7 Reaction Kinetics

ANSWERS TO TUTORIAL QUESTIONS

Deducing order of reaction by analysis of a concentration-time graph and from initial rate data

1 (a) [N13/3/5(c)(d)] Explain the meaning of the following terms.

(i) order of reaction
(ii) half-life [2]

(b) The Harcourt and Esson reaction is that between hydrogen peroxide and acidified potassium iodide.

\[
H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2
\]

The rate of reaction can be followed by measuring the amount of iodine produced after various times, from which the concentration of \(H_2O_2\) remaining can be calculated.

The following reaction mixture was prepared:

\[
\begin{align*}
\text{initial } [H^+] &= 0.200 \text{ mol dm}^{-3} \\
\text{initial } [I^-] &= 0.200 \text{ mol dm}^{-3} \\
\text{initial } [H_2O_2] &= 0.0200 \text{ mol dm}^{-3}
\end{align*}
\]

The following table shows \([H_2O_2]\) at various times.

<table>
<thead>
<tr>
<th>Time /s</th>
<th>([H_2O_2]/\text{mol dm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0200</td>
</tr>
<tr>
<td>80</td>
<td>0.0167</td>
</tr>
<tr>
<td>183</td>
<td>0.0135</td>
</tr>
<tr>
<td>315</td>
<td>0.0103</td>
</tr>
<tr>
<td>490</td>
<td>0.0071</td>
</tr>
<tr>
<td>760</td>
<td>0.0039</td>
</tr>
</tbody>
</table>

Plot these data on suitable axes and, showing all your working and drawing clearly any construction lines on your graph, use your graph to determine:

(i) the order of reaction with respect to \([H_2O_2]\),
(ii) the initial rate, in \(\text{mol dm}^{-3} \text{s}^{-1}\).

Further experiments were carried out changing \([H^+]\) and \([I^-]\), but keeping the initial \([H_2O_2]\) the same as before. The following results were obtained.

<table>
<thead>
<tr>
<th>Initial ([H^+]/\text{mol dm}^{-3})</th>
<th>Initial ([I^-]/\text{mol dm}^{-3})</th>
<th>Initial rate /mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.400</td>
<td>0.200</td>
<td>(8.4 \times 10^{-5})</td>
</tr>
<tr>
<td>0.300</td>
<td>0.200</td>
<td>(6.3 \times 10^{-5})</td>
</tr>
<tr>
<td>0.200</td>
<td>0.100</td>
<td>(2.1 \times 10^{-5})</td>
</tr>
</tbody>
</table>

(iii) Determine the orders with respect to \([H^+]\) and \([I^-]\). Explain your reasoning.

(iv) Hence write the rate equation for the reaction, and calculate a value for the rate constant. Include units in your answer. [9]
1 (a) (i) The overall order of reaction is the sum of the individual powers on each concentration term in the rate equation. It must be experimentally-determined.

(ii) The half-life of a reaction is the time it takes for the concentration of a particular reactant to fall to half its initial value.

(b) (i) Graph shows that the half-life is constant at approximately 330 s.
(\(t_{\frac{1}{2}}\) from 0.0200 to 0.0100 \(\approx\) 325 s; \(t_{\frac{1}{2}}\) from 0.0160 to 0.0080 \(\approx\) 333 s; \(t_{\frac{1}{2}}\) from 0.0100 to 0.0050 \(\approx\) 335 s)

(ii) Approx. \(4.76 \times 10^{-5}\) mol dm\(^{-3}\) s\(^{-1}\) (from graph).

(iii) The reaction is first order with respect to \([H^+]\) and with respect to \([I^-]\).
Reasoning can be by inspection or solved mathematically (by ratios).

(iv) Rate = \(k[H_2O_2][H^+][I^-]\)
\(k = 0.0525\) mol\(^{-2}\) dm\(^6\) s\(^{-1}\)
Deducing order of reaction by analysis of concentration-time graphs

2. [N03/3/2(b) (modified)] A solution of vanadium(V) ions in 1.00 mol dm$^{-3}$ H$_2$SO$_4$ slowly oxidises arsenic(III) oxide to arsenic(V) oxide, according to the following (unbalanced) equation.

$$\text{As}_2\text{O}_3 + \text{VO}_2^+ + \text{H}^+ \rightarrow \text{As}_2\text{O}_5 + \text{VO}^{2+} + \text{H}_2\text{O}$$

(a) Balance this equation. \[1\]

The rate of the reaction was followed by measuring the concentration of the remaining vanadium(V) ions after fixed time intervals. Two experiments were carried out, starting with different concentrations of arsenic(III) oxide. The results obtained are given below.

<table>
<thead>
<tr>
<th>Time /minutes</th>
<th>Experiment 1, with [As$_2$O$_3$] = 0.10 mol dm$^{-3}$</th>
<th>Experiment 2, with [As$_2$O$_3$] = 0.05 mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[VO$_2^+$] /mol dm$^{-3}$</td>
<td>[VO$_2^+$] /mol dm$^{-3}$</td>
</tr>
<tr>
<td>0</td>
<td>0.0050</td>
<td>0.0050</td>
</tr>
<tr>
<td>15</td>
<td>0.0040</td>
<td>0.0045</td>
</tr>
<tr>
<td>30</td>
<td>0.0032</td>
<td>0.0040</td>
</tr>
<tr>
<td>45</td>
<td>0.0026</td>
<td>0.0036</td>
</tr>
<tr>
<td>60</td>
<td>0.0021</td>
<td>0.0032</td>
</tr>
<tr>
<td>75</td>
<td>0.0017</td>
<td>0.0029</td>
</tr>
<tr>
<td>90</td>
<td>0.0014</td>
<td>0.0026</td>
</tr>
</tbody>
</table>

(b) Suggest how the concentration of vanadium(V) ions at fixed time intervals can be determined. \[1\]

(c) Using the same axes, plot graphs of [VO$_2^+$] against time for the two experiments. \[2\]

(d) What do you understand by the term initial rate of reaction? \[1\]

(e) Use your graphs to determine the order of reaction with respect to VO$_2^+$ and to As$_2$O$_3$, showing your working clearly. Hence give the rate equation for the reaction.
(The rate of reaction was found to be independent of the concentration of H$^+$. ) \[3\]

(f) Use the initial rate of reaction and your rate equation to calculate the rate constant for the reaction, including units. \[2\]

2. (a) As$_2$O$_3$ + 4VO$_2^+$ + 4H$^+$ \rightarrow As$_2$O$_5$ + 4VO$^{2+}$ + 2H$_2$O

(b) As vanadium is a transition metal, VO$_2^+$ is likely to be colored. Hence, its concentration may be followed by using a colorimeter. [VO$_2^+$] is directly proportional to the absorbance reading.

Note to tutors: You may wish to discuss that the absorbance is normally monitored at a specific wavelength depending on $\lambda_{max}$ of the ion. As the color of the reactant and the product are different (yellow VO$_2^+$ vs blue VO$^{2+}$) VO$_2^+$ would have a significantly different
\( \lambda_{\text{max}} \) compared to \( \text{VO}^{2+} \), hence the concentration of \( \text{VO}^{2+} \) can be determined.

\[(d)\] Half-life of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value.

Initial rate of reaction is the rate at the start of a reaction, i.e., when time = 0.
In this question, it is the negative of the gradient of the tangent to the concentration-time graph at time = 0.

\[(e)\] - Half-life of the reaction for Experiment 1 is (approximately) constant
- at 48 min.
- \( \therefore \) reaction is first order with respect to \( \text{VO}^{2+} \).

*Examiner report: construction lines for at least two half lives had to be shown.*

- \([\text{VO}^{2+}]\) for both experiments is the same at time zero
- Determine initial rates:

<table>
<thead>
<tr>
<th>experiment</th>
<th>([\text{As}_2\text{O}_3]) / mol dm(^{-3})</th>
<th>initial rate / mol dm(^{-3}) min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.0040 / 59 = (6.8 \times 10^{-5})</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.0025 / 69 = (3.6 \times 10^{-5})</td>
</tr>
</tbody>
</table>

- Initial rate approximately doubles when \([\text{As}_2\text{O}_3]\) doubles
- rate \( \alpha \) \([\text{As}_2\text{O}_3]\), i.e., first order with respect to \(\text{As}_2\text{O}_3\)

Rate = \(k[\text{As}_2\text{O}_3][\text{VO}^{2+}]\)

\[(f)\] \(k = \frac{\text{rate}}{[\text{As}_2\text{O}_3][\text{VO}^{2+}]} = \frac{6.8 \times 10^{-5}}{0.10 \times 0.005} = 0.136 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}\)

*Examiner report: initial rate for experiment 1 = \(7 \times 10^{-5} \pm 2 \times 10^{-5}\) mol dm\(^{-3}\) min\(^{-1}\)*

\(k = 0.15 \pm 0.05 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}\)

*Deducing order of reaction by analysis of a product-time graph*

3 Do Q1(b), parts (i) and (ii), from the “Further Practice” section on p. 20.

3 (b) (ii) - Half-life of the reaction is approximately constant
- at 1.3-1.5 min
- \( \therefore \) a first order reaction

*Remarks: construction lines for at least two half lives had to be shown*
Deducing order of reaction by comparison of relative rates

4  [N09/3/3(d) (modified)] The initial rate of the slow reaction between $\text{H}_2\text{O}_2$ and acidified potassium iodide solution can be studied by the "clock" method, using sodium thiosulfate. The equations for the reactions are as follows.

\[
\text{H}_2\text{O}_2 + 2\Gamma^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{I}_2 \quad \text{reaction I}
\]
\[
\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6 \quad \text{reaction II}
\]

When a small but constant amount of sodium thiosulfate is added to a reaction mixture, the iodine being slowly produced by reaction I will immediately react in reaction II until all the sodium thiosulfate has been used up. At that point, free iodine will be present in the solution, which will cause a sudden appearance of a deep blue colour if starch is present.

A series of experiments was carried out using different volumes of the five reagents, each mixture being made up to the same total volume with water. The following results were obtained.

<table>
<thead>
<tr>
<th>Expt no.</th>
<th>volume of 0.10 mol dm$^{-3}$ $\text{H}_2\text{O}_2$ /cm$^3$</th>
<th>volume of 1.00 mol dm$^{-3}$ KI /cm$^3$</th>
<th>volume of 1.00 mol dm$^{-3}$ HCl /cm$^3$</th>
<th>volume of 0.050 mol dm$^{-3}$ $\text{Na}_2\text{S}_2\text{O}_3$ /cm$^3$</th>
<th>volume of starch solution /cm$^3$</th>
<th>volume of water /cm$^3$</th>
<th>time for the appearance of deep blue colour, $t$ /s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>10</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>65</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>2</td>
<td>3</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>15</td>
<td>10</td>
<td>2</td>
<td>3</td>
<td>65</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>2</td>
<td>3</td>
<td>65</td>
<td>50</td>
</tr>
</tbody>
</table>

(a) How is the rate of consumption of $\Gamma^-$ related to the rate of formation of $\text{I}_2$ in reaction I?  \[1\]

(b) Calculate the initial rate of reaction for Experiment 1.  \[2\]

(c) In this experiment, the volume of the $\text{H}_2\text{O}_2$ solution used is directly proportional to the concentration of $\text{H}_2\text{O}_2$ in the initial reaction mixture (i.e., at $t = 0$). So when the volume of $\text{H}_2\text{O}_2$ solution is increased two times from 5 cm$^3$ (in experiment 2) to 10 cm$^3$ (in experiment 4), $[\text{H}_2\text{O}_2]$ in the initial reaction mixture also increases two times.

Explain why this is so.  \[1\]

(d) What is the simple relationship between the time taken for the blue colour to appear and the initial rate of reaction I?  \[1\]

(e) By comparison of the relative initial rates for the experiments, deduce the order of reaction with respect to each of the three reactants in reaction I. Explain your reasoning.  \[4\]

(f) Hence write an overall rate equation for reaction I, stating the units of the rate constant.  \[2\]
(a) The rate of consumption of $\Gamma^-$ is double the rate of formation of $I_2$.

(b) Change in no. of moles of $I_2$ when blue colour appears
\[
\frac{1}{2} \times \frac{2}{1000} \times 0.050 = 5 \times 10^{-5} \text{ mol}
\]
Change in $[I_2] = 5 \times 10^{-5} / (100/1000) = 5 \times 10^{-4} \text{ mol dm}^{-3}$

Initial rate $= 5 \times 10^{-4} / 33 = 1.52 \times 10^{-5} \text{ mol dm}^{-3} \text{s}^{-1}$

(c) $[H_2O_2]_{\text{initial reaction mixture}} = \frac{\text{Volume of } H_2O_2 \text{ solution} \times 0.10}{\text{Total volume of reaction mixture}}$

Total volume of each reaction mixture was kept constant at 100 cm$^3$ (by adding water)
\[\therefore \text{ Volume of } H_2O_2 \text{ solution used } \alpha [H_2O_2]_{\text{initial reaction mixture}}\]

(d) The initial rate of reaction is inversely proportional to the time taken for the blue colour to appear.

*Examiner report: The answer expected was a little more quantitative than just “a faster reaction takes less time”. Mention of an inverse or reciprocal relationship was needed.*

(e) Experiment | Relative initial rate /s$^{-1}$
---|---
1 | 1/33 = 0.0303
2 | 1/100 = 0.0100
3 | 1/67 = 0.0149
4 | 1/50 = 0.0200

Deduce orders of reaction, show reasoning or calculation working...

E.g. comparing Experiments 2 and 4, when volume and hence $[H_2O_2]$ increases 2 times and $[\Gamma^-]$ and $[H^+]$ remains constant, relative initial rate increases 2 times. Hence, 1st order w.r.t. $H_2O_2$.

Ans: Order of reaction w.r.t. $H_2O_2 = 1, \quad \Gamma^- = 1, \quad H^+ = 0$

(f) Rate $= k [H_2O_2] [\Gamma^-]$ OR Rate $= k [H_2O_2] [KI]$

Units of $k$: $\text{mol}^{-1} \text{dm}^{3} \text{s}^{-1}$
**Deducing order of reaction from initial rate data + half-lives of pseudo-first order reactions**

5  [J92/1/3(b) (modified)] Sucrose has been used as a feedstock in the production of alcohol for use as a motor fuel. The initial reaction is its hydrolysis:

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6
\]

This reaction can be catalysed either by dilute acid or by the enzyme sucrase, which is present in yeast.

The following results were obtained using hydrochloric acid as the catalyst:

<table>
<thead>
<tr>
<th>experiment</th>
<th>initial [HCl] /mol dm(^{-3})</th>
<th>initial [sucrose] /mol dm(^{-3})</th>
<th>initial rate /mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>0.024</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.15</td>
<td>0.036</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.10</td>
<td>0.048</td>
</tr>
</tbody>
</table>

(a) Deduce the order of reaction with respect to both HCl and sucrose and, hence calculate the rate constant for the reaction, stating its units. [4]

(b) The half-life of sucrose in experiment 1 was 3.0 s. Predict the half-life of sucrose in experiment 2 and in experiment 3, giving your reasoning. [2]

(c) Calculate the concentration of sucrose in experiment 1 after
   (i) 9.0 s, and
   (ii) 1.0 s
   from the start of the experiment. [2]
5 (a) Compare experiments 1 and 2, [HCl] unchanged, when [sucrose] increases 1.5 times, rate also increases 1.5 times. \( \therefore \) rate \( \alpha \) [sucrose], reaction is first order with respect to sucrose.

Let rate = \( k [\text{sucrose}] [\text{HCl}]^x \)

Using data from experiments 2 and 3,

\[
\frac{0.048}{0.036} = \frac{k[0.10][0.20]^x}{k[0.15][0.10]^x} \quad \Rightarrow \quad 2^x = 2 \quad \Rightarrow \quad x = 1
\]

\( \therefore \) reaction is first order with respect to HCl.

\[
k = \frac{0.024}{0.10 \times 0.10} = 2.4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}
\]

(b) Rate = \( k [\text{sucrose}] [\text{HCl}] \)

HCl is a catalyst, so [HCl] stays constant during the reaction.

The rate equation is simplified as: rate = \( k' [\text{sucrose}] \) where \( k' = k [\text{HCl}] \)

The reaction may then be considered pseudo-first order overall with

\[
t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[\text{HCl}]}
\]

[HCl] in experiment 2 is the same as that in experiment 1, \( \therefore \) \( t_{\frac{1}{2}} \) is the same at 3.0 s

In experiment 3, [HCl] is increased two times (from 0.10 to 0.20 mol dm\(^{-3}\)).

Using \( t_{\frac{1}{2}} = \frac{\ln 2}{k[\text{HCl}]} \), \( t_{\frac{1}{2}} \) should decrease two times from 3.0 to 1.5 s.

Examiner report: Many candidates arrived at the conclusion that this was a (pseudo) first-order reaction without explicitly stating the reason -- HCl being a catalyst, so its concentration does not change, but then did not appreciate that the half-life of a first-order reaction does not depend on the initial [sucrose].

(c) (i) 9.0 s \( \equiv \) three half-lives

\( \therefore \) [sucrose] = 0.10 \( \times \) \( \left( \frac{1}{2} \right)^3 \) = 0.0125 mol dm\(^{-3}\)

(ii) 1.0 s \( \equiv \) 1/3 half-life

\( \therefore \) [sucrose] = 0.10 \( \times \) \( \left( \frac{1}{2} \right)^{1/3} \) = 0.0794 mol dm\(^{-3}\)
Deducing order of reaction by analysis of rate-concentration graph

6 [N10/2/3] Nitrogen monoxide, NO, is a by-product of the combustion of hydrocarbon fuels in internal combustion engines.

(a) NO is considered to be involved in the formation of 'acid rain'. State one other undesirable consequence of the presence of NO in the atmosphere. [1]

Nitrogen monoxide is readily converted into nitrogen dioxide.

\[ 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \]

In order to determine the rate equation for this reaction, an investigation was carried out at a constant temperature and with the same partial pressure of oxygen, \(p_{\text{O}_2}\), for each experiment. The following results were obtained.

<table>
<thead>
<tr>
<th>initial rate / N m(^{-2})s(^{-1})</th>
<th>16.2</th>
<th>47.2</th>
<th>78.8</th>
<th>124</th>
<th>172</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p_{\text{NO}}) / N m(^{-2})</td>
<td>0.30</td>
<td>0.50</td>
<td>0.66</td>
<td>0.82</td>
<td>0.95</td>
</tr>
<tr>
<td>((p_{\text{NO}})^2) / N(^2) m(^{-4})</td>
<td>0.09</td>
<td>0.25</td>
<td>0.44</td>
<td>0.67</td>
<td>0.90</td>
</tr>
</tbody>
</table>

(b) To determine the order of reaction with respect to \(p_{\text{NO}}\), use these data to plot a suitable graph on the grid below.

(c) What is the order of reaction with respect to \(p_{\text{NO}}\)? Explain your answer. [2]

(d) The partial pressure of oxygen was halved and a new series of experiments carried out and the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the first graph. What is the order of reaction with respect to \(p_{\text{O}_2}\)?

(e) (i) Construct the rate equation for the reaction between NO and \(\text{O}_2\).

(ii) What are the units of the rate constant for this reaction? [2]
6 (a) Formation of photochemical smog that can cause breathing difficulties.

(b) Plot initial rate against \( p_{\text{NO}} \) or initial rate against \( (p_{\text{NO}})^2 \). Graph should pass through origin.

Examiners’ report: There were many very good graphs drawn in this part. Candidates had the option of plotting \( p_{\text{NO}} \) or \( (p_{\text{NO}})^2 \) against initial rate. The former will produce a curve and the latter a straight line. Examiners expected both graphs to go through the origin but this was not always the case in answers seen. Some candidates made the question difficult for themselves by choosing values on their axes that were difficult to plot. A small number tried to plot a graph of time against \( p_{\text{NO}} \) and received no credit.

(c) If initial rate against \( (p_{\text{NO}})^2 \) is plotted:
From graph, since initial rate is directly proportional to \( (p_{\text{NO}})^2 \), reaction is second order with respect to \( \text{NO} \).
If initial rate against \( p_{\text{NO}} \) is plotted:
Show that when the value of \( p_{\text{NO}} \) is doubled, the rate of reaction is increased fourfold.

Examiners’ report: Examiners did not accept the answer ‘since the graph is not a straight line the reaction must be second order with respect to \( p_{\text{NO}} \).’

(d) When \( p_{\text{O}_2} \) is halved, initial rate is halved since gradient at each point was halved. Thus the reaction is first order with respect to \( p_{\text{O}_2} \).

(e) (i) Rate = \( k (p_{\text{NO}})^2 (p_{\text{O}_2}) \)
Examiners’ report: Examiners expected the rate equation to be written in terms of partial pressures rather than concentrations.

(ii) \( \text{rate} = \frac{N^2}{m^4 \text{ s}^{-1}} \)
Reaction mechanism

7  [N94/3/5 (modified)]

(a) What is the oxidation number of nitrogen in the following?
   (i) NO  (ii) ONF

(b) The compound nitrosyl fluoride, ONF, can be produced from nitrogen monoxide and fluorine:

\[
2\text{NO(g)} + \text{F}_2(g) \rightarrow 2\text{ONF(g)}
\]

It is found experimentally that the rate of reaction is directly proportional to [NO] and also directly proportional to [F_2]. The reaction mechanism has two steps. One of these steps produces ONF and the free radical F• in equimolar amounts.

(A free radical is a species with an odd number of electrons e.g. a fluorine atom can be called a fluorine radical because it contains 7 electrons.)

(i) Suggest equations for the two steps of the mechanism, stating which step is the slower one.

(ii) Justify your answer to (b)(i) in terms of the relative reactivities of the species involved.

7  (a)  (i) +2
     (ii) +3

(b) (i) NO + F_2 \rightarrow ONF + F• (slow)
     NO + F• \rightarrow ONF (fast)

(ii) Examiner report: Candidates were asked to justify their answers in terms of the relative reactivities of the species involved. Points expected were: the slow step involves breaking the fluorine molecule into high energy free radicals, the free radicals, F•, will react quickly because they have high energy; NO has an odd number of electrons and can absorb the fluorine radical.

Reaction pathway diagram

8  [N93/1/1(c), N04/2/1] The equation for the partial decomposition of gaseous hydrogen iodide at 400 °C is shown.

\[
2\text{HI(g)} = \text{H}_2(g) + \text{I}_2(g)
\]

This is a second order reaction.

(a) (i) Explain what the phrase, second order reaction, means.
     (ii) If the reactor volume is doubled (all other conditions unchanged), what is the effect on the initial rate of this reaction?

(b) At 400 °C, the activation energy for the forward reaction is 184 kJ mol^{-1} and that for the reverse reaction is 163 kJ mol^{-1}.

   In the presence of a gold catalyst, the activation energy for the reverse reaction is 85 kJ mol^{-1}.
(i) Sketch a labelled reaction pathway diagram for the catalysed and uncatalysed reaction by incorporating all these information on your diagram.

(ii) Using only the above information, calculate the value of the enthalpy change, $\Delta H$, for this reaction. Label this $\Delta H$ value on your reaction pathway diagram.

(iii) Calculate the value for the activation energy for the decomposition of $2\text{HI(g)}$ in the presence of the gold catalyst.

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8 (a) (i) "second order reaction" means that the total or overall order of reaction is 2. One possibility is that the rate of reaction is proportional to the square of the concentration of one reactant, i.e., rate $\alpha [\text{reactant A}]^2$. In this question, rate $\alpha [\text{HI}]^2$ since there is only one reactant, HI.

Another possibility is that the rate is proportional to the product of the concentrations of two reactants, i.e., rate $\alpha [\text{reactant A}]^{1}[\text{reactant B}]^{1}$.

(ii) Initial rate becomes a quarter of the previous value. OR decreases four times.

(b) (i) $\Delta H = 184 - 163 = +21 \text{ kJ mol}^{-1}$ (label value on reaction pathway diagram above)

(ii) $E_a = 85 + 21 = 106 \text{ kJ mol}^{-1}$
Catalysis and activation energy

9 Suggest reasoning for the following observations.

(a) [N90/4/3] When ammonia gas is passed over a platinum gauze, the rate of decomposition into nitrogen and hydrogen is independent of the partial pressure of ammonia. However, at very low pressures, the rate is directly proportional to the partial pressure of ammonia.

(b) The rate of reaction between potassium manganate(VII) and ethanedioic acid

\[ 2\text{MnO}_4^-(aq) + 16\text{H}^+(aq) + 5\text{C}_2\text{O}_4^{2-}(aq) \rightarrow 2\text{Mn}^{2+}(aq) + 10\text{CO}_2(g) + 8\text{H}_2\text{O}(l) \]

increases initially and then decreases.

(c) [N93/1/1] Reaction (1) below must be heated for some time for it to occur whereas reaction (2) takes place almost instantaneously at room temperature.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaOH}(aq) &\rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(aq) + \text{NaCl}(aq) \\
1\text{-chloropropane} &\text{propan-1-ol} \\
\text{HCl}(aq) + \text{NaOH}(aq) &\rightarrow \text{H}_2\text{O}(l) + \text{NaCl}(aq)
\end{align*}
\]

9 (a) At very low pressures, \([\text{NH}_3]\) is very low, active sites on the surface of Pt catalyst (heterogeneous catalyst) are not saturated. More \(\text{NH}_3\) can be adsorbed onto the active sites as \(P_{\text{NH}_3}\) increases. Hence, rate is directly proportional to \(P_{\text{NH}_3}\).

At higher pressures, \([\text{NH}_3]\) is higher, active sites on Pt catalyst are saturated with \(\text{NH}_3\). The product \(\text{N}_2\) and \(\text{H}_2\) molecules must first desorb from the active sites before anymore \(\text{NH}_3\) molecules can be adsorbed. Thus, increasing \(P_{\text{NH}_3}\) has no effect on the catalysis process.

Examiner report: The catalyst is not saturated at low pressures and the rate depends on the pressure of the ammonia. When the pressure of ammonia is high, the sites on the catalyst surface are completely filled, and the rate is independent of increasing ammonia concentration.

(b) - The reaction between KMnO₄(aq) and ethanedioic acid produces Mn²⁺ which acts as a catalyst for the reaction that produces it (this phenomenon is known as autocatalysis).
- As the reaction progresses, \([\text{Mn}^{2+}]\) increases, so rate increases.
- As the reactants are used up, their concentrations decrease, rate then decreases.

Remarks: For normal reactions, rate should decrease over time as concentrations of reactants decrease. For an autocatalysed reaction, rate increases then decreases over time.

(c) POSSIBLE ANSWER POINTS:
- activation energy of reaction (1) is greater than that of (2), possible reasons:
  - relatively large size of 1-chloropropane but it needs to collide with \(\text{OH}^-\) in a correct orientation for reaction,
  - C–C/ bond must be broken during the reaction
- 1-chloropropane is practically non-polar and does not mix well with the aqueous solution containing OH\(^-\). This heterogeneity may make the reaction slow. Hence, heating is required for reaction (1) to increase the rate.

- Reaction (2) is basically H\(^+\)(aq) + OH\(^-\)(aq) → H\(_2\)O(l). The strong acid & soluble NaOH dissociate completely in water, so reaction does not involve bond breaking.
- H\(^+\) & OH\(^-\) are oppositely charged and both are small, they collide with each other easily without much orientation problem
Hence, reaction (2) has low activation energy & takes place instantaneously at room temperature.

**Examiners’ report:** To deduce that the activation energy for reaction (1) is greater than that for (2), due to the energy required to break a C–Cl covalent bond in (1), whereas in (2), the H–Cl covalent bond is already broken and the reaction reduces to H\(^+\) + OH\(^-\) → H\(_2\)O.

### 7 Reaction Kinetics

**ANSWERS TO FURTHER PRACTICE QUESTIONS**

**Deducing order of reaction by analysis of a product-time graph**

1. [J98/2/2 (modified)] A student investigated the rate of reaction between sodium and ethanol. A freshly cut piece of sodium was weighed and added to a large excess of ethanol.

   (a) (i) Sodium metal reacts with ethanol to produce sodium ethoxide, C\(_2\)H\(_5\)O\(^-\)Na\(^+\), and hydrogen gas. Write an equation, including state symbols, for sodium reacting with ethanol.

   (ii) Suggest why the sodium needs to be freshly cut.

   

   The total volume of gas liberated was recorded every minute. The results are tabulated below.

<table>
<thead>
<tr>
<th>Time /min</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total volume of gas /cm(^3)</td>
<td>0</td>
<td>23.0</td>
<td>36.5</td>
<td>46.0</td>
<td>51.0</td>
<td>54.5</td>
<td>57.0</td>
<td>58.5</td>
<td>60.0</td>
<td>60.0</td>
</tr>
</tbody>
</table>

   * (b) *(i)* Plot the experimental results.

   *(ii)* Explain why the experimental results indicate that the overall kinetics are first order.

   *(iii)* In this experiment, the kinetics appear to be zero order with respect to ethanol. Suggest a reason for this.

   [3]

   (c) (i) Calculate how many moles of gas were produced in the experiment, conducted at room temperature and pressure.

   (ii) Calculate the mass of sodium weighed out at the start of the experiment.

   [2]

   (d) The student wishes to modify the experiment by changing the concentration of the ethanol.
(i) Explain, with the aid of an equation, why water should not be used to dilute the ethanol.

(ii) Suggest a suitable solvent the student could use to dilute the ethanol.

Numerical Ans to (c):
(i) \(2.50 \times 10^{-3}\) mol (by molar volume at r.t.p.) OR \(2.45 \times 10^{-3}\) mol (by ideal gas equation);
(ii) 0.115 g OR 0.113 g.

1 (a) (i) \(\text{C}_2\text{H}_5\text{OH}(l) + \text{Na}(s) \rightarrow \text{C}_2\text{H}_5\text{O}^-\text{Na}^+ + \frac{1}{2}\text{H}_2(g)\)

Examiner report: State symbols required only for Na(s) & H\(_2\)(g)

(ii) Na needs to be freshly cut because this metal is very reactive and has a coating of oxide.

(b) (ii) - Half-life of the reaction is approximately constant
- at 1.3-1.5 min
- \(\therefore\) a first order reaction

Remarks: construction lines for at least two half lives had to be shown

(iii) Suggested answers:
- State that ethanol is present in (considerable) excess
- Some elaboration e.g. So its quantity does not change significantly during the reaction and may be regarded as constant. The rate of reaction will appear to be independent of ethanol. The reaction is said to be pseudo zero order with respect to ethanol.

(c) (i) No. of moles of \(\text{H}_2\) produced = \(60 / 24000 = 2.50 \times 10^{-3}\) mol

(ii) No. of moles of Na = \(2.50 \times 10^{-3} \times 2 = 5.00 \times 10^{-3}\) mol
Mass of Na = \(5.00 \times 10^{-3} \times 23.0 = 0.115\) g

(d) (i) Na also reacts with water (and much more readily).
\(\text{Na}(s) + \text{H}_2\text{O}(l) \rightarrow \text{NaOH}(aq) + \frac{1}{2}\text{H}_2(g)\)

(ii) ether
OR any other inert solvent/liquid