

ESAT

Chemistry

Rates of Reaction and Energetics

Free lesson notes

Covers	C10.1 to C10.6 and C11.1 to C11.5
Format	Lesson, worked examples, self-check
Price	Free

About this lesson

Some reactions are over in a flash (a firework) and others take years (iron rusting). Why? And why does a reaction sometimes get hot and sometimes cold? Two ideas answer both questions. *Rate* is about how fast reactants are used up or products appear, and it is controlled by how often particles collide successfully. *Energetics* is about the energy that moves in and out as bonds are broken and made. Both are explained by the same picture: particles must collide, with enough energy, to get over an energy barrier, and the energy of the products compared with the reactants decides whether the surroundings warm up or cool down.

This lesson starts with how rates are measured and read from graphs, then lists the factors that change the rate and explains each one with collision theory. We introduce activation energy and the energy profile diagram, see how a catalyst changes the pathway, then turn to exothermic and endothermic reactions, the calculation of energy changes from temperature changes ($q = mc\Delta T$) and from bond energies. Specification codes: C10.1–C10.6 and C11.1–C11.5. Any data needed (specific heat capacity of water, bond energies) is always given in the exam question, so nothing needs to be memorised apart from the ideas.

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1 Measuring the rate of reaction

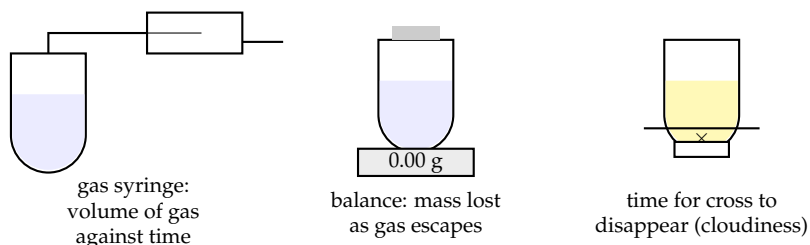
What is the rate? The **rate of reaction** is how quickly the amount of a reactant falls, or the amount of a product rises, with time:

$$\text{mean rate} = \frac{\text{change in amount of a reactant or product}}{\text{time taken}}$$

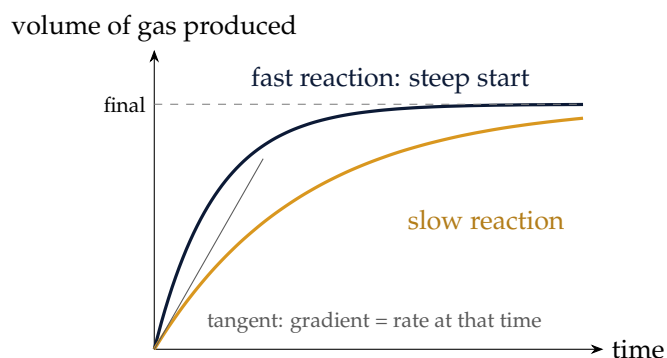
The unit depends on what you measure: cm^3/s for the volume of a gas, g/s for mass, $\text{mol/dm}^3/\text{s}$ for concentration.

Three common methods. Pick the one that suits the reaction:

- **Volume of gas** collected (gas syringe or upturned measuring cylinder), read at regular times: for acid with a carbonate or metal.
- **Mass lost:** if a gas escapes, the flask on a balance gets lighter (for example $\text{CaCO}_3 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$, where CO_2 leaves). This does not work well for a very light gas such as hydrogen, because the change in mass is tiny.
- **Time for a visible change:** for example sodium thiosulfate with acid forms a fine yellow precipitate of sulfur; the time taken for a cross under the flask to disappear is measured. The shorter the time, the faster the rate (rate is proportional to $1/\text{time}$).



Reading a rate graph. Plot the amount of product (or the mass lost) against time. The *steeper* the line, the faster the reaction. The reaction is fastest at the start, when the reactant concentrations are highest, and the line becomes flatter as the reactants are used up. It becomes *horizontal* when the reaction has stopped (one reactant has been completely used up). The final height of the curve shows the total amount of product, which depends on the amount of the limiting reactant, not on the speed.



The rate at any one moment is the **gradient of a tangent** to the curve at that time. The mean rate over an interval is the change divided by the time.

Worked example: mean rate from a graph

A flask of acid and marble chips loses 0.60 g of carbon dioxide in the first 60 s. What is the mean rate over this time, and how much would be lost in 60 s if the rate were constant at that value?
 Mean rate = $0.60/60 = 0.010 \text{ g/s}$. At that constant rate $60 \times 0.010 = 0.60 \text{ g}$, of course; in practice the rate slows, so in the *second* 60 s less than 0.60 g is lost.

Common mistakes

- Reading the final height of a curve as the rate. The final volume depends on the amount of reactant; the *gradient* gives the rate.
- Thinking the rate is constant. It is greatest at the start and falls as the reactants are used up.
- Using the time taken as the rate. Short time means high rate; $\text{rate} \propto 1/\text{time}$.

2 What changes the rate?

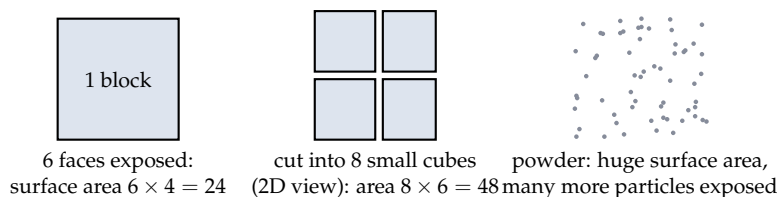
Five factors change the rate of a reaction: concentration, pressure (for gases), temperature, surface area (particle size) and the presence of a catalyst. Whenever you are asked how a change would affect a rate, the answer is the same type of sentence: “the change makes particles collide more often, or makes more collisions successful, so the rate increases”. Here is each factor.

Concentration. A higher concentration of a solution means more particles in the same volume, so they collide more often: the rate rises. Doubling the concentration roughly doubles the number of collisions per second.

Pressure (gases). Raising the pressure squeezes the same number of gas particles into a smaller volume. This is the same as increasing the concentration: more collisions per second.

Temperature. At a higher temperature the particles move faster, so they collide more often *and*, more importantly, a much greater fraction of the collisions have enough energy to react. As a rule of thumb, the rate roughly doubles for every 10°C rise.

Surface area. Reactions between a solid and a liquid or gas happen at the surface of the solid. Cutting a solid into smaller pieces exposes more particles to the other reactant, so there are more collisions per second at the surface. Fine powders react very quickly (flour dust and coal dust can explode).



Catalyst. A catalyst provides an alternative reaction pathway with a lower activation energy (see below), so a bigger fraction of collisions are successful. It is not used up and can be recovered unchanged at the end.

Worked example: which curve?

Marble chips (small and large) react with the same volume and concentration of acid at the same temperature, using the same mass of marble. Which experiment gives the steeper initial curve and which ends with the larger volume of gas?

The smaller chips have the larger total surface area, so they react faster: a steeper curve at the start. Both experiments use the same mass of marble (and the same amount of acid), so the same number of moles of CO_2 are produced and the final volumes are equal.

Exam tip

A change in rate does not change the *amount* of product unless the amount of a reactant changes. In graph questions, check whether the final level is the same (same limiting reactant) or different (more or less reactant).

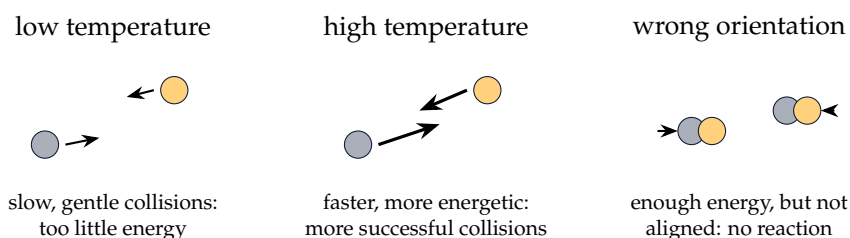
Common mistakes

- Saying that a higher temperature makes the reaction faster “because particles have more energy” and stopping there. Add that they collide more often and a larger fraction have the activation energy.
- Believing a catalyst raises the yield or is used up: it changes the rate only, and is not consumed.
- Thinking that a larger piece of solid has a bigger surface area for the same mass: smaller pieces have the larger area.

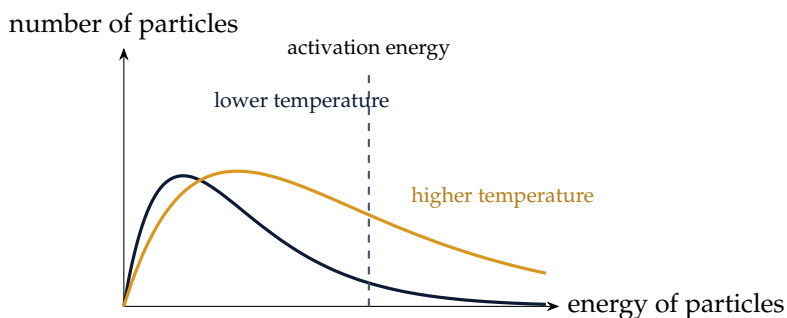
3 Collision theory

Two requirements. Particles can only react if they *collide*, but not every collision leads to a reaction. A collision is **successful** only if

1. the particles have at least a minimum energy, the **activation energy** E_a , which is needed to break the existing bonds, and
2. they hit each other in the right orientation.



Why temperature matters so much. In any sample the particles do not all have the same energy: there is a spread, with a few at low energy, most near an average, and a few at high energy. Raising the temperature shifts the whole spread towards higher energy. The activation energy stays the same, so the fraction of particles beyond it (the area under the curve to the right of the line) increases a lot, even though the average only rises a little.



Explaining each factor with collision theory.

factor increased	effect on collisions
concentration / pressure	more particles per unit volume: collisions more frequent
temperature	particles faster: collisions more frequent <i>and</i> a bigger fraction have energy $\geq E_a$
surface area	more solid particles exposed: collisions more frequent
catalyst	lower E_a : a bigger fraction of collisions have enough energy

Worked example: explaining a rate change

Explain why the rate of reaction is greater at 40 °C than at 20 °C.

At the higher temperature the particles move faster and so collide more often, and more of them have energy greater than or equal to the activation energy. A greater fraction of collisions are therefore successful, so the rate is greater.

Worked example: rate rule of thumb

Using the rule that the rate doubles for every 10 °C, by what factor does the rate increase when the temperature goes from 20 °C to 50 °C?

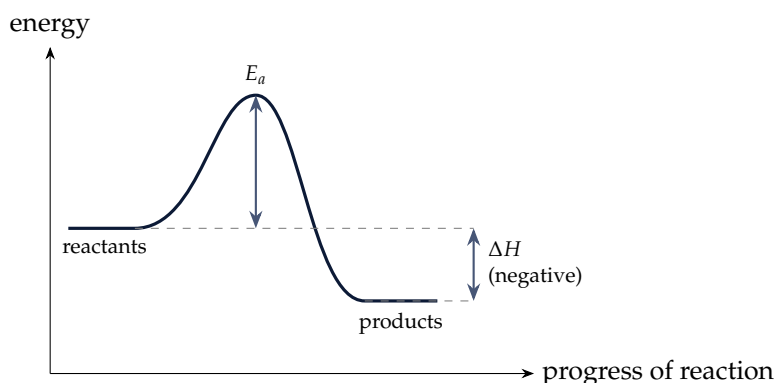
The rise is 30 °C, which is 3 steps of 10. The rate doubles each step: $2^3 = 8$ times faster.

Common mistakes

- Saying that a higher temperature lowers the activation energy. Temperature leaves E_a unchanged; it increases the fraction of particles that reach it.
- Saying particles “collide harder” without saying that the fraction with at least E_a rises.
- Thinking that all collisions between particles lead to a reaction.

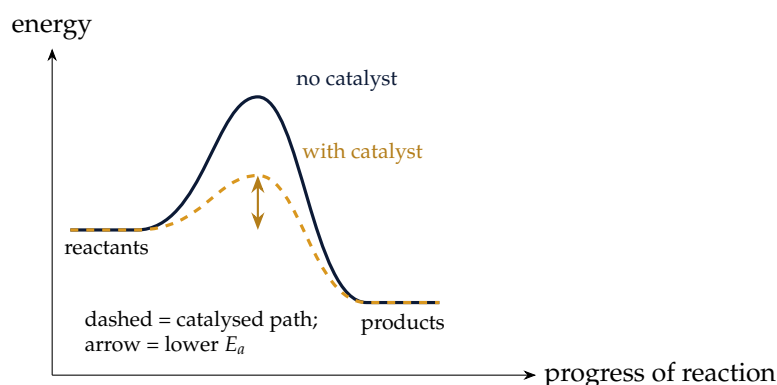
4 Activation energy, energy profiles and catalysts

An **energy profile** (or reaction profile) plots the energy of the particles against the progress of the reaction. The reactants sit at one energy level and the products at another. Between them is a hill, because bonds must be broken (taking in energy) before new bonds form. The height of the hill above the reactants is the **activation energy**, E_a .



The difference in level between the products and the reactants is the **enthalpy change**, ΔH , which we discuss next. Notice that the activation energy and the enthalpy change are different quantities: E_a is the barrier, ΔH is the overall change.

Catalysts. A catalyst speeds up a reaction by providing an alternative pathway with a *lower* activation energy. On the profile the peak is lower; but the reactants and products are at the same levels, so ΔH is *unchanged*. A catalyst does not change the products or the amount formed, and is not used up.



Reverse reactions. For a reversible reaction the profile can be read backwards. The activation energy of the reverse reaction is the height of the peak above the *products*. For an exothermic forward reaction the reverse reaction has the *larger* activation energy, and its ΔH has the opposite sign.

Worked example: reading a profile

On a profile, the reactants are at 50 kJ, the peak is at 130 kJ and the products are at 20 kJ. Find E_a (forward), ΔH , and E_a (reverse).

$E_a(\text{forward}) = 130 - 50 = 80 \text{ kJ}$. $\Delta H = \text{products} - \text{reactants} = 20 - 50 = -30 \text{ kJ}$ (exothermic). $E_a(\text{reverse}) = 130 - 20 = 110 \text{ kJ}$ (and for the reverse reaction $\Delta H = +30 \text{ kJ}$).

Common mistakes

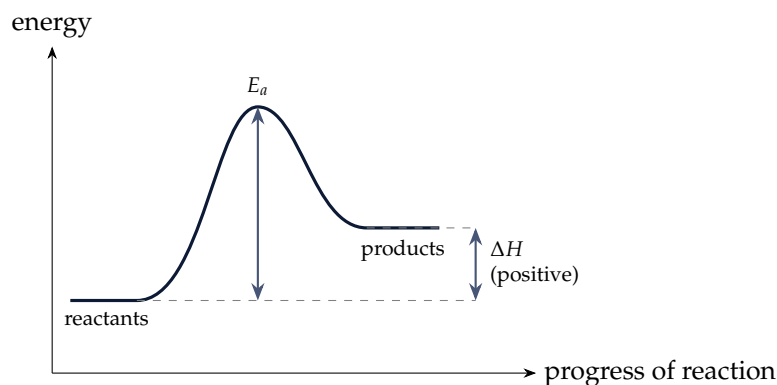
- Measuring the activation energy from the bottom of the graph (the axis) instead of from the reactants' level.
- Saying a catalyst changes ΔH . It does not.
- Thinking that a lower activation energy means the reaction is more exothermic.

5 Exothermic and endothermic reactions

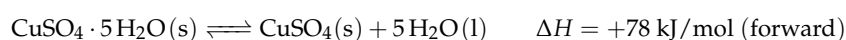
Energy is conserved. Chemical reactions involve a change in the energy stored in the chemicals. The energy comes from or goes to the surroundings as heat, and we measure it as a temperature change.

Exothermic. An **exothermic** reaction gives out energy to the surroundings: the temperature of the surroundings rises. The products have *less* energy than the reactants, so ΔH is **negative**. Examples: combustion (burning fuels), neutralisation, respiration, and many oxidation reactions (rusting, hand warmers).

Endothermic. An **endothermic** reaction takes in energy from the surroundings: the temperature falls. The products have *more* energy than the reactants, so ΔH is **positive**. Examples: thermal decomposition (for example of calcium carbonate), photosynthesis, and dissolving ammonium nitrate (used in cold packs).



Reversible reactions. In a reversible reaction, if the forward reaction is exothermic then the reverse is endothermic by exactly the same amount. For example, heating blue hydrated copper(II) sulfate drives off water (endothermic):



and adding water to white anhydrous copper(II) sulfate makes it blue and warms up (the reverse, exothermic, $\Delta H = -78$).

Remember

Sign convention. $\Delta H < 0$: exothermic, surroundings get hotter. $\Delta H > 0$: endothermic, surroundings get colder. Whenever you reverse a reaction you reverse the sign of ΔH .

Worked example: exo or endo?

A student mixes two solutions in a cup and the temperature falls from 22 °C to 15 °C. Is the reaction exothermic or endothermic, and what is the sign of ΔH ?

The surroundings (the solution) got colder, so the reaction took energy from them: endothermic, and ΔH is positive.

Common mistakes

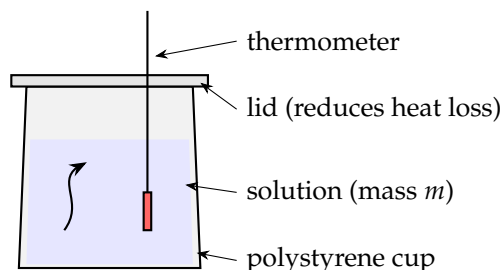
- Mixing up the sign: exothermic means ΔH is *negative*, not positive.
- Saying that an exothermic reaction does not need activation energy. It does: it needs a push to start (a match to light a fuel).
- Thinking the surroundings and the chemicals warm up together. In an exothermic reaction the energy stored in the chemicals decreases as the surroundings warm up.

6 Calculating the energy change from a temperature change

The equation. Heat released or absorbed by a solution is found from the temperature change of the solution:

$$q = mc\Delta T$$

where q is the energy transferred in joules, m is the mass of the solution (in g; for dilute aqueous solutions take the mass of 1 cm³ as 1 g), c is the specific heat capacity (for water, 4.2 J/(g K), given in the question) and ΔT is the temperature change in kelvin (or degrees Celsius; a change of 1 °C equals a change of 1 K).



Energy change per mole. The enthalpy change of a reaction is usually quoted in kJ per mole of a stated substance:

$$\Delta H = \mp \frac{q}{n} \quad (\text{in kJ/mol}), \quad q \text{ in kJ,}$$

negative if the temperature rose (exothermic) and positive if it fell (endothermic); n is the number of moles of the reactant that was completely used up. Convert q from joules to kilojoules by dividing by 1000.

Worked example: neutralisation

50 cm³ of acid is mixed with 50 cm³ of alkali in an insulated cup. The temperature rises by 6.5 K. 0.050 mol of acid reacted. Find ΔH per mole ($c = 4.2 \text{ J/(g K)}$).

$m = 100 \text{ g}$. $q = 100 \times 4.2 \times 6.5 = 2730 \text{ J} = 2.73 \text{ kJ}$. Per mole: $2.73/0.050 = 54.6 \text{ kJ/mol}$. The temperature rose, so $\Delta H = -54.6 \text{ kJ/mol}$.

Worked example: a cold pack

4.0 g of ammonium nitrate dissolves in 50 g of water and the temperature falls by 5 K. What energy was absorbed from the water? ($c = 4.2 \text{ J/(g K)}$; ignore the small mass of solute.)

$q = 50 \times 4.2 \times 5 = 1050 \text{ J} (1.05 \text{ kJ})$ absorbed by the dissolving, which is endothermic.

Common mistakes

- Using the mass of the reacting solid instead of the mass of the *solution* being heated.
- Forgetting to convert joules to kilojoules before dividing by moles.
- Putting a positive sign on ΔH for a reaction in which the temperature rose.

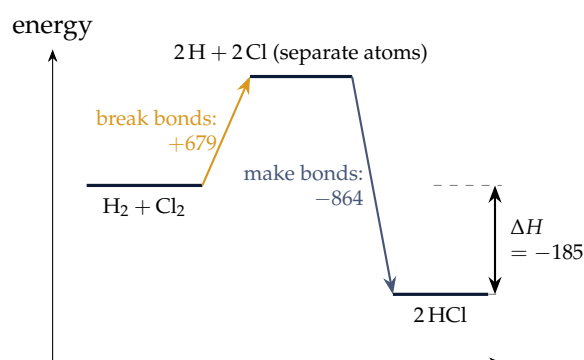
7 Bond energies

Breaking and making bonds. Energy is needed to break a bond (endothermic, +), and energy is released when a bond forms (exothermic, -). A reaction involves both: the old bonds in the reactants are broken, and new bonds in the products are made. The **bond energy** is the energy needed to break one mole of a given bond (given in kJ/mol in a question).

The calculation.

$$\Delta H = \underbrace{\sum(\text{bonds broken})}_{\text{energy in}} - \underbrace{\sum(\text{bonds made})}_{\text{energy out}}$$

If more energy is released making bonds than is needed to break the old ones, ΔH is negative (exothermic); otherwise it is positive. Draw the molecules so that every bond is counted, and remember that a double bond counts as one bond of the double-bond energy (not two single bonds).



In the figure, the reaction $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$ is shown as a trip to separate atoms and back. Breaking one H-H (436) and one Cl-Cl (243) takes 679 kJ; forming two H-Cl bonds (432 each) releases 864 kJ; so $\Delta H = 679 - 864 = -185$ kJ/mol.

Worked example: methane combustion

Use these bond energies in kJ/mol: C-H 410, O=O 500, C=O 800, O-H 460. Calculate ΔH for $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$.

Bonds broken: $4 \times \text{C-H} + 2 \times \text{O=O} = 1640 + 1000 = 2640$. Bonds made: $2 \times \text{C=O} + 4 \times \text{O-H} = 1600 + 1840 = 3440$. $\Delta H = 2640 - 3440 = -800$ kJ/mol: exothermic.

Common mistakes

- Subtracting the wrong way round: it is bonds *broken* minus bonds *made*.
- Forgetting the number of bonds in a molecule: water has two O-H bonds, so $2\text{H}_2\text{O}$ has four.
- Using the bond energies of the whole molecules rather than of each bond type.

8 Putting it together: reading experiments

Many exam questions give a graph of volume or mass against time for two experiments and ask what changed. Use this checklist.

1. **Slope at the start.** Steeper line: faster rate (higher concentration, temperature, surface area, or catalyst).
2. **Final level.** Same final level means the same amount of limiting reactant. A higher final level means more of the limiting reactant (not just a faster reaction).
3. **When it levels off.** The time at which the line becomes flat is when the reaction finishes.

Energy diagrams. Check where the reactants and products are (sign of ΔH), the height of the peak above the reactants (E_a), and whether a dashed line shows a catalysed pathway (lower peak, same start and end).

Explaining answers. A complete explanation of why a rate changes uses three ideas: (a) more collisions per second, (b) a greater fraction of collisions with E_a , (c) so more successful collisions per second. Choose the ones that apply (a for concentration, pressure and surface area; a and b for temperature; b for catalysts).

Worked example: same moles, different speed

1.0 g of magnesium reacts with excess HCl at 20 °C, giving the curve A. In a second experiment the acid is warmed to 40 °C and everything else is unchanged. Describe the new curve.

Same mass of magnesium, so the same final volume of hydrogen. The higher temperature gives a faster rate, so the curve starts steeper and levels off sooner, at the same final level.

Worked example: limiting reactant changes the level

Another experiment uses 2.0 g of magnesium instead of 1.0 g, with plenty of acid. What changes?

The final volume doubles, since twice the moles of magnesium give twice the moles of hydrogen. The initial rate is about the same (the surface area per gram and the acid concentration are the same), but the reaction takes longer to finish.

Exam tip

Draw both experiments on a sketch graph of the same axes. If you are asked about a catalyst: the final level is the same, the curve is steeper. If the question changes the amount of limiting reactant: the final level changes.

Common mistakes

- Saying that a higher temperature produces more product. It reaches the same amount sooner.
- Assuming that a faster reaction is always more exothermic. Rate and energy change are independent.
- Forgetting that doubling the mass of a limiting reactant doubles the final amount of product.

Check yourself

Try these without looking back, then compare with the answers on the next page.

1. A reaction loses 0.90 g of mass in 30 s. Find the mean rate.
2. Give two ways of making magnesium react faster with dilute acid.
3. Why does a higher temperature increase the rate more than the extra collisions alone would suggest?
4. What does a catalyst do to the activation energy and to ΔH ?
5. A reaction has $\Delta H = -45 \text{ kJ/mol}$. Is it exothermic or endothermic? What is ΔH for the reverse?
6. 100 g of water is heated by 10 K. Find q ($c = 4.2 \text{ J/(g K)}$).
7. Bond energies: H–H 436, O=O 500, O–H 460. Find ΔH for $2 \text{ H}_2 + \text{O}_2 \longrightarrow 2 \text{ H}_2\text{O}$.
8. On a graph of volume against time, how can you tell the reaction has finished?

Answers to the self-check

1. $0.90/30 = 0.030 \text{ g/s}$.
2. Any two of: heat the acid, use a more concentrated acid, use magnesium powder instead of ribbon.
3. A much larger fraction of the collisions have energy at least equal to the activation energy.
4. Lowers E_a ; ΔH is unchanged.
5. Exothermic; $+45 \text{ kJ/mol}$.
6. $100 \times 4.2 \times 10 = 4200 \text{ J}$.
7. Broken: $2 \times 436 + 500 = 1372$; made: $4 \times 460 = 1840$; $\Delta H = 1372 - 1840 = -468 \text{ kJ}$.
8. The curve becomes horizontal.

Next step

Heurisco's *ESAT Chemistry: Rates of Reaction and Energetics Practice Set* has twenty original exam-style questions on this lesson, with rate graphs, energy profiles and distribution curves, in order of difficulty, with a full worked solution for each.