08 Reaction Kinetics

Set B **Answer key**

A Multiple choice

5 MARKS

1 **A** 28 minutes [1]

[Reactant] falls from 0.48 to 0.24 to 0.12 to 0.06 mol dm^{-3} in three half-lives, 14 min each.

[Reactant] falls from 0.40 to 0.20 to 0.10 mol dm^{-3} in two half-lives of 14 min each, 28 min in total.

2 **B** 5.0×10^{-3} mol dm^{-3} [1]

$$t_{½} = \frac{\ln 2}{k} = \frac{0.693}{3.6 \times 10^{-3}} = 192.5 \text{ s}$$

$$\text{Number of half-lives} = \frac{385}{192.5} = 2$$

$$c_t = c_0(½)^n = (2.0 \times 10^{-2}) \times (½)^2 = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$$

3 **B** 1 and 2 only [1]

1 Correct. Half-lives of a zero order reaction decrease with concentration, while the half-lives of second and higher order reactions increase with concentration. Only first order reactions have constant half-lives.

2 Correct. Initial rate measurements allow the order with respect to each of the reactants to be determined, and hence the overall order of the reaction.

3 Wrong. Rate has a fixed unit of mol dm^{-3} s^{-1}. Depending on the order of the reaction, the unit for the rate constant will vary, since rate = k[reactant]^n.

4 **C** The rate constant k has units of $atm^{-2}\ s^{-1}$. [1]

Initial pressure of O_2 = initial total pressure – initial pressure of NO = 0.60, 1.20, 1.20 and (x – 0.20) atm.

Let rate = $kp_{NO}^{x}p_{O_2}^{y}$. Experiments I and II: $\frac{2.16}{1.08} = \frac{k(0.40)^x(1.20)^y}{k(0.40)^x(0.60)^y}$, so $2 = 2^y$ and y = 1

Experiments II and III: $\frac{8.64}{2.16} = \frac{k(0.80)^x(1.20)^y}{k(0.40)^x(1.20)^y}$, so $4 = 2^x$ and x = 2

or From experiments I and II, the pressure of NO remained unchanged while the pressure of O_2 doubled. The rate doubled, so the reaction is first order with respect to O_2.

From experiments II and III, the pressure of O_2 remained unchanged while the pressure of NO doubled. The rate quadrupled, so the reaction is second order with respect to NO.

A The reaction is second order with respect to NO.

B The rate equation should be rate = $kp_{NO}^{2}p_{O_2}$.

D Comparing experiments I and IV, when the pressure of NO is halved, the rate remains the same. Since the order with respect to NO is 2, the pressure of O_2 must have quadrupled. Hence the partial pressure of O_2 must be $0.60 \times 4 = 2.40 = x - 0.20$, so x = 2.60.

5 **D** 2, 3 and 4 only [1]

1 Wrong. H^+ is not a catalyst, as it is consumed without being regenerated.

2 Correct. Both are intermediates of the reaction, as they are formed from reactants and consumed to form products in subsequent steps.

3 Correct. Step 1 is the slow step, so it must have the highest E_a. Step 2 must therefore have a lower E_a than step 1.

4 Correct. The slow step (step 1) shows that the reaction is first order with respect to H_2O_2 and first order with respect to I^-.

B Structured questions

32 MARKS

6 **(a)** Let rate = $kp_{NO}^{x}p_{H_2}^{y}$. Experiments 1 and 2: $\frac{3.75 \times 10^{-8}}{1.50 \times 10^{-7}} = \frac{k(0.80)^x(0.64)^y}{k(1.60)^x(0.64)^y}$, so $\frac{1}{4} = (\frac{1}{2})^x$ and x = 2. The order with respect to NO is 2. [1]

Experiments 1 and 3: $\frac{7.50 \times 10^{-8}}{1.50 \times 10^{-7}} = \frac{k(1.60)^x(0.32)^y}{k(1.60)^x(0.64)^y}$, so $\frac{1}{2} = (\frac{1}{2})^y$ and y = 1. The order with respect to H_2 is 1. [1]

or From experiments 1 and 2, as p_{NO} halves and p_{H_2} is kept constant, the rate decreases by 4 times. Hence, the order with respect to NO is 2.

From experiments 1 and 3, as p_{H_2} halves and p_{NO} is kept constant, the rate decreases by 2 times. Hence, the order with respect to H_2 is 1.

rate = $kp_{NO}^{2}p_{H_2}$ [1]

(b) Experiment 1: $k = \frac{1.50 \times 10^{-7}}{(1.60)^2(0.64)}$

= **$9.16 \times 10^{-8}\ atm^{-2}\ s^{-1}$** [1] [1]

7 **(a)**

Let rate = k[isoprene]^x[Br_2]^y. Experiments 2 and 3: $\frac{3.52 \times 10^{-3}}{1.76 \times 10^{-3}} = \frac{k(0.08)^x(0.128)^y}{k(0.08)^x(0.064)^y}$, so 2 = 2^y and y = 1. The order of reaction with respect to Br_2 is one. [1]

Experiments 1 and 2: $\frac{1.76 \times 10^{-3}}{0.88 \times 10^{-3}} = \frac{k(0.08)^x(0.064)^y}{k(0.04)^x(0.064)^y}$, so 2 = 2^x and x = 1. The order of reaction with respect to isoprene is one. [1]

or Using experiments 2 and 3: keeping [isoprene] constant, when [Br_2] doubled, the initial rate doubled. The order of reaction with respect to Br_2 is one.

Using experiments 1 and 2: keeping [Br_2] constant, when [isoprene] doubled, the initial rate doubled. The order of reaction with respect to isoprene is one.

(b)

rate = k[isoprene][Br_2] [1]

8 **(a)**

rate = k[CH_3COCH_3][H^+], second order [1]

(b)

Mechanism A fits the observed kinetic data. The slow step, which is the rate-determining step, is a bimolecular elementary reaction between propanone and the acid. Its rate equation is of the form rate = k′[CH_3COCH_3][H^+], which is similar to the experimentally determined rate equation. [1]

The reaction is zero order with respect to iodine, so iodine is only involved in the fast step (which is not rate-determining). [1]

The rate-determining step in mechanism B is a bimolecular elementary reaction between propanone and iodine, with rate = k″[CH_3COCH_3][I_2]. Since the rate is found to be independent of [I_2], mechanism B is inconsistent with the observed kinetic data. [1]

(c)

Bromine is not involved in the rate-determining step, so the reaction is zero order with respect to bromine. The rate is therefore expected to be identical to that of the reaction between propanone and iodine under the same experimental conditions. [1]

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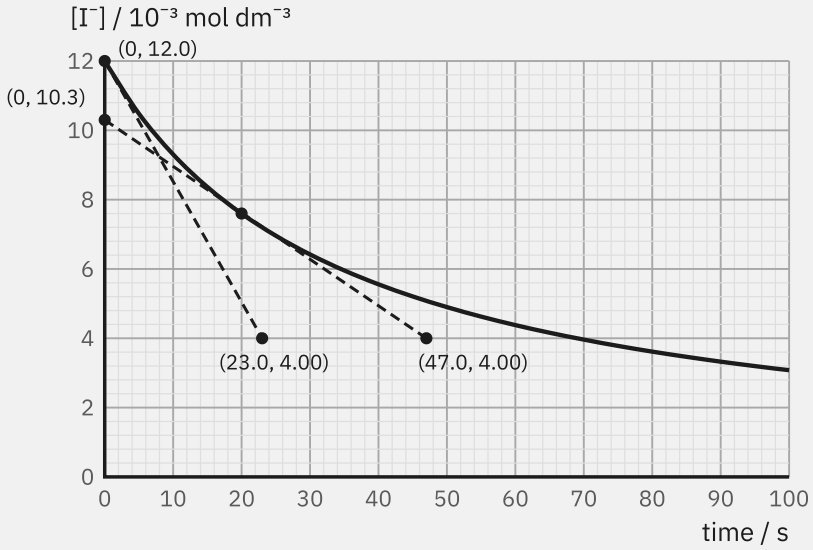
Let the original [NO_2] be c mol dm^{-3}. Then [NO_2] after the 1st half-life = $\frac{c}{2}$ mol dm^{-3}.

1st half-life = $\frac{1}{kc}$, 2nd half-life = $\frac{2}{kc}$

Total time taken = $\frac{3}{kc} = \frac{3}{0.54c} = 46.3$ [1]

c = **0.120 mol dm^{-3}** [1]

10 **(a)**



Initial rate = $-\frac{4.00 \times 10^{-3} - 12.0 \times 10^{-3}}{23.0 - 0}$ = **3.48×10^{-4} mol dm^{-3} s^{-1}** [1]

Rate at 20 s = $-\frac{4.00 \times 10^{-3} - 10.3 \times 10^{-3}}{47.0 - 0}$ = **1.34×10^{-4} mol dm^{-3} s^{-1}** [1]

(b)

Let n be the order with respect to I^-. At 20 s, $[I^-] = 7.60 \times 10^{-3}$ mol dm^{-3}.

$\frac{\text{initial rate}}{\text{rate at 20 s}} = \frac{3.48 \times 10^{-4}}{1.34 \times 10^{-4}} = (\frac{12.0 \times 10^{-3}}{7.60 \times 10^{-3}})^n$

n = 2.09, so the reaction is **second order** with respect to I^-. [1]

(c)

This keeps the concentration of $Fe^{3+}(aq)$ approximately constant, so that the rate is changed by the concentration of $I^-(aq)$ only. [1]

(d)

rate = $k[Fe^{3+}][I^-]^2$ [1]

(e)

$3.48 \times 10^{-4} = k(0.150)(12.0 \times 10^{-3})^2$

k = **16.1 mol^{-2} dm^6 s^{-1}** [1] [1]

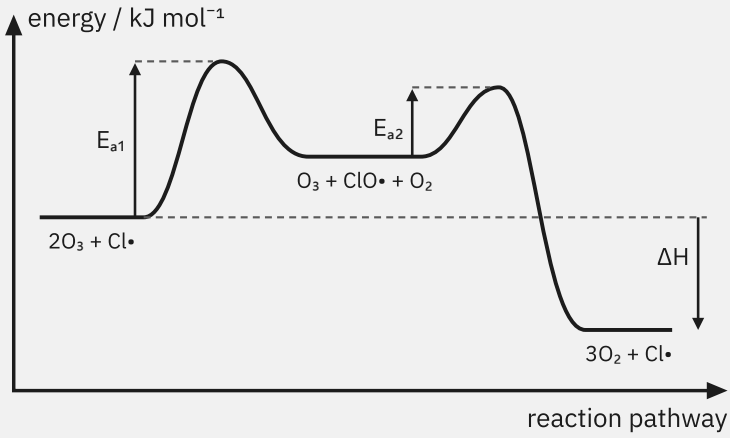
(f)

Since the rate constant of the new experiment is lower than that of the original experiment, the new experiment was carried out at a lower temperature. [1]

11 **(a)**

Cl• acts as a catalyst. It is used in step 1 and regenerated in step 2. [1]

(b)



Correct shape: two steps, with the overall reaction exothermic. [1]

The axis, the balanced species and the enthalpy change are labelled correctly. [1]

NOTE Step 1 is likely to be endothermic, as more energy is taken in to break the stronger O–O bond in ozone than is released in forming the weaker Cl–O bond. Step 2 must then be exothermic for the overall ΔH to be negative.

12 **(a)**

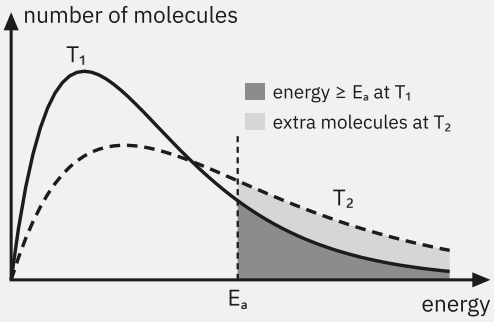
Platinum acts as a heterogeneous catalyst in the decomposition of NH_3 into N_2 and H_2.

At very low pressures, the active sites on the catalyst surface are not saturated with ammonia molecules. Hence, the rate of decomposition of ammonia depends only on the partial pressure of ammonia, and the reaction is first order with respect to ammonia. [1]

At moderate or high pressures, most, if not all, of the active sites on the platinum surface are taken up by ammonia molecules. [1]

Any increase in the partial pressure of ammonia then has no effect on the rate of decomposition, and the reaction is zero order with respect to ammonia. The limiting factor is the availability of active sites. [1]

(b)



As temperature increases, the average speed of the reactant particles increases. This leads to a higher collision frequency, which contributes to an increase in the reaction rate. [1]

However, the large increase in reaction rate from a small rise in temperature is mainly because, at a higher temperature, the proportion of reactant particles with energy greater than or equal to the activation energy increases significantly, as the Maxwell–Boltzmann distribution curve shows. [1]

Consequently, the frequency of effective collisions increases accordingly, and hence the reaction rate increases. An increase in temperature also leads to a larger rate constant. [1]