Chemistry Units 3 & 4

Chapter 5 — Rates of reaction

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Chapter 5 Rates of reaction — 5A Collision theory and activation energy

Theory

The **rate** of a chemical reaction measures how quickly reactants are consumed and products are formed. Some reactions, such as an explosion, are over in a fraction of a second; others, such as the rusting of iron, take years. To understand why reactions occur at all — and why their rates differ so widely — chemists picture reactant particles as being in constant, rapid motion and colliding with one another. This picture is the basis of **collision theory**.

Collision theory. For a reaction to occur, reactant particles must first **collide**. In a mixture of gases or a solution, particles collide with one another billions of times each second, yet only a tiny proportion of those collisions actually results in a reaction. Collision theory explains this by requiring that a collision meet **two conditions at the same time** for it to lead to products:

- the colliding particles must together possess at least a certain minimum amount of energy, the **activation energy** (E_a), and
- the particles must collide with the **correct orientation** — that is, aligned so that the atoms that must bond are brought together.

A collision that satisfies **both** conditions is a **successful** (or *effective*) collision and leads to reaction; a collision that fails either condition is unsuccessful, and the particles simply rebound unchanged. Because most collisions fail at least one of the two conditions, only a small fraction of all collisions are successful.

The energy condition. Reactant particles move with a wide range of kinetic energies. When two particles collide, some of their kinetic energy is momentarily converted into potential energy that begins to stretch and break the bonds within the reactants. Only a collision in which the combined kinetic energy is **at least** E_a provides enough energy to break those bonds and push the reactants over the energy barrier to form products. A collision with less than E_a is too gentle: no bonds break, and the particles separate unchanged.

The orientation condition. Even a collision with sufficient energy will fail if the particles are wrongly aligned. Consider the reaction

$$\mathrm{CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)}$$

An oxygen atom must transfer from $\mathrm{NO_2}$ to CO, so the **carbon** atom of CO must strike one of the **oxygen** atoms of $\mathrm{NO_2}$. A collision in which the oxygen end of CO leads, or in which the carbon meets the nitrogen of $\mathrm{NO_2}$, is incorrectly oriented and cannot react, however energetic it is. For collisions between two single atoms orientation does not matter, but for molecules only a fraction of the possible orientations are productive.

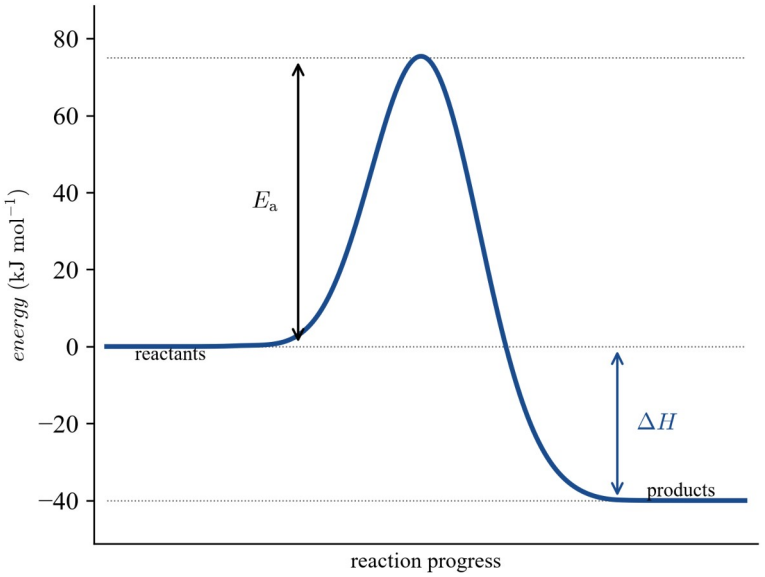
Activation energy. The **activation energy** E_a is the **minimum energy** that colliding particles must possess for a reaction to occur; it is the height of the energy barrier separating reactants from products. Surmounting the barrier requires the particles to pass through a high-energy, unstable arrangement called the **transition state** (or *activated complex*), in which the old bonds are partly broken and the new bonds are partly formed. A reaction with a **low** E_a has a barrier that is easily cleared, so a large fraction of collisions succeed; a reaction with a **high** E_a has few collisions energetic enough to react. The activation energy is always positive and is a property of the reaction pathway: it is **not** changed by altering the temperature or the concentration. (A catalyst provides an alternative pathway of **lower** E_a — this is examined in 5B.)

Energy profile diagrams. An **energy profile** (reaction-coordinate diagram) plots the potential energy of the reacting system against the progress of the reaction. The reactants sit at one energy level and the products at another, separated by a peak at the transition state. Three quantities can be read from it:

- the **forward activation energy** $E_a(\mathrm{fwd})$ = the height from the **reactant** level up to the peak;
- the **enthalpy change** ΔH = product level − reactant level ($\Delta H < 0$ = **exothermic**, products lower; $\Delta H > 0$ = **endothermic**, products higher);
- the **reverse activation energy** $E_a(\mathrm{rev})$ = the height from the **product** level up to the same peak.

Because both activation energies are measured up to the same peak, they are related to the enthalpy change by

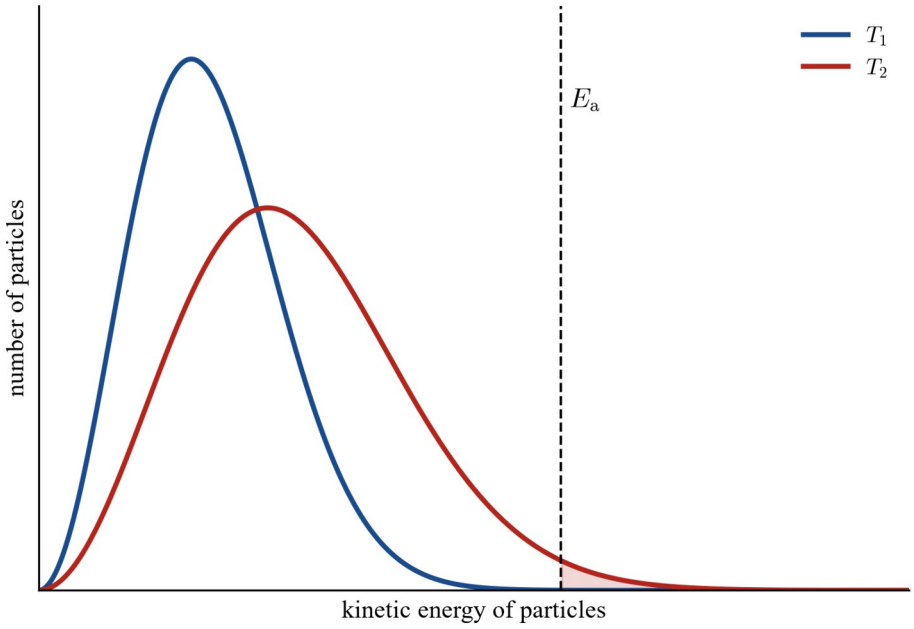
$$E_a(\text{rev}) = E_a(\text{fwd}) - \Delta H$$



The profile above is for an **exothermic** reaction. Taking the reactant level as the zero of energy, the barrier is $E_a(\text{fwd}) = 75\ \text{kJ mol}^{-1}$ and the products lie $40\ \text{kJ mol}^{-1}$ below the reactants, so $\Delta H = -40\ \text{kJ mol}^{-1}$ and $E_a(\text{rev}) = 75 - (-40) = 115\ \text{kJ mol}^{-1}$. For an exothermic reaction the reverse barrier is always the larger of the two.

The Maxwell–Boltzmann distribution. At any given temperature the particles in a sample do not all move with the same energy; their kinetic energies are spread over a wide range described by the **Maxwell–Boltzmann distribution**. Plotting the number of particles against kinetic energy gives a curve that starts at the origin, rises to a peak at the **most probable** energy, and then falls away with a long **tail** at high energy. The **total area** under the curve represents the total number of particles.

Only particles with energy $\geq E_a$ are able to react when they collide, so the fraction of particles that **could** react is the area under the curve **to the right of the E_a line**. Because E_a lies well out along the energy axis, this area is small — one reason why only a small proportion of collisions succeed.

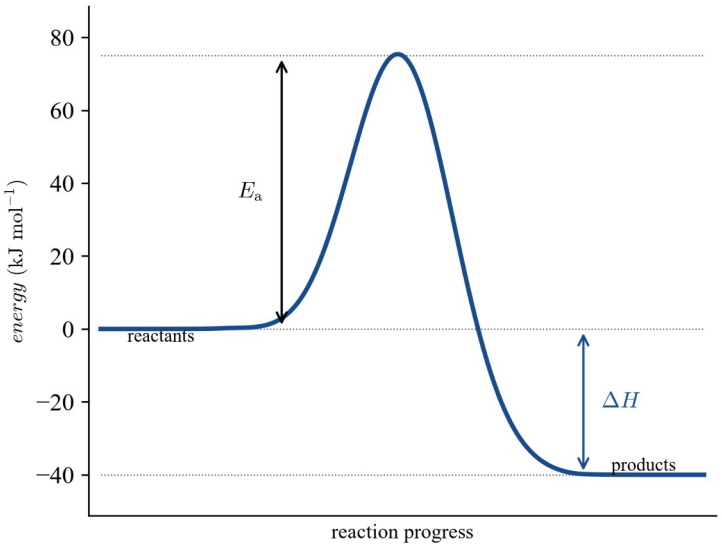


Raising the temperature gives the particles, on average, more kinetic energy. The whole distribution **broadens and shifts to higher energy**; the peak becomes lower and moves to the right, while the total area (the number of particles) stays the same. Critically, the **area beyond E_a grows**: a disproportionately larger fraction of particles now have

$E \geq E_a$. The curve above shows a lower temperature T_1 and a higher temperature T_2; the shaded region is the fraction with $E \geq E_a$ at T_2, which is clearly larger than the corresponding fraction at T_1. This growing high-energy fraction, together with slightly more frequent collisions, is why reactions proceed faster at higher temperature. Temperature is only one of several factors — temperature, concentration, gas pressure, surface area and catalysts — whose systematic effects on rate are treated in 5B.

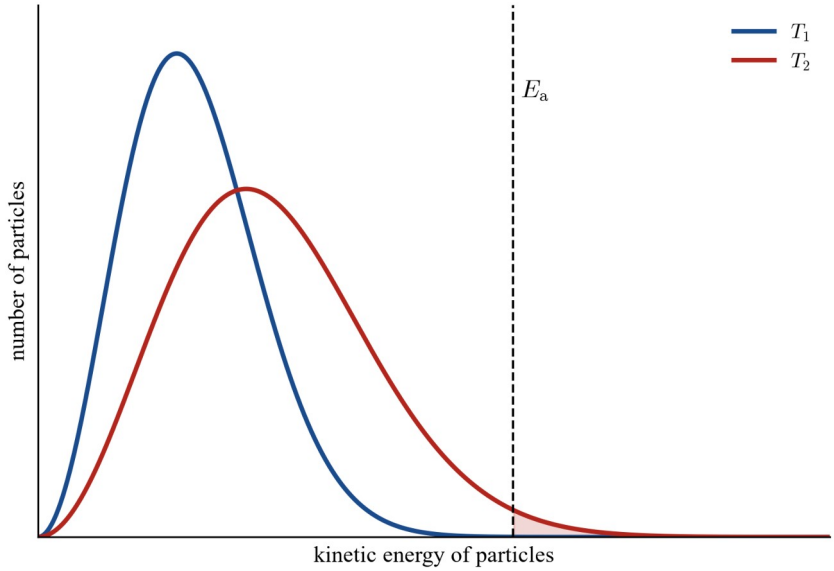
Worked examples

Worked Example 1 — The energy profile below is for a gas-phase reaction. The reactant level is taken as the zero of energy; the transition state lies at $75\ \text{kJ mol}^{-1}$ and the products at $-40\ \text{kJ mol}^{-1}$. Determine the forward activation energy, the enthalpy change (and whether the reaction is exothermic or endothermic), and the reverse activation energy.



Working	Comment
$E_a(\text{fwd}) = 75 - 0 = 75\ \text{kJ mol}^{-1}$	The forward activation energy is the height from the reactant level (0) up to the peak.
$\Delta H = (-40) - 0 = -40\ \text{kJ mol}^{-1}$	Enthalpy change = product level − reactant level.
exothermic	$\Delta H < 0$: the products lie below the reactants, so energy is released.
$E_a(\text{rev}) = E_a(\text{fwd}) - \Delta H = 75 - (-40) = 115\ \text{kJ mol}^{-1}$	Height from the product level up to the same peak; the reverse barrier is larger for an exothermic reaction.

Worked Example 2 — The Maxwell–Boltzmann distribution below shows the particle energies of a reaction mixture at two temperatures, T_1 and T_2 (with $T_2 > T_1$), and the activation energy is marked. Use the distribution to explain what the shaded area represents, why only a small fraction of collisions are successful, and what happens to that fraction when the temperature is raised from T_1 to T_2.



Working	Comment
The shaded area is the region under the curve to the right of the E_a line.	It represents the **fraction of particles with** $E \geq E_a$ — those energetic enough to react on collision.
E_a lies far along the energy axis, so only a small tail of the curve extends beyond it.	Most particles have less than E_a; their collisions are too gentle to break bonds, so only a small fraction of collisions are successful.
At T_2 the whole curve is lower, broader and shifted to higher energy, but encloses the same total area.	Raising the temperature increases the average kinetic energy; the number of particles is unchanged, so the peak falls as the spread widens.
The area beyond E_a is larger at T_2 than at T_1.	A greater fraction of particles now have $E \geq E_a$, so a greater fraction of collisions succeeds and the reaction is faster.

Worked Example 3 — In a mixture of two reactant gases at room temperature, each particle undergoes billions of collisions every second, yet the reaction proceeds only slowly. Explain, using collision theory, why the reaction is slow despite this enormous collision frequency.

For a collision to lead to reaction it must meet two conditions at once: the colliding particles must together have energy of at least the activation energy E_a, and they must be correctly oriented. At room temperature only a small fraction of particles have kinetic energy $\geq E_a$ — in the Maxwell–Boltzmann distribution the area beyond E_a is small — so the great majority of collisions are too gentle to break the reactant bonds and the particles simply rebound unchanged. Of the minority of collisions that are energetic enough, only those with the correct orientation actually react; the wrongly oriented ones also fail. The rate depends on the frequency of **successful** collisions, not on the total collision frequency, and successful collisions are only a tiny fraction of the total.

$\therefore$ a high collision frequency does not by itself make a reaction fast; this reaction is slow because only a small fraction of the many collisions satisfies both the energy and the orientation requirements.

Worked Example 4 — For the reaction $\mathrm{CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)}$ the forward activation energy is $60\ \mathrm{kJ\ mol^{-1}}$ and the reverse activation energy is $95\ \mathrm{kJ\ mol^{-1}}$. Determine ΔH for the forward reaction and state whether it is exothermic or endothermic. Then explain why, even at a temperature at which many collisions have energy greater than $60\ \mathrm{kJ\ mol^{-1}}$, a large number of these collisions still fail to produce products.

Rearranging $E_a(\mathrm{rev}) = E_a(\mathrm{fwd}) - \Delta H$ gives

$$\Delta H = E_a(\mathrm{fwd}) - E_a(\mathrm{rev}) = 60 - 95 = -35\ \mathrm{kJ\ mol^{-1}}$$

Since $\Delta H < 0$, the forward reaction is exothermic.

A collision succeeds only if **both** the energy and the orientation conditions are satisfied. Having energy $\geq E_a$ meets the first condition but not the second: in this reaction the carbon atom of CO must strike one of the oxygen atoms of $\mathrm{NO_2}$ so that an oxygen atom can transfer. Collisions in which CO approaches with its oxygen end leading, or in which the carbon meets the nitrogen of $\mathrm{NO_2}$, are wrongly oriented and rebound without reacting even though they are energetic enough.

$\therefore \Delta H = -35\ \mathrm{kJ\ mol^{-1}}$ (exothermic), and many energetic collisions still fail because they lack the correct orientation.

Practice questions

Question 1 — Collisions between reactant particles do not all lead to reaction.

a. State the two conditions that must both be met for a collision between reactant particles to result in a reaction.
b. Define the term *activation energy*.
c. Using your answers to part a, explain why not every collision between reactant particles leads to a reaction.

Question 2 — In a certain reaction the reactants have a potential energy of $20\ \mathrm{kJ\ mol^{-1}}$, the transition state has an energy of $90\ \mathrm{kJ\ mol^{-1}}$, and the products have an energy of $45\ \mathrm{kJ\ mol^{-1}}$.

a. Determine the forward activation energy.
b. Determine ΔH and state whether the reaction is exothermic or endothermic.
c. Determine the reverse activation energy.

Question 3 — A reaction mixture is represented by a Maxwell–Boltzmann distribution of particle energies, with the activation energy marked on the energy axis.

a. State what the area under the curve beyond the activation-energy line represents.
b. State how this area changes when the temperature of the mixture is increased.
c. Explain, in terms of the distribution of particle energies, why the area changes in this way.

Question 4 — Orientation is one of the two requirements for a successful collision.

a. Explain what is meant by the requirement that colliding particles have the *correct orientation*.
b. For the reaction $\mathrm{NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)}$, in which an oxygen atom transfers to NO, describe one collision orientation that would **not** lead to reaction.
c. State whether the orientation requirement is more important for a reaction between two molecules or between two single atoms, giving a reason.

Question 5 — A reaction has a forward activation energy of $45\ \mathrm{kJ\ mol^{-1}}$ and a reverse activation energy of $78\ \mathrm{kJ\ mol^{-1}}$.

a. Determine ΔH for the forward reaction.
b. State whether the forward reaction is exothermic or endothermic.
c. State whether the forward or the reverse reaction has the larger fraction of successful collisions at a given temperature, and justify your answer.

Question 6 — Consider a reaction mixture whose temperature is raised.

a. Using the Maxwell–Boltzmann distribution, explain why raising the temperature increases the fraction of collisions that are successful.
b. State one reason, other than insufficient energy, why a collision may fail to produce products.
c. State whether raising the temperature changes the activation energy of the reaction, and justify your answer.

Question 7 — State the central idea of collision theory, and the two requirements it places on a collision for that collision to result in a reaction.

Question 8 — For a reaction, the reactants lie at $50\,\text{kJ mol}^{-1}$, the transition state at $148\,\text{kJ mol}^{-1}$ and the products at $92\,\text{kJ mol}^{-1}$. Determine the forward activation energy, the reverse activation energy and ΔH, and state whether the reaction is exothermic or endothermic.

Question 9 — A forward reaction has an activation energy of $62\,\text{kJ mol}^{-1}$ and an enthalpy change of $-20\,\text{kJ mol}^{-1}$. Determine the activation energy of the reverse reaction.

Question 10 — Explain why, in a typical reaction mixture, only a small fraction of the collisions between reactant particles lead to the formation of products. In your answer refer to both requirements for a successful collision and to the distribution of particle energies.

Question 11 — Sketch a Maxwell–Boltzmann distribution of particle energies for a reaction mixture at a lower temperature T_1 and a higher temperature T_2, marking the activation energy E_a on the energy axis. Use your sketch to explain what happens to the fraction of particles able to react as the temperature is raised from T_1 to T_2.

Question 12 — For the gas-phase reaction $\text{H}_2(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{HI}(\text{g}) + \text{HCl}(\text{g})$, explain, with reference to orientation, why some energetic collisions between H_2 and ICl molecules do not lead to reaction.

Question 13 — A reaction has a forward activation energy of $118\,\text{kJ mol}^{-1}$ and a reverse activation energy of $80\,\text{kJ mol}^{-1}$. Determine ΔH for the forward reaction and state whether it is exothermic or endothermic.

Question 14 — A Maxwell–Boltzmann distribution of particle kinetic energies is drawn for a reaction mixture at a single temperature, with the activation energy E_a marked well to the right of the peak. State what the **peak** of the curve represents and what the **total area** under the curve represents, and explain what the position of the E_a line shows about the proportion of the particles that are able to react.

Question 15 — Explain the difference between the activation energy of a reaction and its enthalpy change ΔH, and describe how each is shown on an energy profile diagram.

Question 16 — Two reactions, X and Y, have the same enthalpy change, but reaction X has a larger activation energy than reaction Y. At the same temperature, state which reaction has the larger fraction of successful collisions, and explain your answer with reference to the Maxwell–Boltzmann distribution.

Question 17 — An energy profile for reaction P shows the reactants at $40\,\text{kJ mol}^{-1}$, the transition state at $130\,\text{kJ mol}^{-1}$ and the products at $70\,\text{kJ mol}^{-1}$.

a. Determine the forward activation energy, the reverse activation energy and ΔH for reaction P.
b. A second reaction, Q, has the same reactant and product energies as P but a transition state at $110\,\text{kJ mol}^{-1}$. State, with a reason, which of P and Q proceeds faster at the same temperature.

Question 18 — Define *activation energy*, and use both an energy profile diagram and the Maxwell–Boltzmann distribution to explain the role that activation energy plays in determining whether a collision between reactant particles is successful.

Answers

1 a the colliding particles together have energy $\geq E_a$, **and** they collide with the correct orientation; b the minimum energy that colliding particles must possess for a reaction to occur; c a collision reacts only if it meets both conditions, and most collisions meet neither or only one. **2** a $70\ \text{kJ mol}^{-1}$; b $\Delta H = +25\ \text{kJ mol}^{-1}$ (endothermic); c $45\ \text{kJ mol}^{-1}$. **3** a the fraction of particles with $E \geq E_a$ (those able to react); b it increases; c raising T broadens and shifts the distribution to higher energy, enlarging the area beyond E_a. **4** a the particles must be aligned so that the atoms that must bond are brought together; b e.g. NO approaching with its oxygen end leading rather than its nitrogen, or NO striking the central oxygen of O_3 rather than a terminal oxygen — wrongly oriented, no reaction; c more important for molecules — single atoms have no orientation requirement. **5** a $\Delta H = -33\ \text{kJ mol}^{-1}$; b exothermic; c the forward reaction — it has the smaller E_a, so a larger fraction of collisions has $E \geq E_a$. **6** a raising T enlarges the fraction of particles with $E \geq E_a$ (larger area beyond E_a); b the collision has the wrong orientation; c no — E_a is fixed by the reaction pathway and is unchanged by temperature. **7** reactions occur when particles collide; a collision reacts only if the particles have combined energy $\geq E_a$ **and** collide with the correct orientation. **8** $E_a(\text{fwd}) = 98\ \text{kJ mol}^{-1}$; $E_a(\text{rev}) = 56\ \text{kJ mol}^{-1}$; $\Delta H = +42\ \text{kJ mol}^{-1}$ (endothermic). **9** $E_a(\text{rev}) = 82\ \text{kJ mol}^{-1}$. **10** model answer: energy condition (small area beyond E_a) + orientation condition; only collisions meeting both react. **11** sketch: at T_2 the curve is lower, broader and shifted right; the area beyond E_a (fraction able to react) is larger than at T_1. **12** H_2 must meet ICl broadside, with the H–H axis roughly parallel to the I–Cl bond, so that one hydrogen reaches the iodine and the other the chlorine; any other alignment — for example H_2 approaching end-on at one end of ICl — is wrongly oriented and fails even when energetic. **13** $\Delta H = +38\ \text{kJ mol}^{-1}$ (endothermic). **14** the peak = the most probable energy (the energy held by the greatest number of particles); the total area = the total number of particles in the sample; because E_a lies well to the right of the peak, only the small tail area beyond the line represents particles with $E \geq E_a$, so only a small proportion is able to react. **15** E_a = height of the barrier from the reactant level up to the peak; ΔH = product level − reactant level (the net vertical gap between reactants and products). **16** reaction Y — its smaller E_a lies further left on the energy axis, so a larger area of the distribution (fraction of particles) lies beyond it. **17** a $E_a(\text{fwd}) = 90\ \text{kJ mol}^{-1}$, $E_a(\text{rev}) = 60\ \text{kJ mol}^{-1}$, $\Delta H = +30\ \text{kJ mol}^{-1}$ (endothermic); b reaction Q — it has the lower activation energy, so a larger fraction of collisions succeeds. **18** model answer: E_a = minimum energy = barrier height on the profile; only particles in the tail beyond E_a can react, so E_a sets the fraction of collisions that are energetic enough.

Fully-worked solutions

Question 1 a. (1) The colliding particles must together possess at least the activation energy, E_a; and (2) they must collide with the correct orientation, so that the atoms that must bond are aligned. b. The activation energy is the **minimum** energy that colliding particles must have for a reaction to occur — the height of the energy barrier between reactants and products. c. A collision leads to reaction only when **both** conditions are met at once. Many collisions are too gentle (combined energy below E_a) and simply rebound; of the energetic ones, many are wrongly oriented and also fail. Only the collisions that are both sufficiently energetic and correctly oriented are successful, so most collisions do not lead to reaction.

Question 2 a. $E_a(\text{fwd}) = 90 - 20 = 70\ \text{kJ mol}^{-1}$ (transition state − reactant level). b. $\Delta H = 45 - 20 = +25\ \text{kJ mol}^{-1}$ (product level − reactant level). Since $\Delta H > 0$, the reaction is **endothermic**. c. $E_a(\text{rev}) = 90 - 45 = 45\ \text{kJ mol}^{-1}$ (transition state − product level). Check: $E_a(\text{rev}) = E_a(\text{fwd}) - \Delta H = 70 - 25 = 45\ \text{kJ mol}^{-1}$. ✓

Question 3 a. It represents the **fraction of particles whose kinetic energy is at least** E_a — the particles able to react when they collide. b. The area **increases**. c. Raising the temperature increases the average kinetic energy of the particles, so the whole distribution broadens and shifts towards higher energy (the peak falls and moves right, but the total area stays the same). Because the curve now extends further to the right, a disproportionately larger fraction of particles has $E \geq E_a$, so the area beyond the E_a line grows.

Question 4 a. The particles must approach one another so that the atoms which need to form new bonds are brought together (and the bonds that must break are suitably exposed). Only a fraction of the possible approach geometries

achieves this; the rest cannot react even if energetic. b. In $NO + O_3 \rightarrow NO_2 + O_2$, an oxygen atom must transfer from ozone to the **nitrogen** of NO. A collision in which the oxygen end of NO leads, or in which NO strikes the central oxygen of O_3 rather than a terminal oxygen, is wrongly oriented and rebounds without reacting. c. Orientation matters more for a reaction between two **molecules**. Molecules have distinct reactive sites, so only some alignments allow the correct atoms to meet; two single atoms are spherically symmetric and have no orientation requirement (every approach is equivalent).

Question 5 a. $\Delta H = E_a(\text{fwd}) - E_a(\text{rev}) = 45 - 78 = -33\ \text{kJ mol}^{-1}$. b. Since $\Delta H < 0$, the forward reaction is **exothermic**. c. The **forward** reaction has the smaller activation energy ($45 < 78\ \text{kJ mol}^{-1}$). A smaller E_a lies further to the left on the energy axis, so a larger fraction of particles has $E \geq E_a$; hence the forward reaction has the larger fraction of successful collisions at a given temperature.

Question 6 a. Raising the temperature broadens the distribution and shifts it to higher energy, so a larger fraction of particles has energy $\geq E_a$. The area under the curve beyond the E_a line therefore increases, meaning a larger fraction of collisions is energetic enough to be successful. b. The colliding particles may have the **wrong orientation**, so the atoms that must bond are not brought together. c. **No.** The activation energy is fixed by the reaction pathway (the height of its energy barrier); temperature changes the *energies of the particles*, not the barrier. Raising the temperature increases the fraction of particles that can clear the barrier, but the barrier height E_a itself is unchanged.

Question 7 Collision theory states that reactant particles must **collide** in order to react, and that a collision leads to products only when two conditions are met simultaneously: the colliding particles must together have kinetic energy of at least the activation energy E_a, and they must collide with the correct orientation. Collisions that fail either condition do not react.

Question 8 $E_a(\text{fwd}) = 148 - 50 = 98\ \text{kJ mol}^{-1}$. $E_a(\text{rev}) = 148 - 92 = 56\ \text{kJ mol}^{-1}$. $\Delta H = 92 - 50 = +42\ \text{kJ mol}^{-1}$. Since $\Delta H > 0$, the reaction is **endothermic**. (Check: $E_a(\text{fwd}) - E_a(\text{rev}) = 98 - 56 = 42 = \Delta H$. ✓)

Question 9 $E_a(\text{rev}) = E_a(\text{fwd}) - \Delta H = 62 - (-20) = 82\ \text{kJ mol}^{-1}$. (For an exothermic forward reaction the reverse barrier is larger than the forward barrier, as expected.)

Question 10 For a collision to lead to products it must satisfy both requirements at once: the colliding particles must have combined energy of at least E_a, and they must be correctly oriented. In the Maxwell–Boltzmann distribution of particle energies, E_a lies far out along the energy axis, so only a small tail of the curve — a small fraction of particles — has $E \geq E_a$; most collisions are therefore too gentle and rebound unchanged. Of the energetic collisions, only those with the correct orientation actually react, which removes a further proportion. The fraction of collisions that is both sufficiently energetic and correctly oriented is small, so only a small fraction of all collisions leads to the formation of products.

Question 11 The sketch shows two curves that both begin at the origin and enclose the **same total area**. The lower-temperature curve T_1 is taller with its peak further left; the higher-temperature curve T_2 is lower and broader, with its peak shifted to higher energy. A vertical line marks E_a well to the right of both peaks. As the temperature rises from T_1 to T_2, the area under the curve beyond the E_a line becomes larger, showing that a greater fraction of particles now has energy $\geq E_a$ and is able to react. (See the distribution in the Theory section.)

Question 12 A successful collision needs both sufficient energy and the correct orientation. In $H_2 + ICl \rightarrow HI + HCl$ one hydrogen atom bonds to the iodine while the other hydrogen bonds to the chlorine, so the two molecules must meet **broadside** — with the H–H axis roughly parallel to the I–Cl bond — bringing one hydrogen up to the iodine end and the other up to the chlorine end at the same time. A collision in which H_2 approaches **end-on**, its axis pointing at just one end of the ICl molecule, brings only one hydrogen within reach, so the atoms that must bond are not all brought together; such a collision is wrongly oriented and rebounds without reacting even if it carries more than enough energy.

Question 13 $\Delta H = E_a(\text{fwd}) - E_a(\text{rev}) = 118 - 80 = +38\ \text{kJ mol}^{-1}$. Since $\Delta H > 0$, the forward reaction is **endothermic** (the forward barrier is the larger of the two, as expected for an endothermic reaction).

Question 14 The curve plots the number of particles against kinetic energy, and at any temperature the particles are spread over a wide range of energies. The **peak** of the curve is the **most probable energy** — the kinetic energy possessed by the greatest number of particles. The **total area** under the curve represents the **total number of particles** in the sample. The activation energy is drawn as a vertical line, and only the particles lying to its **right**, with $E \geq E_a$, carry enough energy to react when they collide. Because E_a is marked well to the right of the peak, out in the high-energy tail, the area beyond the line is only a small part of the total area: only a small proportion of the particles is energetic enough to react, which is one reason why only a small fraction of collisions is successful. (Those energetic particles must also collide with the correct orientation.)

Question 15 The **activation energy** E_a is the minimum energy needed for a collision to react — the height of the barrier from the reactant level up to the peak (transition state) of the energy profile. The **enthalpy change** ΔH is the net energy difference between products and reactants — the vertical gap from the reactant level to the product level (products below reactants for an exothermic reaction, above for an endothermic one). E_a concerns the barrier that must be climbed to react; ΔH concerns only the start and end levels and says nothing about the barrier height.

Question 16 Reaction Y has the larger fraction of successful collisions. Both reactions are at the same temperature, so they share the same Maxwell–Boltzmann distribution of particle energies. Reaction Y has the smaller activation energy, so its E_a line sits further to the left on the energy axis; the area under the curve beyond that line is therefore larger. A larger area means a larger fraction of particles has $E \geq E_a$, so a larger fraction of collisions is energetic enough to succeed (the equal ΔH does not affect this — only E_a does).

Question 17 a. $E_a(\text{fwd}) = 130 - 40 = 90\ \text{kJ mol}^{-1}$; $E_a(\text{rev}) = 130 - 70 = 60\ \text{kJ mol}^{-1}$; $\Delta H = 70 - 40 = +30\ \text{kJ mol}^{-1}$ (endothermic). b. **Reaction Q** proceeds faster. Q has the same reactant and product levels as P but a lower transition state (110 versus $130\ \text{kJ mol}^{-1}$), so its forward activation energy is smaller ($E_a(\text{fwd,Q}) = 110 - 40 = 70\ \text{kJ mol}^{-1}$, compared with $90\ \text{kJ mol}^{-1}$ for P). A smaller E_a means a larger fraction of collisions has $E \geq E_a$, so Q has more successful collisions per second and reacts faster.

Question 18 The activation energy E_a is the minimum energy that colliding particles must possess for a reaction to occur. On an **energy profile diagram** it appears as the height of the barrier from the reactant level up to the peak (the transition state); to react, the reactants must gain enough energy on collision to reach this peak. On a **Maxwell–Boltzmann distribution** of particle energies, E_a is a vertical line, and only the particles in the tail to its right — those with $E \geq E_a$ — carry enough energy to react. The size of this high-energy fraction, set by where E_a falls, determines what proportion of collisions is energetic enough to be successful: a high E_a leaves only a tiny fraction beyond the line and a slow reaction, while a low E_a leaves a larger fraction and a faster reaction. (Energy alone is not sufficient — a successful collision must also have the correct orientation.)

Chapter 5 Rates of reaction — 5B Factors affecting reaction rate

Theory

The **rate** of a chemical reaction is a measure of how quickly reactants are consumed and products are formed. It can be followed by measuring any property that changes as the reaction proceeds — the volume of gas released, the mass lost as a gas escapes, a change in colour, or the concentration of a reactant or product — and is found from the **gradient** of the resulting graph plotted against time. The rate is usually greatest at the very start, when reactant concentrations are highest, and falls towards zero as the reactants are used up.

Collision theory (the model from 5A). Reactant particles can only react when they **collide**. A collision leads to reaction — a **successful** (or *effective*) collision — only if it satisfies two conditions at once: the colliding particles must have a combined kinetic energy of at least the **activation energy** E_a (the minimum energy needed to break the existing bonds and begin forming new ones), **and** they must collide with the correct **orientation**, so that the reacting parts of the particles come together. The rate of a reaction therefore depends on two things: the **frequency** of collisions (how many occur each second) and the **success** of those collisions (the fraction that have enough energy and the right orientation). Anything that increases either the frequency or the success of collisions increases the rate.

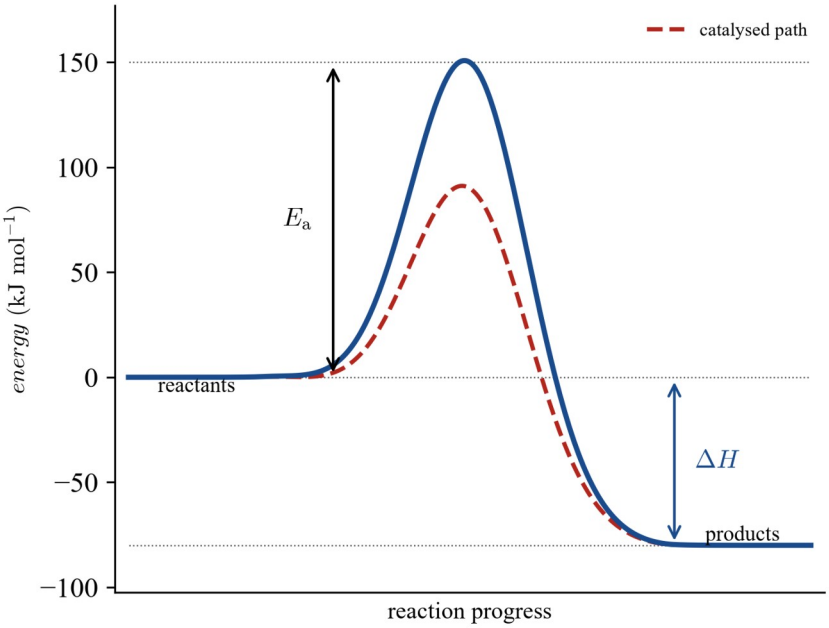
Temperature. Raising the temperature increases the average kinetic energy of the particles. This has two effects. First, faster particles collide more often, so the collision **frequency** rises. Second, and more importantly, a much larger **proportion** of the particles now have energy greater than E_a: on a Maxwell–Boltzmann distribution the curve broadens and shifts to higher energy, so the area beyond the E_a line — the fraction of particles able to react — grows steeply. Because the success fraction rises far more sharply than the collision frequency, the increase in the fraction of successful collisions is the **dominant** reason a reaction speeds up when it is heated.

Concentration. Increasing the concentration of a reactant in solution packs more reactant particles into the same volume. Collisions between reactant particles then occur **more frequently**, so the number of successful collisions each second rises and the rate increases. Concentration changes the collision *frequency* only; it does not change the fraction of collisions that have enough energy.

Gas pressure. For a reaction involving gases, increasing the pressure — by pushing the same amount of gas into a smaller volume, or by pumping in more gas — increases the number of gas particles per unit volume. This is the gaseous equivalent of increasing concentration: the particles collide **more frequently** and the rate increases.

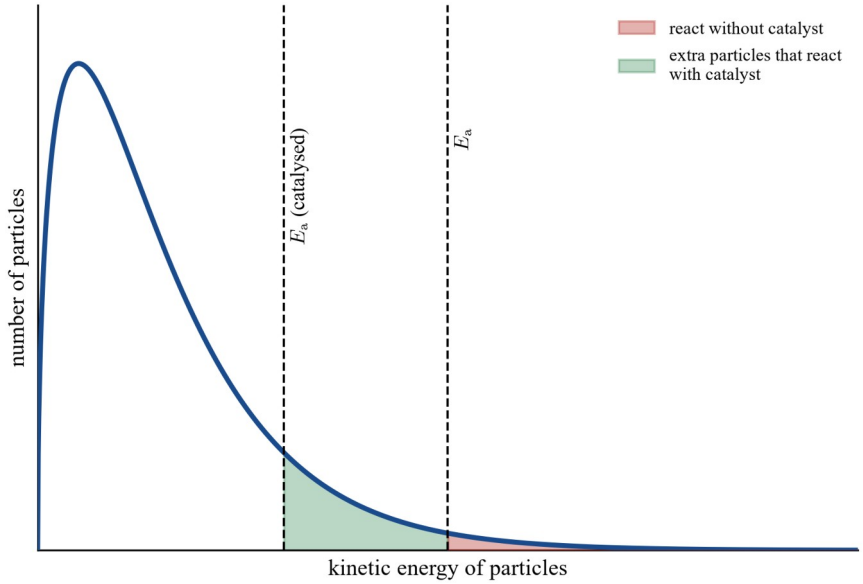
Surface area. When a solid reactant takes part in a reaction, only the particles at its **surface** are exposed to the other reactant and able to collide. Breaking a solid into smaller pieces, or grinding it to a powder, greatly increases the total surface area, exposing many more particles and creating many more **collision sites**. Collisions between the reactants therefore occur more frequently and the rate increases. The same mass of solid is present, so the total amount that can react is unchanged — only the *rate* changes.

Catalysts. A **catalyst** is a substance that increases the rate of a reaction without being consumed overall — it is regenerated and can be recovered unchanged at the end. A catalyst works by providing an **alternative reaction pathway of lower activation energy**. On the energy-profile diagram below, the catalysed pathway (dashed) has a lower barrier than the uncatalysed pathway.



Because the barrier is lower, a **greater fraction** of the colliding particles now have energy of at least E_a, so a greater fraction of collisions are successful and the rate increases. Importantly, a catalyst lowers the **forward and reverse** activation energies by the **same** amount, so it does **not** change the enthalpy change ΔH of the reaction: in the diagram the reactant and product levels — and hence ΔH — are identical for both pathways. (A catalyst likewise does not change the position of an equilibrium; equilibrium is treated in Chapter 6.)

The effect of a catalyst on the fraction of particles able to react is seen clearly on a Maxwell–Boltzmann distribution. Because a catalyst does not change the temperature, the distribution curve is **unchanged**; only the activation-energy line moves to a lower value. The shaded area beyond the catalysed barrier is much larger than the area beyond the uncatalysed barrier — many more particles now have enough energy to react.



Activation energy and orientation. Activation energy and the orientation requirement are properties of the reaction itself. A reaction with a **low** activation energy is intrinsically fast, because at any temperature a large fraction of collisions clear the low barrier; a reaction with a high E_a is slow. A catalyst speeds a reaction precisely by lowering this barrier. The **orientation** requirement explains why not every collision that has enough energy leads to reaction: the particles must also be aligned so that the correct atoms meet. Only collisions that satisfy **both** the energy and the orientation requirements are successful.

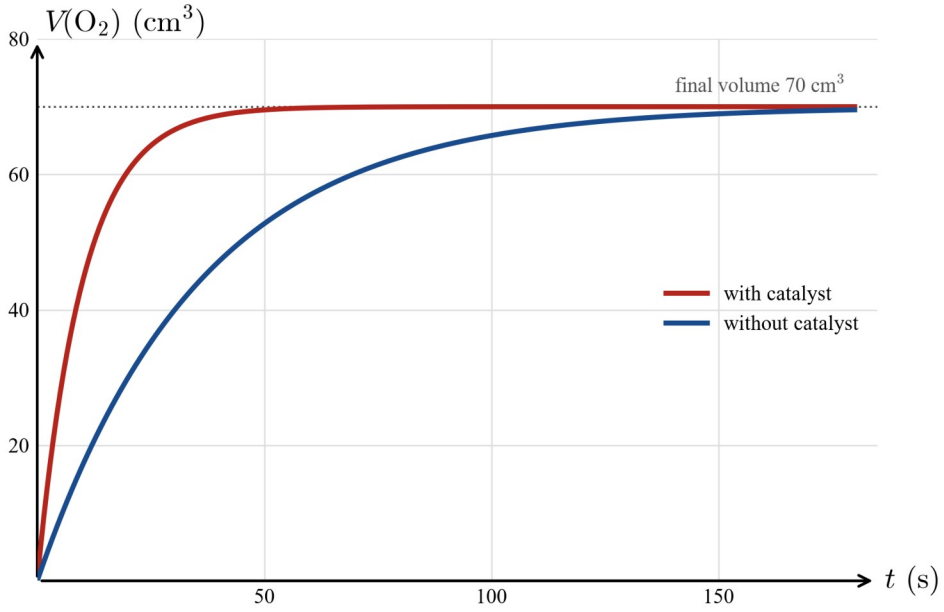
Open and closed systems. In a **closed system** no matter can enter or leave, so gases produced are retained and the pressure of a gaseous mixture can be used as a variable to change the rate. In an **open system** matter can escape to the surroundings: a gaseous product leaves the vessel, the pressure stays close to atmospheric, and gas pressure cannot be

used to control the rate. The rate of a reaction that releases a gas can still be followed in an open system by placing the flask on a balance and recording the **loss of mass** as the gas escapes.

The table below summarises how each factor acts through collision theory.

Factor increased	Effect on collisions	Effect on rate
Temperature	more frequent **and** a much greater fraction have $E \geq E_a$	large increase
Concentration (solution)	more frequent (more particles per unit volume)	increase
Gas pressure	more frequent (more particles per unit volume)	increase
Surface area of a solid	more collision sites exposed → more frequent	increase
Catalyst added	greater fraction have $E \geq E_a$ (lower barrier)	increase

Rate-versus-time graphs — telling rate apart from yield. When the volume of a gaseous product is plotted against time, the **gradient** at any instant is the rate at that moment. The graph below compares the decomposition of the *same* amount of hydrogen peroxide, H_2O_2, carried out with and without a catalyst at the *same* temperature.



The catalysed run (red) has a much **steeper initial gradient** — a faster initial rate — and reaches its final volume sooner. Both curves flatten to a plateau as a reactant is used up, and both level off at the **same final volume** (70 cm³): the amount of oxygen produced depends only on the amount of H_2O_2 decomposed, not on how quickly it reacts. This illustrates a key distinction: the **rate** of a reaction (how fast product forms) and the **yield** of a reaction (how much product forms) are different quantities. For a reaction that goes to completion, a catalyst — or a higher temperature, or a larger surface area — changes the **rate** but not the final amount of product.

Worked examples

Worked Example 1 — A strip of magnesium is added to excess dilute hydrochloric acid and the volume of hydrogen gas collected is recorded at 10-second intervals:

Time (s)	0	10	20	30	40	50	60	70
Volume of H_2	0	20	34	44	50	52	52	52

Time (s)	0	10	20	30	40	50	60	70
(cm^3)								

Calculate the average rate over the first 10 s and over the interval 20–30 s, describe how the rate changes with time, and state the final volume of hydrogen with a reason.

Working	Comment
$\text{rate}_{0-10} = \dfrac{20-0}{10-0} = 2.0\,\text{cm}^3\,\text{s}^{-1}$	Average rate = change in volume ÷ time interval.
$\text{rate}_{20-30} = \dfrac{44-34}{30-20} = 1.0\,\text{cm}^3\,\text{s}^{-1}$	Rate over the later interval, same method.
The rate **falls** with time (2.0 → 1.0 $cm^3\ s^{-1}$).	As the acid is consumed its concentration drops, so collisions become less frequent.
Final volume $= 52\,\text{cm}^3$.	The readings at 50, 60 and 70 s are identical, so the volume has stopped rising: all of the magnesium (the limiting reactant, as the acid is in excess) has reacted and the reaction is complete.
$\text{Mg(s)} + 2\,\text{HCl(aq)} \rightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{(g)}$	Balanced equation, with states.

Worked Example 2 — The energy profile shown earlier is for an exothermic reaction. The uncatalysed forward activation energy is $150\,\text{kJ mol}^{-1}$ and the products lie $80\,\text{kJ mol}^{-1}$ below the reactants. Adding a catalyst provides an alternative pathway with a forward activation energy of $90\,\text{kJ mol}^{-1}$. Determine ΔH, the reverse activation energies for both pathways, and the amount by which the catalyst lowers each barrier.

Working	Comment
$\Delta H = -80\,\text{kJ mol}^{-1}$	Products are $80\,\text{kJ mol}^{-1}$ below reactants; exothermic, so $\Delta H < 0$.
$E_a(\text{reverse, uncat}) = E_a(\text{fwd}) - \Delta H = 150 - (-80) = 2$	The reverse barrier is measured from the product level up to the same peak.
$E_a(\text{fwd, cat}) = 90\,\text{kJ mol}^{-1}$	Given: the catalysed forward barrier.
$E_a(\text{reverse, cat}) = 90 - (-80) = 170\,\text{kJ mol}^{-1}$	Reverse barrier for the catalysed pathway.
Forward lowered by $150 - 90 = 60\,\text{kJ mol}^{-1}$; reverse lowered by $230 - 170 = 60\,\text{kJ mol}^{-1}$	The catalyst lowers **both** barriers by the same amount.
$\therefore \Delta H$ is unchanged at $-80\,\text{kJ mol}^{-1}$	ΔH is the difference between the reactant and product **levels**, not a barrier height; the catalyst lowers only the peak between them, so ΔH is unaffected.

Worked Example 3 — Zinc reacts with dilute sulfuric acid, $\text{Zn(s)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{ZnSO}_4\text{(aq)} + \text{H}_2\text{(g)}$. A fixed mass of zinc, which is the limiting reactant, is added to excess acid. Using collision theory, explain why (i) using powdered zinc rather than a single lump and (ii) using a more concentrated acid each increase the initial rate, yet neither changes the final volume of hydrogen collected.

Powdering the zinc greatly increases the **surface area** of the solid, exposing far more zinc atoms at the surface. There are then many more sites where acid particles can collide with the zinc, so collisions between the reactants are **more frequent**, more successful collisions occur each second, and the initial rate increases.

Using a more concentrated acid packs more H^+ particles into each unit of volume. Collisions between the acid and the zinc surface therefore occur **more frequently**, again raising the number of successful collisions per second and increasing the initial rate.

Both changes increase only the **rate** at which the reaction occurs, not the amount that can react. The zinc is the limiting reactant, so the final volume of hydrogen is fixed by the amount of zinc. Neither powdering the zinc (the same mass is used) nor concentrating the acid (still in excess) changes the amount of zinc, so the final volume of hydrogen is unchanged — the reactions simply reach that same volume at different speeds.

∴ increasing surface area and increasing concentration both increase the initial rate by raising the collision frequency, but the final volume of hydrogen depends only on the fixed amount of the limiting reactant and is unchanged.

Worked Example 4 — With reference to an energy-profile diagram and a Maxwell–Boltzmann distribution, explain how a catalyst increases the rate of a reaction. State one quantity that a catalyst does **not** change, and identify one green-chemistry benefit of using a catalyst in an industrial process.

A catalyst provides an **alternative reaction pathway with a lower activation energy**, as shown by the lower barrier on the catalysed (dashed) energy profile. On the Maxwell–Boltzmann distribution the temperature — and therefore the distribution curve — is unchanged, but the activation-energy line moves to a lower value, so a **greater fraction of the colliding particles have energy of at least** E_a. For the distribution drawn earlier, lowering the barrier increases this fraction roughly six-fold. A greater fraction of collisions are therefore successful, and the rate of reaction increases.

A catalyst does **not** change the enthalpy change ΔH of the reaction, because it lowers the forward and reverse barriers by the same amount and leaves the reactant and product energy levels unmoved. (Nor does it change the amount of product formed in a reaction that goes to completion.)

A green-chemistry benefit is improved **energy efficiency**: because the catalysed reaction reaches a useful rate at a **lower temperature**, less energy needs to be supplied to heat the reaction mixture, reducing the energy demand and the associated emissions of the process.

∴ a catalyst speeds a reaction by offering a lower-E_a pathway that makes more collisions successful, without altering ΔH, and allows industrial processes to run faster at lower temperatures.

Practice questions

Question 1 — A reaction between two solutions is carried out at a higher temperature.

a. State the effect of increasing the temperature on the rate of reaction.
b. Explain, in terms of collision theory, the **two** reasons the rate increases when the temperature is raised.
c. State which of the two reasons is the more important, and why.

Question 2 — A piece of metal reacts with dilute hydrochloric acid, producing hydrogen gas. The experiment is repeated using acid of twice the concentration.

a. State the effect of doubling the acid concentration on the initial rate of reaction.
b. Explain this effect using collision theory.
c. The metal is the limiting reactant. State whether doubling the acid concentration changes the final volume of hydrogen collected, and explain why.

Question 3 — Marble chips react with hydrochloric acid:
$\mathrm{CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)}$.

a. State the effect on the rate of grinding the chips to a fine powder.
b. Explain this effect using collision theory.
c. The same mass of marble is used. State whether the final volume of carbon dioxide changes, and explain why.

Question 4 — An exothermic reaction has an uncatalysed forward activation energy of $100\,\mathrm{kJ\,mol^{-1}}$, and its products lie $60\,\mathrm{kJ\,mol^{-1}}$ below the reactants. A catalyst provides an alternative pathway with a forward activation energy of $70\,\mathrm{kJ\,mol^{-1}}$.

a. Determine the reverse activation energy for the catalysed pathway.
b. State by how much the catalyst lowers the activation energy.

c. State ΔH for the reaction and explain why it is unchanged by the catalyst.

Question 5 — The Maxwell–Boltzmann diagram in the Theory shows the distribution of particle kinetic energies at a fixed temperature, with two activation-energy lines.

a. State what the shaded area to the right of an activation-energy line represents.
b. Explain how adding a catalyst changes this shaded area, given that the temperature does not change.
c. Link your answer in part b to the effect of the catalyst on the reaction rate.

Question 6 — Use the volume-of-oxygen versus time graph in the Theory (decomposition of hydrogen peroxide with and without a catalyst).

a. State which curve corresponds to the catalysed reaction and how you can tell.
b. Explain why both curves level off at the same final volume.
c. Explain, using collision theory, why the gradient of each curve decreases with time.

Question 7 — A reaction between two gases is carried out in a sealed vessel of fixed volume. Explain, in terms of collision theory, the effect on the reaction rate of increasing the pressure inside the vessel by pumping in more of the reacting gases.

Question 8 — Distinguish between an open system and a closed system. Explain why gas pressure can be used to change the rate of a gaseous reaction only in a closed system, and describe how the rate of a reaction that releases a gas could be followed in an open system.

Question 9 — Not every collision in which the particles have a combined energy greater than the activation energy results in a reaction. Explain why, referring to the orientation of the colliding particles.

Question 10 — Hydrogen peroxide solution decomposes slowly into water and oxygen. Solid manganese dioxide, $\mathrm{MnO_2}$, greatly speeds up the reaction.

a. Write a balanced equation, including states, for the decomposition of hydrogen peroxide.
b. Explain why $\mathrm{MnO_2}$ is described as a catalyst rather than as a reactant.

Question 11 — Define the term *catalyst* with reference to activation energy. State **two** quantities that a catalyst does not change for a reaction that goes to completion.

Question 12 — A student observes that marble chips react much faster with hydrochloric acid when the chips are first crushed **and** the acid is warmed. Using collision theory, explain each of these two observations.

Question 13 — The decomposition of the same amount of hydrogen peroxide is carried out twice at the same temperature: once with a $\mathrm{MnO_2}$ catalyst and once without. In the first 10 s, 28 cm³ of oxygen is collected in the catalysed run and 4.0 cm³ in the uncatalysed run; both runs eventually produce 70 cm³ of oxygen.

a. Calculate the average rate of reaction over the first 10 s for each run.
b. State how many times faster the catalysed reaction is initially.
c. Explain why both runs produce the same final volume of oxygen.

Question 14 — The initial rate of a reaction is found by drawing a tangent to the volume–time graph at $t = 0$. At 30 °C the initial rate is $0.80\,\mathrm{cm^3\,s^{-1}}$ and at 50 °C it is $4.0\,\mathrm{cm^3\,s^{-1}}$.

a. Determine how many times faster the reaction is at 50 °C than at 30 °C.
b. Explain, in terms of the distribution of particle energies, why a rise of only 20 °C can increase the rate so markedly.

Question 15 — A manufacturer adds a catalyst to a reaction that goes to completion. Explain the effect of the catalyst on (a) the rate at which the product forms and (b) the final amount (yield) of product obtained, and use your answers to distinguish clearly between the rate and the yield of a reaction.

Question 16 — A single cube of a solid reactant has a side length of 2.0 cm. It is ground into small cubes of side length 0.5 cm.

a. Calculate the total surface area of the solid before and after grinding.
b. State the factor by which the total surface area increases.
c. Explain, using collision theory, the effect of this change on the reaction rate.

Question 17 — Use the shape of the Maxwell–Boltzmann distribution of particle kinetic energies to explain why raising the temperature increases both the frequency of collisions and the fraction of collisions that are successful, and why the second effect is the more important of the two.

Question 18 — The energy profile for an **endothermic** reaction shows an uncatalysed forward activation energy of $120\,\text{kJ mol}^{-1}$, with the products $40\,\text{kJ mol}^{-1}$ above the reactants. A catalyst provides a pathway with a forward activation energy of $75\,\text{kJ mol}^{-1}$.

a. State ΔH for the reaction.
b. Determine the reverse activation energy for both the uncatalysed and the catalysed pathways.
c. State by how much the catalyst lowers the activation energy.

Question 19 — In many industrial processes a catalyst allows a reaction to proceed at a useful rate at a much lower temperature than would otherwise be required. With reference to the green-chemistry principles of **catalysis** and **designing for energy efficiency**, evaluate the use of a catalyst in such a process. Refer to activation energy and to energy use, and finish with a concluding statement.

Question 20 — A student wants to investigate the effect of temperature on the rate of the reaction between magnesium and hydrochloric acid. In one trial they increase the temperature **and** replace the magnesium ribbon with powdered magnesium.

a. Explain, using collision theory, why each of these two changes would increase the rate.
b. Explain why changing both variables at once means the student cannot validly conclude that temperature affects the rate.
c. State one change to the method that would make the investigation valid.

Answers

1 a the rate increases; b more frequent collisions **and** a greater fraction of collisions with $E \geq E_a$; c the greater fraction with $E \geq E_a$ (the energy effect), because the tail of the distribution rises steeply with temperature. **2** a the initial rate increases; b more acid particles per unit volume → more frequent collisions; c no — the metal is limiting, so the final volume of H_2 is unchanged. **3** a the rate increases; b a larger surface area exposes more particles → more collision sites → more frequent collisions; c no — the same mass of marble gives the same final volume of CO_2. **4** a $130\ \text{kJ mol}^{-1}$; b $30\ \text{kJ mol}^{-1}$; c $\Delta H = -60\ \text{kJ mol}^{-1}$, unchanged because both barriers are lowered equally and the reactant/product levels are unmoved. **5** a the fraction of particles with $E \geq E_a$; b the curve is unchanged but the E_a line moves lower, so the shaded fraction increases; c more successful collisions per second → faster rate. **6** a the catalysed run is the steeper curve that reaches the plateau sooner; b the same amount of H_2O_2 gives the same amount of O_2; c as reactant is used up its concentration falls, so collisions become less frequent and the rate (gradient) decreases. **7** more gas particles per unit volume → more frequent collisions → faster rate. **8** open = matter can leave, closed = it cannot; pressure is only a usable variable when gas is retained (closed); in an open system follow the loss of mass as gas escapes. **9** the particles must also collide with the correct orientation; wrongly oriented collisions do not react even with enough energy. **10** a $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$; b it is regenerated and not used up overall, so it does not appear in the equation. **11** a substance that speeds a reaction by providing an alternative pathway of lower activation energy, without being consumed; the two quantities are ΔH and the final amount (yield) of product. **12** crushing ↑ surface area → more collision sites; warming ↑ energy → more collisions with $E \geq E_a$ (and more frequent) — both give more successful collisions per second. **13** a catalysed $2.8\ \text{cm}^3\text{s}^{-1}$, uncatalysed $0.40\ \text{cm}^3\text{s}^{-1}$; b 7.0 times; c the same amount of H_2O_2 decomposes, giving the same amount of O_2. **14** a 5.0 times; b a small temperature rise moves many particles past E_a because the high-energy tail of the distribution rises steeply. **15** a the rate increases; b the yield is unchanged; rate = how fast product forms, yield = how much forms. **16** a $24\ \text{cm}^2$ then $96\ \text{cm}^2$; b factor of 4; c four times the surface area → more collision sites → faster rate. **17** raising T makes particles move faster (more frequent collisions) and shifts the distribution to higher energy so a much larger fraction exceed E_a; the energy effect dominates. **18** a $\Delta H = +40\ \text{kJ mol}^{-1}$; b uncatalysed $80\ \text{kJ mol}^{-1}$, catalysed $35\ \text{kJ mol}^{-1}$; c $45\ \text{kJ mol}^{-1}$. **19** evaluation: a catalyst lowers E_a, allowing a useful rate at a lower temperature, cutting energy use and emissions (energy efficiency + catalysis principles); concluding statement that catalysis makes the process more sustainable. **20** a powder ↑ surface area, warming ↑ fraction with $E \geq E_a$; b two variables change together so the cause of the rate change cannot be isolated (not valid); c change only the temperature, keeping the form of the magnesium the same.

Fully-worked solutions

Question 1 a. The rate of reaction increases. b. Two effects act together. (1) At a higher temperature the particles move faster, so collisions occur **more frequently**. (2) A greater proportion of the particles now have a kinetic energy of at least the activation energy E_a, so a greater fraction of collisions have enough energy to be successful. c. The increase in the **fraction of particles with** $E \geq E_a$ is the more important effect. On the Maxwell–Boltzmann distribution the high-energy tail rises steeply as the temperature increases, so even a modest temperature rise produces a large increase in the number of successful collisions — a much larger effect than the smaller rise in collision frequency.

Question 2 a. The initial rate increases. b. A more concentrated acid contains more reactant particles in the same volume. Collisions between the acid particles and the metal therefore occur more frequently, so more successful collisions occur each second and the rate increases. (The fraction of collisions with enough energy is unchanged; only the frequency changes.) c. No. The metal is the limiting reactant, so the final volume of hydrogen is fixed by the amount of metal. Increasing the concentration of the acid (already in excess) does not change the amount of metal, so the same final volume of hydrogen is produced — just more quickly.

Question 3 a. The rate of reaction increases. b. Grinding the chips to a powder greatly increases the total **surface area** of the solid, exposing many more $CaCO_3$ particles at the surface where acid particles can reach them. This creates many more collision sites, so collisions between the reactants are more frequent, and the rate increases. c. No. The same mass of marble contains the same amount of $CaCO_3$, so the same amount of CO_2 is produced and the final volume is unchanged. Only the rate at which that volume is reached is greater.

Question 4 a. $E_a(\text{reverse, cat}) = E_a(\text{fwd, cat}) - \Delta H = 70 - (-60) = 130\ \text{kJ mol}^{-1}$. b. The catalyst lowers the forward activation energy from $100\ \text{kJ mol}^{-1}$ to $70\ \text{kJ mol}^{-1}$, a reduction of $100 - 70 = 30\ \text{kJ mol}^{-1}$ (and it lowers the reverse barrier by the same amount). c. $\Delta H = -60\ \text{kJ mol}^{-1}$ (products $60\ \text{kJ mol}^{-1}$ below reactants, so exothermic). The catalyst leaves the reactant and product energy levels unchanged — it only lowers the barrier between them — so the difference between them, ΔH, is unchanged.

Question 5 a. It represents the **fraction (or number) of particles that have a kinetic energy of at least the activation energy** — the particles able to react on collision. b. A catalyst does not change the temperature, so the distribution curve is unchanged. Instead the activation-energy line moves to a **lower** energy (the catalysed pathway has a lower E_a), so the shaded area to the right of the line becomes **larger**. c. Because a larger fraction of particles now have enough energy, a greater fraction of collisions are successful, so more successful collisions occur each second and the reaction rate increases.

Question 6 a. The catalysed reaction is the curve with the **steeper initial gradient** that reaches the final (plateau) volume in a shorter time; a faster reaction produces gas more quickly at the start. b. Both experiments decompose the same amount of hydrogen peroxide, so both produce the same amount of oxygen. The catalyst changes only the rate, not the amount of product, so both curves level off at the same final volume. c. As the reaction proceeds the reactant is used up and its concentration falls. Collisions between reactant particles therefore become less frequent, so fewer successful collisions occur each second and the rate — the gradient of the curve — decreases, reaching zero when a reactant is exhausted.

Question 7 Pumping in more gas increases the number of gas particles per unit volume inside the fixed vessel. The reactant particles therefore collide **more frequently**, so more successful collisions occur each second and the rate of reaction increases. (Increasing gas pressure in this way is the gaseous equivalent of increasing concentration.)

Question 8 An **open system** can exchange matter with its surroundings, whereas a **closed system** cannot. Gas pressure can only be used to change the rate of a gaseous reaction in a closed system, because only there is the gas contained so that its pressure — and hence the number of particles per unit volume — can be controlled; in an open system a gaseous product simply escapes and the pressure stays close to atmospheric. In an open system the rate of a reaction that releases a gas can be followed by standing the reaction flask on a balance and recording the **decrease in mass** over time as the gas leaves.

Question 9 For a collision to lead to reaction the particles must not only have enough energy ($E \geq E_a$) but must also be **correctly oriented**, so that the parts of the particles that need to bond come together. A collision in which the particles are wrongly aligned will not lead to reaction even if the particles have more than enough energy, because the necessary bonds cannot form. Only collisions that satisfy both the energy and the orientation requirements are successful.

Question 10 a. $2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)$. b. Manganese dioxide provides an alternative pathway of lower activation energy, speeding the reaction, but it is **regenerated** during the reaction and is present unchanged in the same amount at the end. Because it is not consumed overall it is a catalyst, and it does not appear in the balanced equation as a reactant.

Question 11 A **catalyst** is a substance that increases the rate of a reaction by providing an alternative reaction pathway of **lower activation energy**, and that is not consumed overall (it is regenerated). For a reaction that goes to completion, a catalyst does **not** change: (1) the enthalpy change ΔH of the reaction; and (2) the final amount (yield) of product formed. (More generally, a catalyst does not change the position of an equilibrium either — but that case does not arise here, because a reaction that goes to completion does not reach an equilibrium; equilibrium is treated in Chapter 6.)

Question 12 Crushing the chips increases the **surface area** of the marble, exposing many more $CaCO_3$ particles at the surface and creating more collision sites, so collisions between the acid and the solid become more frequent. Warming the acid increases the average kinetic energy of the particles, so a greater fraction of collisions have energy of at least E_a (and collisions are also somewhat more frequent). Both changes increase the number of **successful collisions per second**, so the reaction proceeds faster and the effervescence is more vigorous.

Question 13 a. Catalysed run: $\text{rate} = \frac{28}{10} = 2.8\,\text{cm}^3\,\text{s}^{-1}$. Uncatalysed run: $\text{rate} = \frac{4.0}{10} = 0.40\,\text{cm}^3\,\text{s}^{-1}$. b. $\frac{2.8}{0.40} = 7.0$, so the catalysed reaction is initially **7.0 times** faster. c. The same amount of hydrogen peroxide is decomposed in each run, so the same amount of oxygen is produced. The catalyst changes only the rate, not the amount of product, so both runs reach the same final volume of 70 cm³.

Question 14 a. $\frac{4.0}{0.80} = 5.0$, so the reaction is **5.0 times** faster at 50 °C. b. Raising the temperature shifts the Maxwell–Boltzmann distribution of particle energies to higher energy and broadens it. Because the activation energy lies well out in the high-energy tail of the distribution, even a small temperature rise moves a large number of additional particles past E_a. The fraction of collisions that are successful therefore rises steeply, producing a large increase in rate from only a 20 °C rise.

Question 15 a. The catalyst increases the **rate**: it provides a lower-E_a pathway, so more collisions are successful each second and the product forms more quickly. b. The catalyst does **not** change the **yield**: for a reaction that goes to completion, the final amount of product is fixed by the amounts of reactants, which the catalyst does not alter. The reaction simply reaches that same amount sooner. This shows the distinction between **rate** (how fast the product forms) and **yield** (how much product forms) — a catalyst changes the first but not the second.

Question 16 a. Before grinding: a cube of side 2.0 cm has surface area $6 \times (2.0)^2 = 24\,\text{cm}^2$. After grinding into cubes of side 0.5 cm, the number of small cubes is $(2.0 / 0.5)^3 = 64$, each with surface area $6 \times (0.5)^2 = 1.5\,\text{cm}^2$, giving a total of $64 \times 1.5 = 96\,\text{cm}^2$. b. $\frac{96}{24} = 4$, so the surface area increases by a **factor of 4**. c. The larger surface area exposes four times as many particles at the surface, creating many more collision sites. Collisions between the reactants become more frequent, so more successful collisions occur each second and the reaction rate increases.

Question 17 Raising the temperature increases the average kinetic energy of the particles, so the whole Maxwell–Boltzmann distribution shifts to higher energy and broadens (its peak becomes lower and moves to the right). Two consequences follow. First, faster-moving particles collide **more frequently**. Second, because the activation energy lies in the high-energy tail of the distribution, the shift moves a much greater **fraction** of particles past E_a, so a much greater fraction of collisions are successful. The steep rise of the tail fraction with temperature makes this second effect far larger than the modest increase in collision frequency, so it is the more important reason the rate increases.

Question 18 a. The products are $40\,\text{kJ mol}^{-1}$ above the reactants, so the reaction is endothermic and $\Delta H = +40\,\text{kJ mol}^{-1}$. b. Uncatalysed: $E_a(\text{reverse}) = E_a(\text{fwd}) - \Delta H = 120 - 40 = 80\,\text{kJ mol}^{-1}$. Catalysed: $E_a(\text{reverse}) = 75 - 40 = 35\,\text{kJ mol}^{-1}$. c. The catalyst lowers the forward activation energy from $120\,\text{kJ mol}^{-1}$ to $75\,\text{kJ mol}^{-1}$, a reduction of $120 - 75 = 45\,\text{kJ mol}^{-1}$ (and it lowers the reverse barrier, $80 \rightarrow 35\,\text{kJ mol}^{-1}$, by the same $45\,\text{kJ mol}^{-1}$).

Question 19 A catalyst provides an alternative reaction pathway of **lower activation energy**. Because a greater fraction of collisions then clear the lower barrier, the reaction reaches a useful rate at a **lower temperature** than the uncatalysed process would require.

Against the green-chemistry principle of **catalysis**, using a catalyst is favourable: the catalyst is not consumed and can be recovered and reused, and it avoids the need for the harsher conditions (high temperature) that an uncatalysed reaction would need to run quickly.

Against the principle of **designing for energy efficiency**, the benefit is that heating the reaction mixture to a lower temperature requires **less energy**. Since much industrial energy is generated by burning fossil fuels, a lower operating temperature means lower fuel use, lower cost and lower greenhouse-gas emissions for the same output.

Concluding statement: because a catalyst lets the process run quickly at a lower temperature without being used up, it improves both the energy efficiency and the overall sustainability of the process, so its use is strongly justified on green-chemistry grounds.

Question 20 a. Using powdered magnesium increases the **surface area** of the metal, exposing more magnesium atoms and creating more collision sites, so collisions with the acid are more frequent. Increasing the temperature raises the average kinetic energy of the particles, so a greater fraction of collisions have energy of at least E_a (and collisions are more frequent). Each change increases the number of successful collisions per second, so each increases the rate. b. Because two variables — temperature and surface area — are changed at the same time, any increase in rate could be caused by either change, or by both. The effect of temperature alone cannot be isolated, so the investigation is not **valid** and no sound conclusion about temperature can be drawn. c. Change only the temperature between trials while keeping everything else, including the form and mass of the magnesium (for example, using magnesium ribbon of the same length each time), the same — so temperature is the only independent variable.