "more disorder" and stopping.

That alone earns nothing. Name the particles and their phases: count the moles of *gas* on each side, because making or using gas almost always sets the sign. Counting all moles isn't enough: extra moles of solid add little entropy.

### 9.2 Absolute entropy and entropy change

Entropy has a true zero, a perfect crystal at 0 K, so every pure substance has a positive standard entropy  $S^\circ$  in  $\text{J mol}^{-1} \text{K}^{-1}$ . Unlike its  $\Delta H^\circ_f$ , an element's  $S^\circ$  is **not** zero. (Ions in water are measured against  $\text{H}^+(\text{aq}) = 0$ , so a few have negative values.)

### 9.2 Absolute entropy and entropy change, continued



Gas > liquid > solid for one substance; bigger molecules have more (liquid  $\text{Br}_2$  >  $\text{H}_2$  gas).

#### On the equation sheet

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

each  $S^\circ$  times its coefficient

#### Worked example

$S^\circ$ :  $\text{SO}_2(\text{g})$  248.22,  $\text{O}_2(\text{g})$  205.15,  $\text{SO}_3(\text{g})$  256.77  $\text{J mol}^{-1} \text{K}^{-1}$ . Find  $\Delta S^\circ$  for  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ .

- Predict: 3  $\rightarrow$  2 mol of gas, so  $\Delta S^\circ < 0$
- $2(256.77) - [2(248.22) + 205.15] = 513.54 - 701.59$

$$\Delta S^\circ = -188.05 \text{ J mol}^{-1} \text{K}^{-1}$$

#### Common mistake

Leaving out  $\text{O}_2$  "because it's an element."

Its  $S^\circ$  is 205.15, not zero, and leaving it out flips the sign.

### 9.3 Gibbs free energy and thermodynamic favorability

Under standard conditions, a reaction is **thermodynamically favored** when  $\Delta G^\circ < 0$ .  $\Delta G^\circ$  weighs  $\Delta H^\circ$  against  $T\Delta S^\circ$ , so the signs of  $\Delta H^\circ$  and  $\Delta S^\circ$  show when that happens.

#### On the equation sheet

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (T \text{ in kelvins})$$

$$\Delta G^\circ_{\text{reaction}} = \sum \Delta G^\circ_f \text{ products} - \sum \Delta G^\circ_f \text{ reactants}$$

### 9.3 Gibbs free energy and thermodynamic favorability, continued

#### Not on the equation sheet, so learn it

| $\Delta H^\circ$ | $\Delta S^\circ$ | Favored                  |
|------------------|------------------|--------------------------|
| –                | +                | at every temperature     |
| +                | –                | at no temperature        |
| +                | +                | only at high temperature |
| –                | –                | only at low temperature  |

The last two rows switch at  $T = \Delta H^\circ \div \Delta S^\circ$  if  $\Delta H^\circ$  and  $\Delta S^\circ$  stay nearly constant.

#### Worked example

$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ :  $\Delta H^\circ = +178.3 \text{ kJ/mol}$ ,  $\Delta S^\circ = +160.6 \text{ J mol}^{-1} \text{K}^{-1}$ . Is it favored at 298 K? Above what temperature is it favored?

- $\Delta G^\circ = 178.3 - (298)(0.1606) = +130.4 \text{ kJ/mol}$ , with  $\Delta S^\circ$  in kJ
- $T = 178.3 \div 0.1606 = 1110 \text{ K}$

Not favored at 298 K; favored above about 1110 K

#### How to earn the point

Is  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$  driven by enthalpy or by entropy?

$\Delta H^\circ < 0$ , so the enthalpy term favors it;  $\Delta S^\circ < 0$ , so  $-T\Delta S^\circ > 0$  works against it.  $\Delta G^\circ < 0$  at 298 K, so the reaction is driven by enthalpy.

#### Common mistake

**Mixing kJ and J.** For the  $\text{NH}_3$  reaction,  $\Delta H^\circ = -91.8 \text{ kJ/mol}$  and  $\Delta S^\circ = -198.1 \text{ J mol}^{-1} \text{K}^{-1}$ . Write  $\Delta S^\circ$  as  $-0.1981 \text{ kJ mol}^{-1} \text{K}^{-1}$  before you subtract:  $\Delta G^\circ$  at 298 K is  $-32.8 \text{ kJ/mol}$ , not  $+58,900$ .

### 9.4 Thermodynamic and kinetic control

$\Delta G^\circ$  gives standard-state favorability; the barrier helps set the rate. A favored reaction stuck behind a high barrier, like  $\text{H}_2$  mixed with  $\text{O}_2$ , is under **kinetic control**.

### 9.4 Thermodynamic and kinetic control, continued

#### How to earn the point

Why don't mixed  $\text{H}_2$  and  $\text{O}_2$  react, even though  $\Delta G^\circ < 0$ ?

The reaction is favored, but its activation energy is so large that few collisions at 298 K have enough energy, so the rate is too slow to see.

### 9.5 Free energy and equilibrium

A negative  $\Delta G^\circ$  means  $K > 1$ , so products are favored at equilibrium; a positive  $\Delta G^\circ$  means  $K < 1$ . At 298 K, every 5.7 kJ/mol of  $\Delta G^\circ$  changes  $K$  by a factor of 10.

#### On the equation sheet

$$\Delta G^\circ = -RT \ln K, \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

#### Worked example

$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$  has  $\Delta G^\circ = -32.8 \text{ kJ/mol}$  at 298 K. Find  $K$ .

- Use joules to match  $R$ :  $\Delta G^\circ = -32,800 \text{ J/mol}$
- $-\Delta G^\circ/RT = 32,800 \div [(8.314)(298)] = 13.24$ , so  $K = e^{13.24}$

$K = 5.6 \times 10^5$ , so the equilibrium mixture is mostly  $\text{NH}_3$ .

#### Common mistake

**Leaving  $\Delta G^\circ$  in kJ.** Using 32.8 instead of 32,800 J makes the exponent 0.0132, so  $K$  comes out 1.01 instead of  $5.6 \times 10^5$ . Use  $\ln$  and  $e^x$ , not  $\log$  and  $10^x$ .

### 9.6 Free energy of dissolution

Dissolving breaks solute-solute and solvent-solvent attractions and forms solute-solvent ones.  $\Delta H^\circ$  and  $-\Delta S^\circ$  are often similar in size and opposite in sign, so you need the numbers to know whether a salt dissolves well.

| kJ/mol                   | $\Delta H^\circ$ | $-\Delta S^\circ$ | $\Delta G^\circ$ |
|--------------------------|------------------|-------------------|------------------|
| $\text{NH}_4\text{NO}_3$ | +25.7            | -32.4             | -6.7             |
| $\text{CaCl}_2$          | -81.3            | +13.3             | -68.0            |
| $\text{AgCl}$            | +65.4            | -9.8              | +55.6            |

$\text{NH}_4\text{NO}_3$  dissolves even though dissolving it is endothermic, because  $-\Delta S^\circ$  outweighs  $\Delta H^\circ$ .  $\text{CaCl}_2$  dissolves even though  $\Delta S^\circ < 0$  (its ions order the water), because  $\Delta H^\circ$  is so negative.  $\text{AgCl}$ 's positive  $\Delta G^\circ$  matches its tiny  $K_{sp}$ .

### 9.7 Coupled reactions

An unfavored process runs only while something keeps paying for it: electricity, light, or a favored reaction that shares a species with it. Add the equations so the shared species cancels; their  $\Delta G^\circ$  values add.

#### Worked example

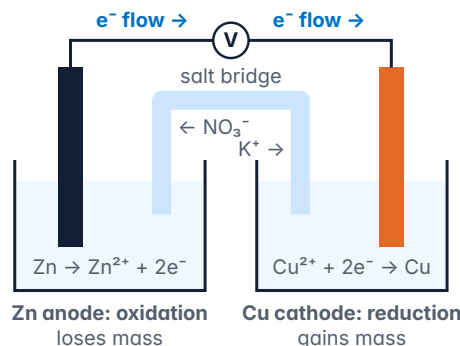
Is  $\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2 \text{Cu} + \text{SO}_2$  favored? Use  $\text{Cu}_2\text{S} \rightarrow 2 \text{Cu} + \text{S}$ ,  $\Delta G^\circ = +86.2 \text{ kJ}$ , and  $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$ ,  $\Delta G^\circ = -300.1 \text{ kJ}$ .

- The S cancels:  $+86.2 + (-300.1)$

$\Delta G^\circ = -213.9 \text{ kJ}$ , so it is favored.

### 9.8 Galvanic (voltaic) and electrolytic cells

Every cell has **oxidation at the anode** and **reduction at the cathode**. In a **galvanic** cell a favored reaction pushes electrons through the wire, while ions in the salt bridge keep each side neutral. An **electrolytic** cell needs a power supply running the whole time to drive an unfavored reaction. The exam never asks you to label an electrode + or -.



#### Not on the equation sheet, so learn it

Electrons move only through the wire, never through the salt bridge. In the bridge, anions move toward the anode and cations toward the cathode.

### 9.9 Cell potential and free energy

#### On the equation sheet

$$\Delta G^\circ = -nFE^\circ, \quad F = 96,485 \text{ C per mol } e^-, \quad 1 \text{ V} = 1 \text{ J/C}$$

#### Not on the equation sheet, so learn it

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ , both as reduction potentials. A positive  $E^\circ$  means  $\Delta G^\circ < 0$ , so the cell is galvanic under standard conditions.

### 9.9 Cell potential and free energy, continued

#### Worked example

Find  $E^\circ$  and  $\Delta G^\circ$  for  $\text{Cu} + 2 \text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2 \text{Ag}$ . Reduction potentials:  $\text{Ag}^+ + e^- \rightarrow \text{Ag}$ ,  $+0.80 \text{ V}$ ;  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ ,  $+0.34 \text{ V}$ .

- $\text{Ag}^+$  is reduced, so silver is the cathode:  $E^\circ = 0.80 - 0.34 = +0.46 \text{ V}$
- Each Cu gives up two electrons, so  $n = 2$ :  $\Delta G^\circ = -(2)(96,485)(0.46) = -8.9 \times 10^4 \text{ J}$ . Don't double  $E^\circ$  for the 2 in  $2 \text{Ag}^+$ .

$E^\circ = +0.46 \text{ V}$  and  $\Delta G^\circ = -89 \text{ kJ/mol}$ , so the reaction is favored.

### 9.10 Cell potential under nonstandard conditions

#### On the equation sheet

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

A working cell's voltage is its push toward equilibrium. Compare  $Q$  with 1: when  $Q < 1$ ,  $E$  is above  $E^\circ$ ; when  $Q > 1$ ,  $E$  is below  $E^\circ$ . At equilibrium,  $Q = K$  and  $E = 0$ .

#### How to earn the point

How does  $E$  of a zinc-copper cell change when  $\text{Cu}^{2+}$  is added?

$Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$  falls, so the cell is farther from equilibrium and  $E$  rises.

### 9.11 Electrolysis and Faraday's law

#### On the equation sheet

$$I = q \div t \text{ (amperes, coulombs, seconds)}$$

Divide the charge by 96,485 for moles of electrons, then by the electrons each ion takes for moles of metal.

#### Worked example

How long must 2.0 A run to plate 2.8 g of Rh (102.9 g/mol) from  $\text{Rh}^{3+}$ ?

- $0.0272 \text{ mol Rh}$  ( $2.8 \div 102.9$ )  $\times 3$  electrons each =  $0.0816 \text{ mol } e^-$
- Charge =  $0.0816 \times 96,485 = 7.88 \times 10^3 \text{ C}$ ; time = charge  $\div 2.0 \text{ A}$

$3.9 \times 10^3 \text{ s}$ , a little over an hour

#### Common mistake

**Treating moles of Rh as moles of electrons.** Each  $\text{Rh}^{3+}$  needs 3 electrons; without the  $\times 3$  the time comes out  $1.3 \times 10^3 \text{ s}$ , a third of the true value.

## The free-response questions

Seven questions in 105 minutes: three long questions worth 10 points each and four short ones worth 4 points each. Most questions mix units: they start from one experiment or data set and ask parts from several units, so a titration question can also want a net ionic equation, a particle drawing and an error analysis.

### What the question's verb asks for

|                              |                                                                                                                            |
|------------------------------|----------------------------------------------------------------------------------------------------------------------------|
| <b>Calculate</b>             | The setup with numbers substituted, then the answer with units and significant figures.                                    |
| <b>Determine</b>             | An answer reached by reasoning or a calculation. Briefly show the reasoning or math you used.                              |
| <b>Estimate</b>              | A rough value, or only a comparison (greater, less, equal) or a sign, read from the data.                                  |
| <b>Explain</b>               | How or why it happens. The cause has to be in the sentence: "because the outer electrons are farther from the nucleus ..." |
| <b>Justify</b>               | The evidence, then how that evidence supports the claim.                                                                   |
| <b>Identify</b>              | Just name it. No reason is needed, and a wrong extra reason can cost the point.                                            |
| <b>Describe</b>              | The features that matter, such as the glassware and the volumes in a procedure.                                            |
| <b>Make a claim, predict</b> | Your answer first, then the evidence for it.                                                                               |
| <b>Draw, represent</b>       | A labeled particle drawing, Lewis diagram, equation or graph that agrees with your earlier answers.                        |

### Say it precisely

| Write                                                      | Instead of                        |
|------------------------------------------------------------|-----------------------------------|
| "the attractions between the molecules are overcome"       | "the bonds break when it boils"   |
| "more occupied electron shells"                            | "more orbitals" or "it's heavier" |
| "the distance between the ion centers"                     | "the radius"                      |
| "the acid ionizes"                                         | "the acid dissolves"              |
| "the concentrations are constant"                          | "the concentrations are equal"    |
| "a greater fraction of collisions have energy $\geq E_a$ " | "the molecules move faster"       |
| "gas particles are far more spread out"                    | "more disorder"                   |

### A part that asks you to ...

### What earns the points

|                                                                      |                                                                                                                                                                                                                                                                                                    |
|----------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Calculate through moles:</b> grams, gas, solution, heat or charge | Change what you're given into moles, use the coefficient ratio once, then change moles into what is asked, with a unit on every number.                                                                                                                                                            |
| <b>Explain why one substance differs from another</b>                | Name the particles and the force or distance involved, and compare both substances: "Ethanol and dimethyl ether both have dispersion and dipole-dipole forces, but only ethanol's O-H can hydrogen-bond, and hydrogen bonds are stronger, so more energy is needed to separate ethanol molecules." |
| <b>Draw particles, a Lewis diagram or a cell</b>                     | Count first: valence electrons, ions in the formula's ratio, or particles per volume. Show every bond, lone pair and charge. Point water's oxygen end toward cations. In a cell, electrons move through the wire and ions through the salt bridge.                                                 |
| <b>Read or sketch a graph</b>                                        | Read the axes and units before the shape. To sketch a curve after a change, keep everything the change doesn't affect: a titrant twice as concentrated halves the equivalence volume but leaves the starting pH unchanged.                                                                         |
| <b>Describe a lab procedure</b>                                      | Name the glassware and what you measure: "To make 0.340 M NaCl, weigh 1.99 g, dissolve it in some water in a 100.0 mL volumetric flask, then add water to the mark." "Add 100 mL of water" loses the point.                                                                                        |
| <b>Say how an error changes the result</b>                           | Follow the error through the math in one chain: say what physically went wrong, how it changed the measured value, and how that changed the calculated result. "Human error" earns nothing.                                                                                                        |
| <b>Find a pH or an equilibrium amount</b>                            | Write the reaction. Let any strong acid or base react completely, in moles, then pick the model from what is left: excess strong species, a weak acid or base, a buffer, or an ICE table with K.                                                                                                   |
| <b>Say which way a reaction goes, or whether it is favored</b>       | For a shift, name what changed, its effect on Q or on K, and the direction. For favorability, use the signs of both $\Delta H^\circ$ and $\Delta S^\circ$ in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , and remember that favored doesn't mean fast.                                    |

### Worked example

A student overfills a 25.0 mL volumetric flask while diluting a colored sample, then uses a calibration line to find the original concentration. Is the result too high, too low or unchanged?

- Too much water makes the diluted solution less concentrated, so its absorbance is lower.
- A lower absorbance gives a lower diluted concentration. The calculation still assumes exactly 25.0 mL, so the original concentration comes out lower too.

Too low

### Worked example

Show the setup: how much heat is released when 0.250 mol of  $H_2$  burns?  
 $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$ ,  $\Delta H = -483.6 \text{ kJ/mol}$  of reaction.

$$1 \quad 0.250 \text{ mol } H_2 \times \frac{483.6 \text{ kJ}}{2 \text{ mol } H_2}$$

60.5 kJ released ( $q = -60.5 \text{ kJ}$ )

### "Do you agree or disagree?"

Start with "I agree" or "I disagree," then give the evidence. A correct reason under the wrong verdict earns nothing, and so does a verdict with no reason.