16 Kinetics II

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1 **a)** $H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$ [1]

b) Rate = $k[H_2O_2(aq)][I^-(aq)]$ [2]

c) Second order [1]

d) The first step [1], which includes the two species that feature in the rate equation. [1]

2 **a)** Labelled axes [1]; accurate plot [1]; smooth curve. [1]

b) Three half-lives = 40×10^3 s [2]; half-life of first order reaction independent of initial concentration. [1]

c) Method of calculating gradient [1]; values for gradients [2]; units: mol dm^{-3} s^{-1}. [1]

d) Axes [1]; accurate plot with straight line. [1]

$k = 1.8 \times 10^{-5}$ s^{-1} [1] for value, [1] for units

3 **a)** Axes [1]; plot and curve. [1]

Half-life from 20×10^{-3} mol dm^{-3}: 3.6×10^3 s [1]

Half-life from 12×10^{-3} mol dm^{-3}: 7.6×10^3 s [1]

Lower starting concentration – higher half-life. [1]

b) Tangents drawn [1]; gradients calculated [1]; concentration units included. [1]

c) Log (rate) and log (concentration) values quoted. [2]

Graph correctly plotted with labelled axes. [2]

Order 2 derived from line of best fit. [2]

4 **a)** **i)** Changing [X] does not affect the rate [1]; zero order. [1]

ii) Rate quadruples if [Y] doubles [1]; second order. [1]

b) Rate = $k[Y]^2$ [2]

c) $k = \dfrac{(1 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1})}{(1 \times 10^{-1}\ \text{mol dm}^{-3})^2} = 1 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ [1] for value, [1] for units

d) Rate-determining step involves two Y molecules. [1]

$Y + Y \rightarrow Y_2$ *slow* [1]

$Y_2 + X \rightarrow XY_2$ *fast* [1]

e) Range of answers possible (*1 mark for each point made up to 3*). Such as:

- Rate equations help to deduce reaction mechanisms; this information can inform methods of chemical synthesis.
- Understanding catalytic activity (including enzymes) can lead to the development of more efficient manufacturing processes or guide drug design and development.
- Rate measurements are important in controlling chemical changes in laboratory and industrial processes; chemical engineers use rate data when designing chemical plants.

5 **a)** The concentrations of all the reacting chemicals are known at the start before they have begun to be used up. [1] It is then only necessary to follow the concentrations of one of the reactants long enough to determine the initial rate from a concentration–time graph. [1]

b) **i)** The reaction is second order with respect to hydrogen. [1]

ii) The reaction is first order with respect to NO. [1]

c) Rate = $k[H_2]^2[NO]$ [1]

d) $$k = \frac{(1.20\ \text{mol dm}^{-3}\ \text{s}^{-1})}{(0.012\ \text{mol dm}^{-3})^2(0.002\ \text{mol dm}^{-3})} = 4.2 \times 10^5\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

[1] for value, [1] for units

e) Most reactions take place in several steps. Only one of these steps is rate determining. [1] It is the concentrations of the molecules or ions involved in the rate-determining step that appear in the rate equation. [1]

f) **i)** As the temperature rises the value of the rate constant gets larger. [1]

ii) The rate of reaction increases as the temperature rises. This happens because as it gets hotter the mean kinetic energy of the molecules increases. [1] This is shown by a shift in the curve of the Maxwell–Boltzmann distribution to the right. The consequence is that there are more molecules with enough energy to react when they collide. [1] The collisions have enough energy to exceed the activation energy for the reaction. [1] The rate increases even if the concentrations of reactants stays the same. This is explained, in the rate equation, by the fact that the value of the rate constant increases. [1]

6 **a)** The clock procedure measures the initial rate – in this case by finding the time taken for a small, fixed amount of iodine to form. [1] At first the thiosulfate ions immediately turn the iodine back to iodide ions [1]; but once all the thiosulfate is used up the iodine produces a deep blue-black colour with the starch indicator. [1]

b) Completion of table as in Figure 16.10 [3]:

Temperature, *T*/K	288	292.5	299	308	315
Time, *t*, for the blue colour to appear/s	10.0	7.0	5.0	3.5	2.5
ln (1/*t*)	–2.30	–1.95	–1.61	–1.25	–0.92
1/*T* /K^{-1}	0.00347	0.00342	0.00334	0.00325	0.00318

Plot of graph of ln (1/*t*) against 1/*T* with appropriate scales and accurate linear plot. [3]

Gradient = –4180 K [1] = $\frac{-E_a}{R}$

E_a = 35 kJ mol^{-1} [1]

c) The catalyst provides an alternative reaction pathway with a lower activation energy. [1] One possible alternative route is that when the catalyst is present, the iron(III) ions oxidise iodide ions to iodine [1], and that peroxodisulfate(VI) ions then oxidise the resulting iron(II) ions back to iron(III), thus regenerating the catalyst. [1] Perhaps the negative peroxodisulfate(VI) ions react more readily with positive iron(II) ions than with negative iodide ions. [1]

7 a) $3ClO^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq)$ [1]

Chlorate(I) (+1) is oxidised to chlorate(V) (+5) and reduced to chloride (–1). [2]

b) The rate decreases by a factor of 4. [1]

c) The rate-determining step appears to involve two chlorate(I) ions. [1]

Step 1: *slow – rate-determining* [1]

$2ClO^-(aq) \rightarrow ClO_2^-(aq) + Cl^-(aq)$ [1]

Step 2: fast [1]

$ClO_2^-(aq) + ClO^-(aq) \rightarrow ClO_3^-(aq) + Cl^-(aq)$ [1]

d) One possibility is to look for evidence that $ClO_2^-(aq)$ exists as an intermediate. [1] It might be detected spectroscopically. [1] This might be hard to do since the second step is fast and so the intermediate disappears very quickly.

8 a) Reactions happen when molecules collide. Collisions with an energy greater than the activation energy lead to reaction. [1] Typically the activation energy is to the right-hand end of the Maxwell–Boltzmann distribution, so that only a small proportion of collisions lead to reaction. [1] Raising the temperature shifts the Maxwell–Boltzmann distribution to the right. [1] The value of the activation energy does not change but the area under the curve of the distribution representing the number of molecules with enough energy to react can increase markedly for a small rise in temperature. [1]

b) Raising the temperature increases the speed with which molecules in a gas move so it increases their kinetic energy. [1] Raising the temperature increases not only the number of collisions per second, but also the energy of the collisions. [1] So the increase in reaction rate is the result of two factors: collision rate and the energy per collision. [1]

c) Plot of graph of ln $(1/t)$ against $1/T$ with appropriate scales and accurate linear plot. [3]

The gradient of the graph = -2.24×10^4 K [2]

$E_a = 2.24 \times 10^4 \text{ K} \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ [1]

$= 186\,000 \text{ J mol}^{-1} = 186 \text{ kJ mol}^{-1}$ [1]