Suggested Answers for Self-Check

1 **(a)** $5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

Method 1: Measuring change in colour intensity with time

MnO_4^- is purple. Since colour intensity $\propto$ $[MnO_4^-]$, the change in the colour intensity of MnO_4^- over time may be used to follow the rate of reaction.

1. The reactants are mixed and the colour intensity of the reaction mixture may be measured using a colorimeter and the readings are taken at regular time intervals.
2. Samples of $KMnO_4(aq)$ of various concentrations (e.g., 0.001, 0.005, 0.100 mol dm^{-3}) are prepared and their colour intensities measured using the colorimeter. A calibration curve is obtained by plotting colour intensity against concentration. The concentration of $KMnO_4$ corresponding to each colour intensity obtained in Step 1 is found using the calibration curve. The concentration of $KMnO_4$ is then plotted against time.
3. Instantaneous rate is found by drawing a tangent to the curve and finding its gradient g_1, where rate = $-g_1$.

   (Note: If the graph of colour intensity is plotted against time, then instantaneous rate is proportional to the gradient, g_1, of the tangent drawn to the curve at that particular time, where rate $\propto -g_1$.)

Method 2: Sampling, quenching and titration

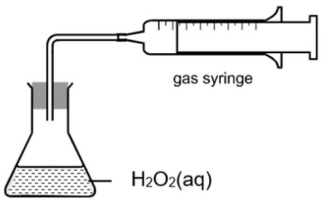
1. The reactants are mixed, and the stopwatch is started simultaneously.
2. Aliquots (same volume) of the reactant mixture are withdrawn and quenched at regular time intervals (e.g., two-minute intervals) using excess KI(aq). I^- reacts with MnO_4^- instantaneously and quantitatively to form I_2.
3. The amount of I_2 formed in each aliquot is found by titrating against a standard solution of $Na_2S_2O_3$.
4. Volume of $Na_2S_2O_3(aq)$ $\propto$ amount of I_2 formed $\propto$ amount of unreacted MnO_4^- $\propto$ $[MnO_4^-]$ remaining (since each aliquot has the same volume). Hence a graph of volume $Na_2S_2O_3(aq)$ against time is plotted, which is similar to a graph of $[MnO_4^-]$ against time.
5. Instantaneous rate is proportional to the gradient, g_1, of the tangent drawn to the curve at that particular time, where rate $\propto -g_1$.

(Other possible method: Volume of CO_2 evolved can be measured over time.)

(b) $2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

Method 1: Measuring volume of oxygen gas evolved

Since a gas is evolved, the change in volume of oxygen evolved over time may be monitored.



1. Set up the apparatus as shown and measure the volume of O_2 gas collected in the syringe at regular time intervals.
2. A graph of volume of $O_2(g)$ against time is plotted.
3. Instantaneous rate is proportional to the gradient, g_1, of the tangent drawn to the curve at that particular time, where rate $\propto g_1$.

Method 2: Sampling, quenching and titration

1. Aliquots of the H_2O_2 solution are pipetted at suitable time intervals into conical flasks.
2. At a suitable time, ice-cold water is added to the conical flask to slow down or quench the reaction.

3. Each quenched aliquot is then titrated against a standard solution of acidified $KMnO_4$.
4. Volume of $KMnO_4 \propto$ amount of unreacted $H_2O_2 \propto [H_2O_2]$ remaining (since each aliquot has the same volume). Hence, a graph of the volume of $KMnO_4$ used against time can be plotted, which is similar to a graph of $[H_2O_2]$ against time.
5. Instantaneous rate is proportional to the gradient, g_1, of the tangent drawn to the curve at that particular time, where rate $\propto -g_1$.

2 *See last page*.

3 Ans: C

Change in pH cannot be used as the reaction is **catalysed** by H^+, which implies that $[H^+]$ (and hence pH) remains unchanged in the reaction $\Rightarrow$ **A** is incorrect

Measuring rate of reaction several times but with a different concentration of ethyl ethanoate each time allows the order of reaction with respect to ethyl ethanoate (but not H^+) to be found $\Rightarrow$ **B** is incorrect

Measuring rate of reaction several times but with a different concentration of H_2SO_4 each time allows the order of reaction with respect to H^+ to be found $\Rightarrow$ **C** is correct

Since the reaction is **catalysed** by H^+, $[H^+]$ remains unchanged in the reaction. Hence, the removal of samples at various time intervals and titration against standard aq NaOH would not allow the order of reaction with respect to H^+ to be found $\Rightarrow$ **D** is incorrect

4 Ans: B

Time/min	Amount of XY_2	Amount of X	Amount of Y
0	n	-	-
45	0.5n	0.5n	n
90	**0.25n**	**0.5n + 0.25n = 0.75n**	**n + 0.5n = 1.5n**
135	0.125n	0.75n + 0.125n = 0.875n	1.5n+0.25n = 1.75n
180	0.0625n	0.875n + 0.0625n = 0.9375n	1.75n+0.125n = 1.875n

At 90 min, mole ratio of XY_2: Y is 0.25n : 1.5n which is 1 : 6.

5 rate = $k[A]^2[B]$ and original rate = $\boldsymbol{R} = k[A]_0^2[B]_0$

	(a)	**(b)**	**(c)**	**(d)**
change	double partial pressures of A & B	double partial pressure of A	double volume of reacting vessel	double total pressure with inert gas
new rate	$8\boldsymbol{R}$	$4\boldsymbol{R}$	$\frac{1}{8}\boldsymbol{R}$	$\boldsymbol{R}$
reason	doubling partial pressure ≡ doubling concentration	doubling partial pressure ≡ doubling concentration	doubling volume ≡ halving concentration	partial pressure of reactants remain constant = no change
working	new rate $= k(2[A]_0)^2(2[B]_0) = 8\boldsymbol{R}$	new rate $= k(2[A]_0)^2([B]_0) = 4\boldsymbol{R}$	new rate $= k(\frac{1}{2}[A]_0)^2(\frac{1}{2}[B]_0) = \frac{1}{8}\boldsymbol{R}$	new rate $= k([A]_0)^2([B]_0) = \boldsymbol{R}$

6 rate = $-\,d[I_2]/dt$ = –gradient of graph
For each experiment, $-d[I_2]/dt$ = constant.
Order of reaction with respect to I_2 = 0

To determine order of reaction wrt **J**, we compare rates of reaction when [**J**] = a and [**J**] = 2a
When [**J**] =a, rate = y/10
When [**J**] = 2a, rate = 2y/5
So, when [**J**] × 2, rate × $\left(\frac{\frac{2y}{5}}{\frac{y}{10}} = 4\right)$
$\Rightarrow$ rate $\propto$ [**J**]^2
Hence order of reaction with respect to **J** = 2.

7 **Ans: D**
When only $[H_2O_2]$ × 2, initial rate × 2 $\Rightarrow$ Rxn is first order wrt H_2O_2.
When $[H_2O_2]$ × 1.5 and $[I^-]$ × 2, initial rate × 3 $\Rightarrow$ Rxn is first order wrt I^-.
When $[H_2O_2]$ × 3, and both $[I^-]$ and $[H^+]$ × 2, initial rate × 6 $\Rightarrow$ Rxn is zero order wrt H^+.

Thus, rate = $k[H_2O_2][I^-]$, where units of k are mol^{-1} dm^3 min^{-1} $\Rightarrow$ **A** is incorrect

H^+ is a reactant that is converted to H_2O (i.e., H^+ does not remain unchanged at the end of reaction) so it cannot be a catalyst. Furthermore, we have insufficient information as to the effect of H^+ on the reaction (e.g. experiment with no H^+). Thus, from the results obtained, we cannot conclude that H^+ is a catalyst. $\Rightarrow$ **B** is incorrect.

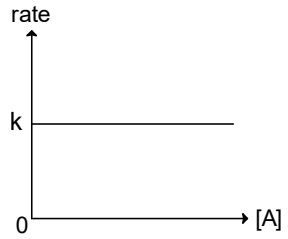
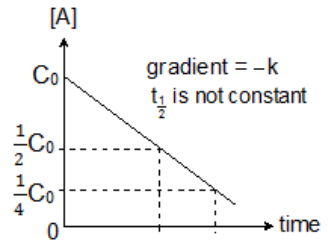
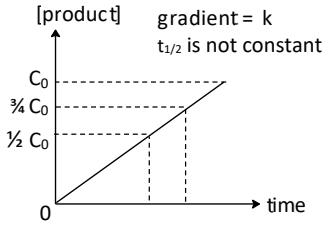
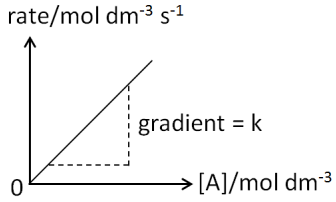
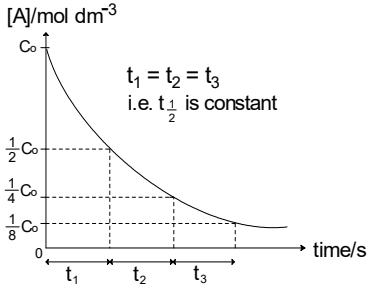
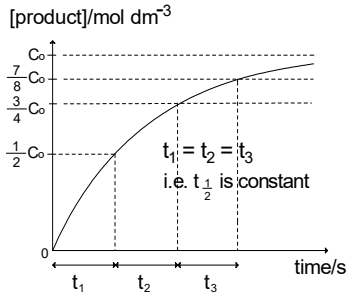
The magnitude of the rate constant increases when a catalyst is used or when temperature is increased $\Rightarrow$ **C** is incorrect

When both $[H_2O_2]$ and $[I^-]$ × 3, the initial rate × 9. Changing $[H^+]$ does not affect the initial rate $\Rightarrow$ **D** is correct

8 **Ans: C**
Note : For a mechanism to be valid,
1. *the mechanism must be consistent with the rate law, and*
2. *the elementary steps must add up to the overall balanced equation.*

A	Incorrect. rate = $k[NO_2]$ Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$
B	Incorrect. rate = $k[NO_2]^2$ Overall eqn: $CO + 2NO_2 \rightarrow CO_2 + 2NO + O$
C	Correct. rate = $k[NO_2]^2$ Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$
D	Incorrect. rate = $k[NO_2][CO]$ Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$

2

Overall order of reaction	Rate equation	Common units of k	Half-life	Rate-[reactant] Graph	[reactant]-Time Graph	Other Graphs
zero	rate = k	mol dm^{-3} s^{-1}	$t_{1/2}$ is <u>not constant</u>			
one	rate = k [A]	s^{-1}	$t_{1/2} = \frac{\ln 2}{k}$ $t_{1/2}$ is <u>constant</u>			
two	rate = k $[A]^2$	mol^{-1} dm^3 s^{-1}	$t_{1/2}$ is <u>not constant</u>