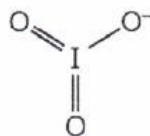


## Reaction Kinetics - 2021

### 1. March/2021/Paper\_42/No.3

Iodates are compounds that contain the  $\text{IO}_3^-$  anion.

(a) The  $\text{IO}_3^-$  anion is shown.



Explain, with reference to the qualitative model of electron-pair repulsion, why the  $\text{IO}_3^-$  anion has a pyramidal shape.

I has 3 bonding pairs and a lone pair of electron on iodine.

[1]

(b) The reaction of iodine and hot aqueous sodium hydroxide is similar to that of chlorine and hot aqueous sodium hydroxide. Sodium iodate,  $\text{NaIO}_3$ , is formed as one of the products.

Suggest an equation for the reaction of iodine and hot aqueous sodium hydroxide.

$3\text{I}_2 + 6\text{NaOH} \rightarrow 2\text{NaIO}_3 + 5\text{NaI} + 3\text{H}_2\text{O}$

[1]



(c) The decomposition of hydrogen peroxide,  $\text{H}_2\text{O}_2$ , is catalysed by acidified  $\text{IO}_3^-$ .

$\text{H}_2\text{O}_2$  reduces acidified  $\text{IO}_3^-$  as shown.



This reaction is followed by the oxidation of  $\text{I}_2$  by  $\text{H}_2\text{O}_2$ .

half-equation	$E^\circ/\text{V}$
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.77
$\text{IO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightleftharpoons \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$	+1.19
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2$	+0.68

(i) Use the data to show that the separate reactions of  $\text{H}_2\text{O}_2$  with  $\text{IO}_3^-$  and with  $\text{I}_2$  are both feasible under standard conditions.

In your answer, give the equation for the reaction of  $\text{H}_2\text{O}_2$  with  $\text{I}_2$ .

$$\text{IO}_3^- / \text{H}_2\text{O}_2 = -0.68 + 1.19$$

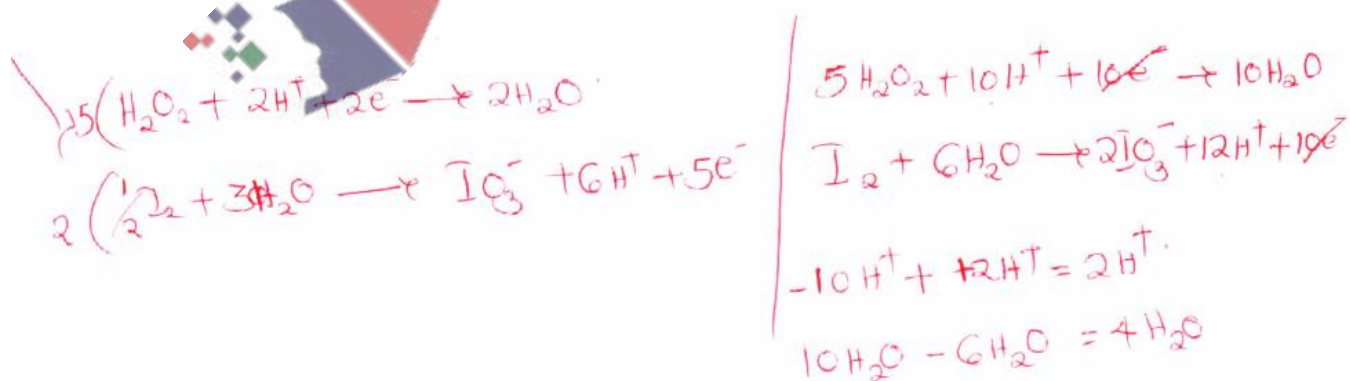
$$= +0.51 \rightarrow \text{feasible (it has a positive sign)}$$

$$\text{H}_2\text{O}_2 / \text{I}_2 = +1.77 - 1.19$$

$$= +0.58 \rightarrow \text{feasible}$$



(ii) Write the overall equation for the decomposition of  $\text{H}_2\text{O}_2$  catalysed by acidified  $\text{IO}_3^-$ .



(d) A student collects some data for the reaction of  $\text{H}_2\text{O}_2$  with acidified  $\text{IO}_3^-$ , as shown in the table.

experiment	$[\text{H}_2\text{O}_2]$ / $\text{mol dm}^{-3}$	$[\text{IO}_3^-]$ / $\text{mol dm}^{-3}$	$[\text{H}^+]$ / $\text{mol dm}^{-3}$	initial rate of reaction / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.0500	0.0700	0.025	$1.47 \times 10^{-5}$
2	0.100	0.0700	0.050	$2.94 \times 10^{-5}$
3	0.100	0.140	0.025	$5.88 \times 10^{-5}$
4	0.150	0.140	0.025	$8.82 \times 10^{-5}$

(i) Use the data to determine the order of reaction with respect to  $[\text{H}_2\text{O}_2]$ ,  $[\text{IO}_3^-]$  and  $[\text{H}^+]$ .

Show your reasoning.

order with respect to  $[\text{H}_2\text{O}_2]$  = *Its first order. (Experiment 3 & 4)*  
*When the concentration changes by 1.5*  
*the rate also changes by 1.5.*

order with respect to  $[\text{IO}_3^-]$  = *First order (Experiment 1 and 3)*  
*As the concentration changes by 2, the*  
*rate also changes by 2.*

order with respect to  $[\text{H}^+]$  = *Zero order.*  
*Change in concentration has no effect*  
*on the rate.*

[3]

(ii) Use your answer to (d)(i) to write the rate equation for this reaction.

rate =  *$k [\text{H}_2\text{O}_2] [\text{IO}_3^-]$*  [1]

(iii) Calculate the value of the rate constant,  $k$ , using data from experiment 4 and your answer to (d)(ii).

Give the units of  $k$ .

$$\begin{aligned}
 &= \frac{\text{Rate}}{[\text{H}_2\text{O}_2][\text{I}_3^-]} \\
 &= \frac{8.82 \times 10^{-5}}{0.15 \times 0.14} \\
 &= 4.20 \times 10^{-3}
 \end{aligned}$$

units:

$$\frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}$$

$$k = 4.20 \times 10^{-3}$$

$$\text{units} = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

[2]

(e)  $\text{Pb}(\text{IO}_3)_2$  is only sparingly soluble in water at 25 °C.

The solubility product,  $K_{\text{sp}}$ , of  $\text{Pb}(\text{IO}_3)_2$  is  $3.69 \times 10^{-13} \text{ mol}^3 \text{ dm}^{-9}$  at 25 °C.

(i) Write an expression for the solubility product of  $\text{Pb}(\text{IO}_3)_2$ .

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{IO}_3^-]^2$$

[1]

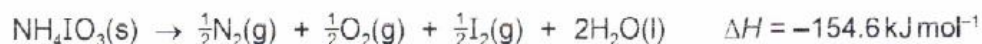
(ii) Calculate the solubility, in  $\text{mol dm}^{-3}$ , of  $\text{Pb}(\text{IO}_3)_2$  at 25 °C.

$$\begin{aligned}
 3.69 \times 10^{-13} &= x(2x)^2 \\
 3.69 \times 10^{-13} &= 4x^3 \\
 \sqrt[3]{3.69 \times 10^{-13}} &= \sqrt[3]{4x^3} \\
 x &= 4.52 \times 10^{-5}
 \end{aligned}$$

$$\text{solubility} = 4.5 \times 10^{-5} \text{ mol dm}^{-3} \quad [2]$$



- (f)  $\text{NH}_4\text{IO}_3$  is an unstable compound that readily decomposes when warmed. The decomposition reaction is shown.



- (i) Use the data in the table to calculate the entropy change of reaction,  $\Delta S$ , of the decomposition of  $\text{NH}_4\text{IO}_3(\text{s})$ .

compound	$S/\text{JK}^{-1} \text{ mol}^{-1}$
$\text{NH}_4\text{IO}_3(\text{s})$	42
$\text{N}_2(\text{g})$	192
$\text{O}_2(\text{g})$	205
$\text{I}_2(\text{g})$	261
$\text{H}_2\text{O}(\text{l})$	70

$$\Delta S = \Delta S_p - \Delta S_a.$$

$$\left( \frac{1}{2}(192) + \frac{1}{2}(205) + \frac{1}{2}(261) + (2 \times 70) \right) - 42.$$

$$= +427$$

$$\Delta S = \dots + 427 \dots \text{ JK}^{-1} \text{ mol}^{-1} \quad [2]$$

- (ii) This reaction is feasible at all temperatures.

Explain why, using the data in (f) and your answer to (f)(i).

$\Delta G$  is always negative because  
 $\Delta H < 0$  hence negative  
 $\Delta S > 0$  positive  $-T\Delta S < 0$  for all  $T$ . [1]

[Total: 18]

Dinitrogen pentoxide,  $\text{N}_2\text{O}_5$ , is dissolved in an inert solvent (solv) and the rate of decomposition of  $\text{N}_2\text{O}_5$  is investigated. This reaction produces nitrogen dioxide, which remains in solution, and oxygen gas.



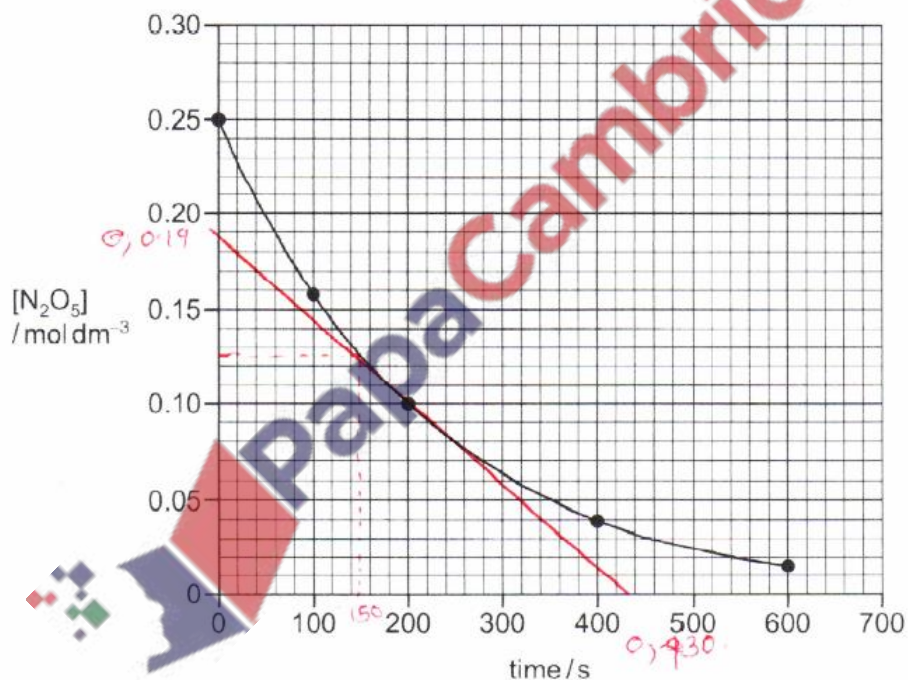
- (a) Suggest what measurements could be used to follow the rate of this reaction from the given information.

- Measure the volume of oxygen produced or mass lost by loss of oxygen against time. [1]  
 - Measure absorbance against time.

- (b) In a separate experiment, the rate of the decomposition of  $\text{N}_2\text{O}_5(\text{g})$  is investigated.



The graph shows the results obtained.



The reaction is first order with respect to  $\text{N}_2\text{O}_5$ . This can be confirmed from the graph using half-lives.

- (i) Explain the term *half-life of a reaction*.

Its the time taken for the concentration of the reactants to fall to half its original value. [1]

(ii) Determine the half-life of this reaction. Show your working on the graph.

$$\frac{0.25}{2} = 0.125$$

half-life = 1.50 s [1]

(iii) Suggest the effect on the half-life of this reaction if the initial concentration of  $N_2O_5$  is halved.

No change (It would decrease at the same rate) [1]

(c) (i) Use the graph in 5(b) to determine the rate of reaction at 200 s. Show your working.

Draw a tangent at 200 s.

$$= \frac{0.19 - 0}{430 - 0} \frac{\text{mol dm}^{-3}}{\text{s}}$$

$$= 4.41 \times 10^{-4}$$

$$\text{rate} = 4.41 \times 10^{-4}$$

$$\text{units} = \text{mol dm}^{-3} \text{s}^{-1}$$

[2]

The rate equation for this reaction is shown.

$$\text{rate} = k[N_2O_5]$$

(ii) Use your answer to (c)(i) to calculate the value of the rate constant,  $k$ , for this reaction and state its units.

$$k = \frac{\text{Rate}}{[N_2O_5]} = \frac{4.41 \times 10^{-4}}{0.10}$$

$$k = 4.41 \times 10^{-3} \text{ units } \text{s}^{-1} [1]$$

(d) Nitrogen dioxide reacts with ozone,  $O_3$ , as shown.



The rate equation for this reaction is  $\text{rate} = k[NO_2][O_3]$ .

Suggest a possible two-step mechanism for this reaction.



[2]

[Total: 9]



3. June/2021/Paper\_42/No.7

(a) In aqueous solution, chlorine dioxide,  $\text{ClO}_2$ , reacts with hydroxide ions as shown.



A series of experiments is carried out using different concentrations of  $\text{ClO}_2$  and  $\text{OH}^-$ . The table shows the results obtained.

experiment	$[\text{ClO}_2]$ / $\text{mol dm}^{-3}$	$[\text{OH}^-]$ / $\text{mol dm}^{-3}$	initial rate / $\text{mol dm}^{-3} \text{min}^{-1}$
1	0.020	0.030	$7.20 \times 10^{-4}$
2	0.020	0.120	$2.88 \times 10^{-3}$
3	0.050	0.030	$4.50 \times 10^{-3}$

(i) Explain the term *order of reaction*.

It's the power to which a concentration of a reactant is raised to in a rate equation [1]

(ii) Use the data in the table to determine the order of reaction with respect to each reactant,  $\text{ClO}_2$  and  $\text{OH}^-$ .

Explain your reasoning

$\text{ClO}_2$  - Experiment 1 and 3. As the concentration increases by 2.5, the rate increases by 6.25. The order is second order.

$\text{OH}^-$  - Experiment 1 and 2. As the concentration increases by 4, the rate increases by 4. The first order. [2]

(iii) Use your answer to (a)(ii) to construct the rate equation for this reaction.

rate =  $k[\text{ClO}_2]^2[\text{OH}]$  [1]

(iv) Use your rate equation and the data from experiment 1 to calculate the rate constant,  $k$ , for this reaction.

Include the units of  $k$ .

$$k = \frac{\text{rate}}{[\text{ClO}_2]^2[\text{OH}]}$$

$$= \frac{7.20 \times 10^{-4}}{[0.02]^2 [0.03]}$$

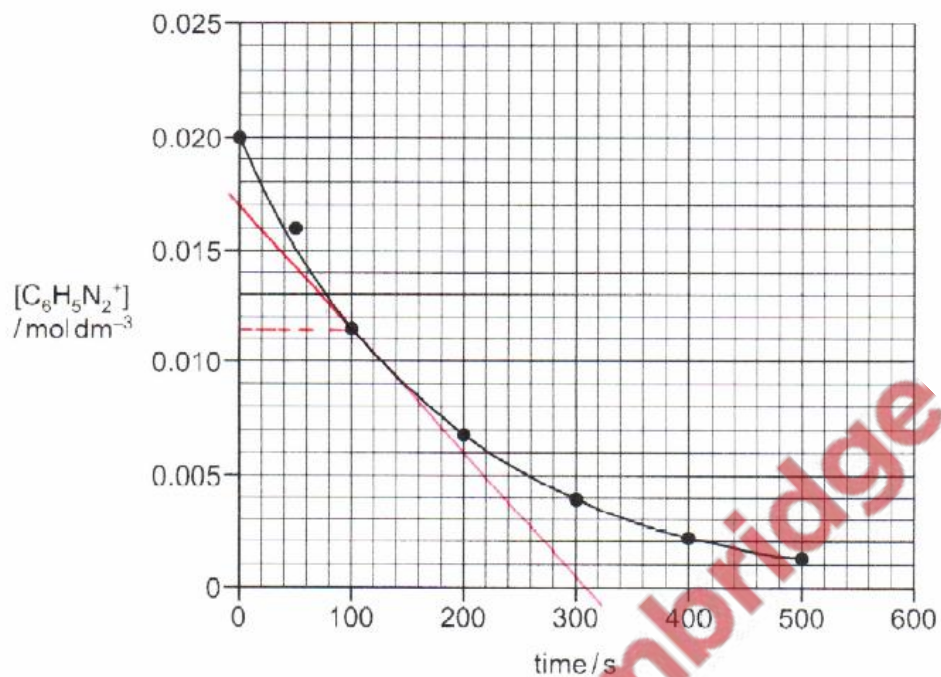
units  $\frac{\text{mol dm}^{-3} \text{min}^{-1}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3} \times \text{mol dm}^{-3}}$

$k = 60$  units  $\text{mol}^{-2} \text{dm}^3 \text{min}^{-1}$  [2]



- (b) The decomposition of benzenediazonium ions,  $C_6H_5N_2^+$ , using a large excess of water, is a first-order reaction.

The graph shows the results obtained.



- (i) Draw the structure of the organic product formed in this reaction.



[1]

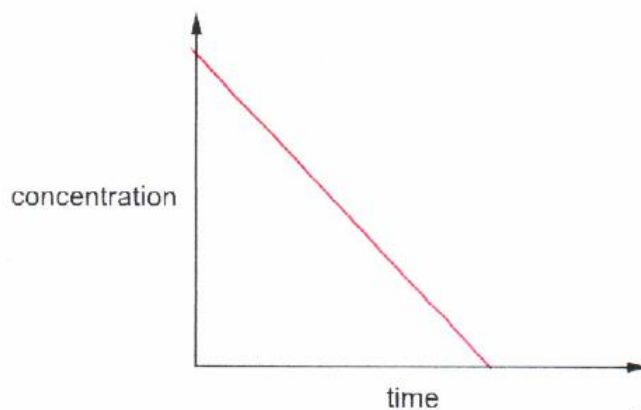
- (ii) Use the graph to determine the rate of reaction at 100s. Show your working.

$$\frac{0.17}{3.0} = 5.48 \times 10^{-4}$$

rate = 5.48 .....  $\text{mol dm}^{-3} \text{s}^{-1}$  [1]

(c) Sketch a concentration–time graph for a **zero-order** reaction.

Use your graph to suggest how successive half-lives for a zero-order reaction vary as the concentration of a reactant decreases. Indicate this by placing a tick (✓) in the appropriate box in the table.



successive half-lives decrease	no change in successive half-lives	successive half-lives increase
✓		

[1]

[Total: 9]

