08 Reaction Kinetics

Set A **Answer key**

A From the lesson

10 MARKS

1 $\frac{4}{2} \times 2.0 \times 10^{-4} = \mathbf{4.0 \times 10^{-4}\ mol\ dm^{-3}\ s^{-1}}$ [1]

2 Overall order 3: $k = \frac{\text{mol dm}^{-3}\ \text{min}^{-1}}{(\text{mol dm}^{-3})^3} = \mathbf{mol^{-2}\ dm^{6}\ min^{-1}}$ [1]

3 Let rate = $k[A]^a[B]^b$. Experiments 1 and 2: $\frac{2.0 \times 10^{-3}}{2.0 \times 10^{-3}} = \frac{k(0.20)^a(0.10)^b}{k(0.10)^a(0.10)^b}$, so $1 = 2^a$ and a = 0. The reaction is zero order with respect to A. [1]

Experiments 1 and 3: $\frac{1.8 \times 10^{-2}}{2.0 \times 10^{-3}} = \frac{k(0.10)^a(0.30)^b}{k(0.10)^a(0.10)^b}$, so $9 = 3^b$ and b = 2. The reaction is second order with respect to B. [1]

or Comparing experiments 1 and 2: when [A] is doubled and [B] is kept constant, the initial rate is unchanged, so the reaction is zero order with respect to A.

Comparing experiments 1 and 3: when [B] is tripled and [A] is kept constant, the initial rate increases 9 times, so the reaction is second order with respect to B.

Rate equation: $\mathbf{rate = k[B]^2}$ [1]

4 As temperature increases, the average kinetic energy of the reactant particles increases, so a greater proportion of reactant particles have energy greater than or equal to the activation energy, E_a. [1]

Hence, the frequency of effective collisions increases, and the rate of reaction increases. [1]

5 The power of its concentration term in the experimentally determined rate equation. [1]

6 $k = \ln 2 \div 20 = \mathbf{0.0347\ s^{-1}}$ [1]

7 A catalyst in the same phase as the reactants. [1]

B Practice

23 MARKS

8 **A** rate = k[Y] [1]

Since rate $\propto \frac{1}{t}$, let rate = $k[X]^x[Y]^y$. Rows 1 and 3: $\frac{1/44}{1/44} = \frac{k(0.10)^x(0.05)^y}{k(0.05)^x(0.05)^y}$, so $1 = 2^x$ and x = 0

Rows 1 and 2: $\frac{1/22}{1/44} = \frac{k(0.05)^x(0.10)^y}{k(0.05)^x(0.05)^y}$, so $2 = 2^y$ and y = 1

or Comparing experiments 1 and 3: when [X] was doubled and [Y] kept constant, the time taken remained unchanged, hence the rate remained unchanged. The reaction is zero order with respect to X.

Comparing experiments 1 and 2: when [Y] was doubled and [X] kept constant, the time taken was halved, hence the rate doubled. The reaction is first order with respect to Y.

9 **A** rate = $k[CH_3COCH_3][H^+]$ [1]

To keep the total volume of every experiment the same, halve the volume of all reactants for experiment 4: 5, 20, 10 and 15 cm^3, a total of 50 cm^3. The rate remains unchanged, as the proportion of each reactant in the solution does not change when the volumes are halved.

Let relative rate = $k(V_{propanone})^m(V_{H^+})^n(V_{Br_2})^p$ at the same total volume. Experiments 1 and 2: $\frac{1}{2} = (\frac{10}{20})^m$, so m = 1. Experiments 1 and 3: $\frac{1}{2} = (\frac{5}{10})^n$, so n = 1

Experiment 4 with all volumes halved (5, 20, 10, 15 cm^3) and experiment 1: $\frac{2}{2} = (\frac{5}{10})^p$, so p = 0

or By comparing experiments 1 and 2, when the volume of CH_3COCH_3 is halved, the rate is halved. The reaction is thus first order with respect to CH_3COCH_3.

By comparing experiments 1 and 3, when the volume of H^+ is halved, the rate is halved. The reaction is thus first order with respect to H^+.

By comparing experiment 1 and experiment 4 (after halving all volumes), when the volume of Br_2 is halved, the rate remains the same. The reaction is thus zero order with respect to Br_2.

10 **(a)** Let rate = $k[NO]^x[H_2]^y$. Experiments 1 and 2: $\frac{0.013}{0.0033} = \frac{k(0.0040)^x(0.012)^y}{k(0.0020)^x(0.012)^y}$, so $4 = 2^x$ and x = 2. The reaction is **second order** with respect to NO. [1]

Experiments 4 and 5: $\frac{0.040}{0.020} = \frac{k(0.012)^x(0.0040)^y}{k(0.012)^x(0.0020)^y}$, so $2 = 2^y$ and y = 1. The reaction is **first order** with respect to H_2. [1]

or Comparing experiments 1 and 2: when [NO] was doubled and $[H_2]$ kept constant, the rate increased to 4 times the original rate, so the reaction is second order with respect to NO.

Comparing experiments 4 and 5: when $[H_2]$ was doubled and [NO] kept constant, the rate doubled, so the reaction is first order with respect to H_2.

(b) rate = $k[NO]^2[H_2]$ [1]

Using values from experiment 6: $0.060 = k(0.012)^2(0.0060)$

k = **6.94×10^4 mol^{-2} dm^6 s^{-1}** [1]

11 **(a)(i)**

rate = $k[NO]^2[O_2]$ [1]

(ii)

The rate constant is a proportionality constant for a given reaction at a specified temperature, denoted by k in (i). [1]

The order of reaction is the power to which the concentration of that reactant is raised in the experimentally determined rate equation. The order of reaction with respect to NO is 2 and with respect to O_2 is 1. [1]

The rate-determining step is the slowest step in a sequence of elementary reactions, and it determines the rate of the reaction. Here, it is $N_2O_2 + O_2 \rightarrow 2NO_2$. [1]

(b)(i)

A catalyst lowers the E_a by providing an alternative pathway for the reaction. [1]

A greater proportion of reactant particles have energy greater than or equal to the lowered E_a. Hence, the frequency of effective collisions increases and the reaction rate increases. [1]

(ii)

A catalyst increases the rate of reaction. From the rate equation, rate = k[A], where A is the reactant, if the rate increases while all concentrations remain the same, then the value of k must also increase. Hence, the rate constant is increased by the presence of a catalyst. [1]

or From the Arrhenius equation, $k = Ae^{-E_a/RT}$, the rate constant is affected by E_a.

12 **(a)**

Doubling the partial pressure doubles the concentration, so new rate = $k(2[A]_0)^2(2[B]_0)$ = **8R** [1]

(b)

new rate = $k(2[A]_0)^2([B]_0)$ = **4R** [1]

(c)

Doubling the volume halves the concentration, so new rate = $k(½[A]_0)^2(½[B]_0)$ = **⅛R** [1]

(d)

The partial pressures of the reactants remain constant, so there is no change: new rate = $k([A]_0)^2([B]_0)$ = **R** [1]

13 **(a)**

Let rate = $k[\text{sucrose}]^x[HCl]^y$. Experiments I and II: $\frac{0.036}{0.024} = \frac{k(0.15)^x(0.10)^y}{k(0.10)^x(0.10)^y}$, so $1.5 = 1.5^x$ and x = 1. The reaction is first order with respect to sucrose. [1]

Experiments I and III: $\frac{0.048}{0.024} = \frac{k(0.10)^x(0.20)^y}{k(0.10)^x(0.10)^y}$, so $2 = 2^y$ and y = 1. The reaction is first order with respect to HCl. Hence rate = k[sucrose][HCl]. [1]

or Comparing experiments I and II: when the initial [sucrose] was increased 1.5 times, the initial rate increased 1.5 times, so rate ∝ [sucrose]. The reaction is first order with respect to sucrose.

Comparing experiments I and III: when the initial [HCl] was doubled, the initial rate also doubled, so rate ∝ [HCl]. The reaction is first order with respect to HCl.

Using data from experiment I, $k = \frac{0.024}{(0.10)(0.10)}$ = **2.40 mol^{-1} dm^3 s^{-1}** [1]

(b)

0.048 = 2.40(0.25)(y), so y = **0.08** [1]

(c)

Since HCl is a catalyst, its concentration is effectively constant during the reaction, so rate = k′[sucrose], where k′ = k[HCl]. The reaction is pseudo first order, with a constant half-life. **[1]**

In experiment II, [HCl] is the same as in experiment I, so $t_{½}$ = **3.0 s**. In experiment III, [HCl] is double that of experiment I, so $t_{½}$ = **1.5 s**. **[1]**