

Question 8

(a) A reasonable rate equation would be:

$$J = k_R [S_2O_3^{2-}]^\alpha [IO_3^-]^\beta [H^+]^\gamma$$

where α , β and γ are partial orders of reaction and k_R is the rate constant.

The initial rate of reaction can be expressed as:

$$J_0 = k_R [S_2O_3^{2-}]_0^\alpha [IO_3^-]_0^\beta [H^+]_0^\gamma$$

Experiments are therefore performed in which the initial concentrations of selected reagents are kept constant; it is not really necessary to have reagents in excess.

The initial rates of reaction are measured as a function of:

- (i) $[S_2O_3^{2-}]_0$ with $[IO_3^-]_0$ and $[H^+]_0$ held fixed;
- (ii) $[IO_3^-]_0$ with $[S_2O_3^{2-}]_0$ and $[H^+]_0$ held fixed;
- (iii) $[H^+]_0$ with $[S_2O_3^{2-}]_0$ and $[IO_3^-]_0$ held fixed.

For example, for the first set of experiments:

$$J_0 = k_R' [S_2O_3^{2-}]_0^\alpha \quad (k_R' = k_R [IO_3^-]_0^\beta [H^+]_0^\gamma)$$

so that

$$\ln J_0 = \ln k_R' + \alpha \ln [S_2O_3^{2-}]_0$$

so a plot of $\ln J_0$ versus $\ln [S_2O_3^{2-}]_0$ will be a straight line with slope α .

A similar strategy can be used to determine both β and γ .

(If α , β and γ are integers, then their values could be found by inspecting a table of results, rather than graphical plotting.)

Once the partial orders of reaction are known, the data collected in experiments (i), (ii) and (iii) can then be used to find an average value of the rate constant, k_R . The rate equation has then been fully established.

Since the measurement of initial rates depends only on the species present initially in the reaction mixture, the method is generally used to study reactions in which a product decomposes, or interferes in some way with the progress of reaction.

(b) (i) Using the reaction variable, $[I^-] = x$; $[H^+] = [H^+]_0 - 6x$

so that

$$[H^+] = [H^+]_0 - 6[I^-]$$

When $t = 0.5$ s,

$$\begin{aligned} [H^+] &= 1.0 \times 10^{-4} \text{ mol dm}^{-3} - 6 \times 2.5 \times 10^{-6} \text{ mol dm}^{-3} \\ &= 8.5 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

(ii) The experimental rate equation given in the question is second order in $[H^+]$, so the appropriate integrated form (given on the data sheet) is:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = ak_R t \quad (\text{with } a = 6 \text{ in this case})$$

Given that $[H^+] = 8.5 \times 10^{-5} \text{ mol dm}^{-3}$ after 0.5 s of reaction, and also that $[H^+]_0 = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, then

$$\frac{1}{8.5 \times 10^{-5} \text{ mol dm}^{-3}} - \frac{1}{1.0 \times 10^{-4} \text{ mol dm}^{-3}} = 6 \times k_R \times 0.5 \text{ s}$$

or

$$\frac{(1.176 - 1.0) \times 10^4 \text{ mol}^{-1} \text{ dm}^3}{6 \times 0.5 \text{ s}} = k_R$$

so

$$k_R = 5.9 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$