Unit 3 · Chemical Kinetics

ANSWER KEY · FOR TEACHERS

Full marks 33

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 Key words

1. rate constant → **e.** the rate of a reaction when every reactant is at 1 mol/L
2. order of reaction → **j.** the sum of the powers of the concentrations in the rate law
3. molecularity → **i.** the number of particles that collide in an elementary step
4. activation energy → **b.** the least energy colliding particles need for a reaction
5. activated complex → **c.** the short-lived, high-energy arrangement at the top of the energy profile
6. half-life → **d.** the time in which half of a reactant is used up
7. catalyst → **a.** a substance that speeds up a reaction by giving it a path of lower activation energy
8. rate-determining step → **f.** the slowest step of a reaction's mechanism

K · 4

Each carries 0.5 mark.

2 Label the diagram

1. activated complex
2. E_a
3. ΔH
4. products

K · 2

Each carries 0.5 mark.

3 Multiple choice

i. **b.** s^{-1} — K · 1

The unit is $(\text{mol L}^{-1})^{1-}\text{Cs}^{-1}$; for n = 1 the concentration cancels and it is $\mathbf{s^{-1}}$ (or min^{-1}). mol L^{-1} s^{-1} is a zero-order constant's, L mol^{-1} s^{-1} a second-order one's.

ii. **c.** 3.0×10^{-5} mol L^{-1} s^{-1} — A · 1

Rate = $-\frac{1}{2}$ d[NO]/dt = $-$d[O_2]/dt, so oxygen is used up at half the rate of NO: $\frac{1}{2} \times 6.0 \times 10^{-5} = \mathbf{3.0 \times 10^{-5}}$ **mol $\mathbf{L^{-1}}$ $\mathbf{s^{-1}}$**.

iii. **c.** 12.5% — A · 1

75 min is three half-lives: 100% → 50% → 25% → **12.5%**.

iv. **c.** gives the reaction a path of lower activation energy — U · 1

A catalyst gives another path with a lower E_a, so more collisions have enough energy. ΔH and the position of equilibrium are unchanged: it speeds up the forward and backward reactions alike.

v. **b.** directly proportional to the starting concentration — U · 1

For a zero-order reaction $t_{½} = [A]_0/2k$: twice the starting concentration takes twice as long to halve. A first-order half-life, 0.693/k, is independent of it; a second-order one is inversely proportional to it.

4 Short answers

a. MARKING SCHEME — U · 2

- ✓ Order from experiment (the rate law); molecularity from the mechanism (an elementary step).
- ✓ Order may be zero or a fraction; molecularity is a whole number, never zero.

b. MARKING SCHEME — U · 2

- ✓ Only collisions with energy at least E_a react.
- ✓ At a higher temperature a much larger share of molecules has energy beyond E_a.

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c. MARKING SCHEME A · 3

✓ Second order in A.
✓ First order in B.
✓ $k = 2.0\ L^2\ mol^{-2}\ s^{-1}$.

5 Long answer

ANSWER U · 4

Enzymes are proteins made by living cells that catalyze the reactions of life.
They are **specific**: each acts on one substrate or one kind of reaction. They are **very efficient**, speeding reactions up enormously in small amounts, and work best at an optimum temperature and pH (about 37 °C for ours); heated much above it, their protein shape is destroyed and they stop working.
The substrate fits into the **active site** of the enzyme as a key fits a lock, forming an **enzyme–substrate complex**; the substrate reacts there, the products leave, and the enzyme is set free unchanged for the next molecule:
$E + S \rightleftharpoons ES \rightarrow E + P$ (E the enzyme, S the substrate, P the products)

MARKING SCHEME

✓ Enzymes are proteins of living cells that act as biological catalysts.
✓ Two characteristics (specific, very efficient, best at a certain temperature and pH).
✓ The substrate fits the active site like a key in a lock, forming the enzyme–substrate complex.
✓ $E + S \rightleftharpoons ES \rightarrow E + P$, the enzyme set free unchanged.

6 Numerical problems

a. ANSWER A · 4

i. $k = 0.693/t_{1/2} = 0.693/35.0 = \mathbf{0.0198\ min^{-1}}$.

ii. 10% is left: $t = \frac{2.303}{k}\log\frac{a}{a-x} = \frac{2.303}{0.0198}\log 10 = \mathbf{116\ min}$.

iii. 120 min is 120/35.0 = 3.43 half-lives: $(½)^{3.43} = \mathbf{0.093}$ (9.3% is left).

iv. $\log\frac{0.80}{[A]} = \frac{0.0198 \times 50.0}{2.303} = 0.430$, so 0.80/[A] = 2.69 and [A] = **0.30 mol/L**.

MARKING SCHEME

✓ $k = 0.0198\ min^{-1}$.
✓ 116 min for 90% to decompose.
✓ 0.093 of it left after 2 hours.
✓ 0.30 mol/L after 50 min.

b. ANSWER A · 4

i. $k = A\,e^{-E_a/RT}$: A is the frequency (pre-exponential) factor, E_a the activation energy.

ii. $E_a = 2.303R\log\frac{k_2}{k_1} \times \frac{T_1T_2}{T_2-T_1} = 2.303 \times 8.314 \times \log 3 \times \frac{290 \times 310}{20} = 41{,}100$ J/mol = **41.1 kJ/mol**.

iii. $\log\frac{k_3}{6.0 \times 10^{-4}} = \frac{41{,}100}{2.303 \times 8.314}\left(\frac{1}{310} - \frac{1}{330}\right) = 0.42$, so $k_3 = 6.0 \times 10^{-4} \times 2.63 = \mathbf{1.6 \times 10^{-3}\ s^{-1}}$.

iv. $1.6 \times 10^{-3} / 2.0 \times 10^{-4} \approx$ **8 times**.

MARKING SCHEME

✓ The Arrhenius equation, with A and E_a named.
✓ E_a = 41.1 kJ/mol.
✓ $k = 1.6 \times 10^{-3}\ s^{-1}$ at 330 K.
✓ About 8 times faster.

7 Think

ANSWER

The reaction of wood with oxygen is exothermic, but it has a high activation energy: at room temperature almost no collisions between the molecules have that much energy, so the rate is practically zero.

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The match heats a small part of the wood, so there many collisions have energy beyond E_a and the wood starts to burn. The heat given out by the burning part then raises the next part above that energy too, so the fire keeps going without the match.

MARKING SCHEME

- ✓ The reaction is exothermic but has a high activation energy, so at room temperature it is far too slow.
- ✓ The match supplies the energy for some collisions to pass E_a.
- ✓ The heat the burning wood gives out keeps raising the next part past E_a.

8 Activity: Temperature and the speed of a fizz

(not marked)

WHAT STUDENTS SHOULD FIND

The warm water finishes first and the cold water last: the warmer the water, the larger the share of collisions with energy beyond the activation energy. Powder reacts faster still: it has a far larger surface area, so many more particles can collide at once.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	7	10	13	3	**33**

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