IB · DP · Chemistry

2 hours 15 questions

Structured Questions: Paper 2

16.1 Rate Expression & Reaction Mechanism

Easy (5 questions)	/37
Medium (5 questions)	/40
Hard (5 questions)	/39
Total Marks	**/116**

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Easy Questions

1 (a) Outline two ways a rate of a reaction can be expressed and state the units for rate of reaction.

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(2 marks)

(b) Explain what is meant by the *order* of a reaction and how it may be determined.

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(2 marks)

(c) Carbon monoxide and chlorine react together to make phosgene, $COCl_2$. The equation for the reaction is given below:

$$CO\ (g) + Cl_2\ (g) \rightarrow COCl_2\ (g)$$

A possible rate equation for the reaction is:

$$\text{rate} = k[CO\ (g)]^2[Cl_2\ (g)]^{½}$$

What is the overall reaction order?

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(1 mark)

(d) Determine the units of the rate constant, *k*, for the following rate equation:

$$\text{rate} = k[NO]^2[O_2]$$

.....

(1 mark)

2 (a) The rate of hydrolysis of sucrose under acidic conditions can be determined experimentally. The following data was obtained:

Experiment	Initial [HCl] / mol dm^{-3}	Initial [sucrose] / mol dm^{-3}	Rate of reaction / mol dm^{-3} s^{-1}
1	0.10	0.10	0.024
2	0.10	0.15	0.036
3	0.20	0.10	0.048

Determine the order of reaction with respect to HCl.

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(1 mark)

(b) Determine the order of reaction with respect to sucrose.

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(1 mark)

(c) Determine the overall order of reaction, write the rate expression and state the units of the rate constant, *k*.

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(3 marks)

(d) Determine the following:

i) The value of k, using Experiment 1

[1]

ii) The rate of reaction if the concentration of HCl and sucrose are both 0.20 mol dm^{-3}

[1]

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(2 marks)

3 (a) Sketch graphs of a first order and second order reaction of concentration against time.

(2 marks)

(b) Draw sketch graphs for a first and second order reaction of rate against concentration.

(2 marks)

(c) Deduce the units of the rate constant, k, for a first order reaction.

(1 mark)

(d) State, with a reason, how the value of the rate constant, *k*, varies with increased temperature for a reaction.

(4 marks)

4 (a) State what is meant by the terms *rate determining step* and *molecularity* in a chemical reaction.

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(2 marks)

(b) The following reaction mechanism has been proposed for the formation of nitrosyl bromide, NOBr, from nitrogen monoxide and bromine:

Step 1: $NO + NO \rightarrow N_2O_2$

Step 2: $N_2O_2 + Br_2 \rightarrow 2NOBr$

Deduce the overall reaction equation and comment on the molecularity of Step 1 and 2.

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(2 marks)

(c) A student proposes an alternative one step mechanism for the formation of nitrosyl bromide.

$NO + NO + Br_2 \rightarrow NOBr_2$

Explain why this mechanism is not likely to take place.

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(2 marks)

(d) State the role of N_2O_2 in the mechanism in part b).

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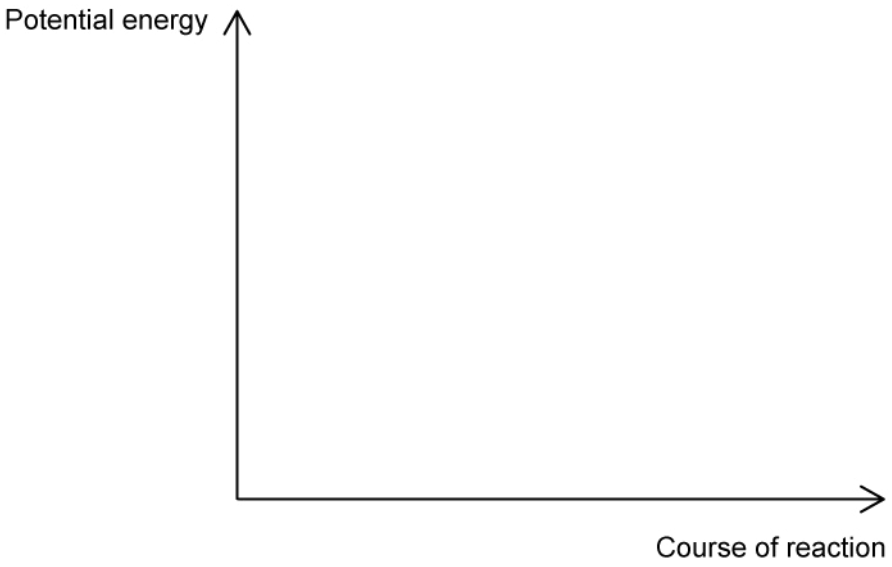
(1 mark)

5 (a) Draw a labelled diagram, on the follow grid, showing a potential energy profile in a two step reaction. The second step is the slow step of the reaction.



(3 marks)

(b) State which step of the mechanism in a) is affected by the addition of a catalyst.

(1 mark)

(c) A reaction mechanism is shown below.

Step 1: $NO_2 + NO_2 \rightarrow NO + NO_3$ (slow)

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

Deduce the overall reaction equation and the rate equation for the reaction.

(2 marks)

(d) State the overall reaction order in part c) and state the units of the rate constant.

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(2 marks)

Medium Questions

1 (a) For the reaction below, consider the following experimental data.

$$X\ (aq) + Y\ (aq) \rightarrow Z\ (aq)$$

Experiment	Initial [X] / mol dm^{-3}	Initial [Y] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.030	0.040	4.0×10^{-4}
2	0.045	0.040	6.0×10^{-4}
3	0.060	0.120	2.4×10^{-3}

Deduce the order of reaction with respect to X.

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(2 marks)

(b) Deduce the order of the reaction with respect to Y.

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(2 marks)

(c) Write the rate expression for the reaction between X and Y.

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(1 mark)

(d) Determine the rate constant, *k*, correct to three significant figures and state its units, using data from Experiment 2.

Experiment	Initial [X] / mol dm^{-3}	Initial [Y] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.030	0.040	4.0×10^{-4}
2	0.045	0.040	6.0×10^{-4}
3	0.060	0.120	2.4×10^{-3}

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(3 marks)

2 (a) Explain why the reaction represented below is a redox reaction.

$$2ClO_2\ (aq) + 2NaOH\ (aq) \rightarrow NaClO_3\ (aq) + NaClO_2\ (aq) + H_2O\ (l)$$

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(2 marks)

(b) For the reaction below, consider the following experimental data.

$$2ClO_2\ (aq) + 2OH^-\ (aq) \rightarrow ClO_3^-\ (aq) + ClO_2^-\ (aq) + H_2O\ (l)$$

Experiment	Initial $[ClO_2]$ / mol dm^{-3}	Initial $[OH^-]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.85	1.70	9.30×10^{-5}
2	1.70	1.70	3.72×10^{-4}
3	1.70	0.85	1.86×10^{-4}

Deduce the rate expression.

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(3 marks)

(c) Determine the rate constant, *k*, and state its units, using data from Experiment 3.

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(3 marks)

(d) Calculate the rate when [ClO_2 (aq)] = 3.10 x 10^{-2} mol dm^{-3} and [OH^- (aq)] = 1.50 x 10^{-2} mol dm^{-3}.

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(2 marks)

3 (a) Sketch a graph to show how the rate constant, *k*, varies with temperature.

(1 mark)

(b) The following mechanism is proposed for the reaction where ethanal dimerises in dilute alkaline solution to form 3-hydroxybutanal:

Step 1: $CH_3CHO + :OH^- \rightarrow :CH_2CHO + H_2O$
Step 2: $CH_3CHO + :CH_2CHO \rightarrow CH_3CH(O:^-)CH_2CHO$
Step 3: $CH_3CH(O:^-)CH_2CHO + H_2O \rightarrow CH_3CH(OH)CH_2CHO + :OH^-$

Classify OH^-, CH_2CHO and $CH_3CH(O:^-)CH_2CHO$ as reactant, product, catalyst or intermediate, based on the proposed mechanism.

(3 marks)

(c) Using the following information about the proposed mechanism, deduce the rate expression.

Step 1: $CH_3CHO + :OH^- \rightarrow :CH_2CHO + H_2O$ slow step
Step 2: $CH_3CHO + :CH_2CHO \rightarrow CH_3CH(O:^-)CH_2CHO$ fast step
Step 3: $CH_3CH(O:^-)CH_2CHO + H_2O \rightarrow CH_3CH(OH)CH_2CHO + :OH^-$ fast step

(1 mark)

(d) Calculate the initial rate of reaction for experiment 2, if measured under the same conditions.

Experiment	Initial [CH_3CHO] / mol dm^{-3}	Initial [OH^-] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.25	0.20	4.2×10^{-2}
2	0.25	0.30	

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(1 mark)

(e) State the effect, if any, increasing the concentration of a reactant would have on the value of the rate constant, *k*.

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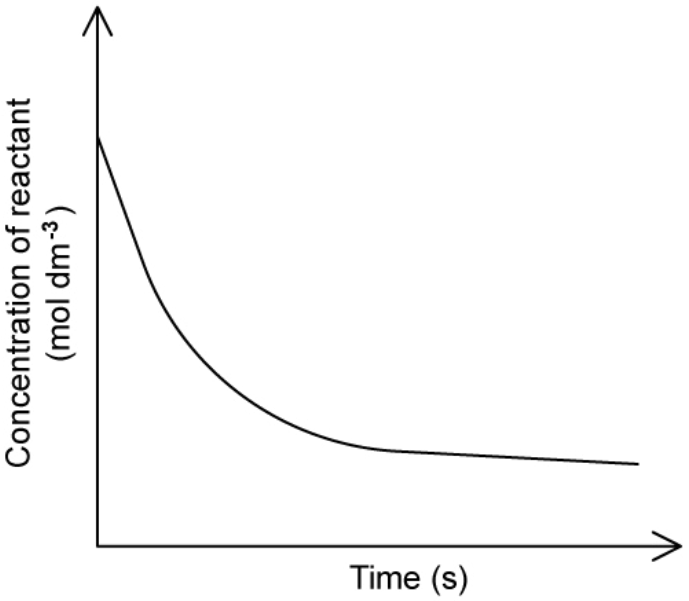
(1 mark)

4 (a) Nitrogen dioxide and carbon monoxide react according to the following equation.

$$NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g)$$

Using the following graph, what is the order with respect to NO_2?



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(1 mark)

(b) The rate expression for the reaction of nitrogen dioxide and carbon monoxide at $T < 227\ ^{O}C$ is:

$$\text{Rate} = k\ [NO_2]^2$$

Sketch a labelled graph of concentration against time for carbon monoxide.

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(2 marks)

(c) A student proposed the following single step mechanism for the reaction of nitrogen dioxide and carbon monoxide.

$$NO_2 + CO \rightarrow NO + CO_2 \qquad \text{slow}$$

$$\text{Rate} = k\,[NO_2]^2$$

Justify whether the student's proposed mechanism is correct.

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(2 marks)

(d) Another student proposed the following mechanism for the reaction of nitrogen dioxide and carbon monoxide.

Step 1: $NO_2 + NO_2 \rightarrow NO + NO_3$
Step 2: $NO_3 + 2CO \rightarrow NO + 2CO_2$

$$\text{Rate} = k\,[NO_2]^2$$

Explain which of the student's proposed mechanism steps is the rate determining step.

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(1 mark)

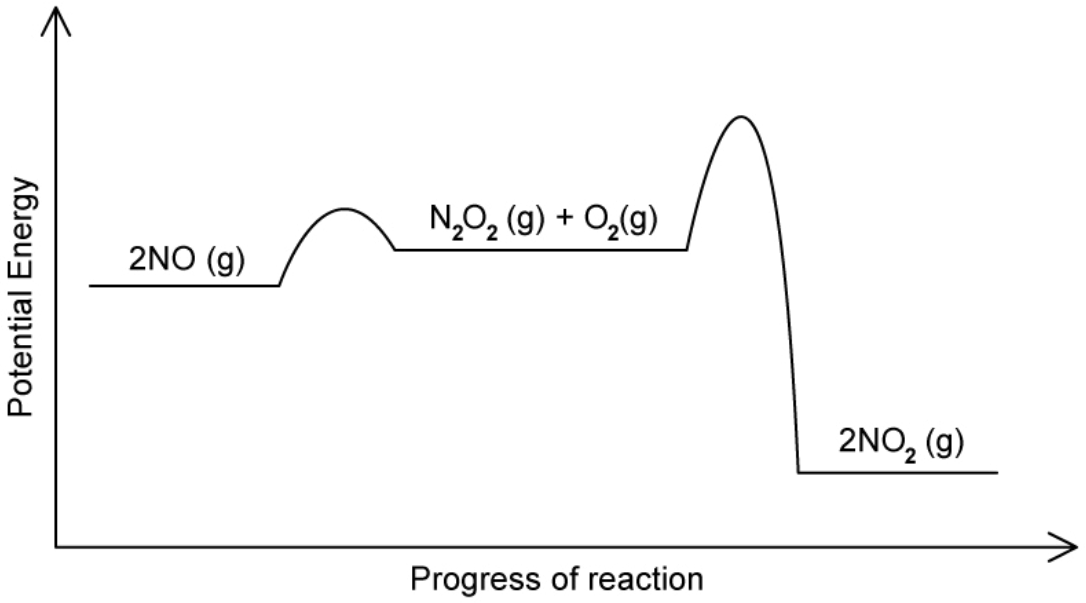
5 (a) Nitrogen(II) oxide is oxidised according to the following equation.

$$2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$$

The following mechanism is proposed for the two-step oxidation of nitrogen(II) oxide.

Step 1: $NO\ (g) + NO\ (g) \rightarrow N_2O_2\ (g)$
Step 2: $N_2O_2\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$

The potential energy profile for this two-step reaction is shown.



Explain which step is the rate determining step.

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(1 mark)

(b) Energy profile diagrams give evidence for or against a proposed mechanism or proposed rate expression.

i) Explain why the rate expression for the oxidation of nitrogen(II) oxide is **not** rate = $k\ [N_2O_2]\ [O_2]$.

ii) Deduce the rate expression for the oxidation of nitrogen(II) oxide.

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(3 marks)

(c) Explain why the following reaction between iodide ions and peroxodisulfate ions has a high activation energy.

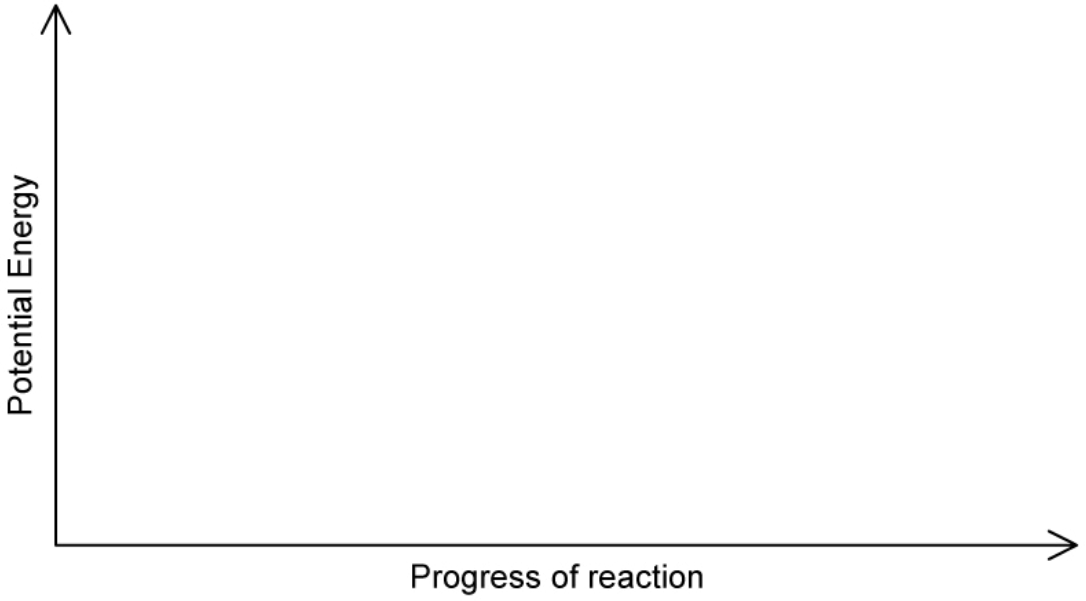
$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

(2 marks)

(d) Sketch the potential energy diagram for the reaction of iodide ions with peroxodisulfate ions catalysed by iron(II) ions according to the following mechanism.

$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$ slow

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ fast



(2 marks)

(e) Deduce the rate expression for the reaction of iodide ions with peroxodisulfate ions catalysed by iron(II) ions according to the following mechanism.

$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$ slow

$2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ fast

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(1 mark)

Hard Questions

1 (a) The conversion of hydrogen and iodine into hydrogen iodide proceeds via a three step reaction mechanism:

1. I_2 (g) $\rightleftharpoons$ 2I (g) fast
2. H_2 (g) + I (g) $\rightleftharpoons$ H_2I (g) fast
3. H_2I (g) + I (g) $\rightarrow$ 2HI (g) slow

Write the rate equation for this reaction and show how the mechanism is consistent with the stoichiometric equation.

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(2 marks)

(b) An investigation into the rate of reaction between hydrogen and iodine was carried out at 298 K and the data obtained is shown below.

Experiment	$[H_2]$ / mol dm^{-3}	$[I_2]$ / mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.0258	0.0137	6.43×10^{-22}
2	0.0258	0.0274	1.29×10^{-21}
3	0.0516	0.0137	1.29×10^{-21}

Determine the rate equation for the reaction and justify your answer.

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(3 marks)

(c) Calculate the rate constant using Expt 2 data, including its units.

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(1 mark)

(d) Using section 11 of the Data booklet, determine whether the forward reaction is favoured by an increase in temperature.

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(1 mark)

2 (a) The reaction between iodide ions and persulfate ions is a 'clock' reaction and often used to study reaction kinetics.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

Deduce the redox changes taking place in the reaction.

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(2 marks)

(b) A persulfate-iodide clock reaction was studied and the following rate data obtained.

Experiment	$[S_2O_8^{2-}]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.25	0.10	8.0×10^{-3}
2	0.10	0.10	3.2×10^{-3}
3	0.20	0.30	1.92×10^{-2}

Deduce the order with respect to persulfate ions and iodide ions.

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(2 marks)

(c) Determine the rate equation for the reaction and calculate rate constant, including the units.

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(2 marks)

(d) Four mechanisms are proposed for the persulfate-iodide reaction. Deduce which mechanism(s) is/are consistent with the rate equation in part c) and justify your answer.

Mechanism 1:

1. $I^-(aq) + I^-(aq) \rightarrow I_2^{2-}(aq)$ *slow*
2. $I_2^{2-}(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$ *fast*

Mechanism 2:

1. $I^-(aq) + S_2O_8^{2-}(aq) \rightarrow S_2O_8I^{3-}(aq)$ *slow*
2. $S_2O_8I^{3-}(aq) + I^-(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$ *fast*

Mechanism 3:

1. $I^-(aq) + S_2O_8^{2-}(aq) \rightarrow S_2O_8I^{3-}(aq)$ *fast*
2. $S_2O_8I^{3-}(aq) + I^-(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$ *slow*

Mechanism 4:

1. $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$ *slow*

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(3 marks)

3 (a) The reaction between nitrogen monoxide and hydrogen produces nitrogen and water:

$$2NO\,(g) + 2H_2\,(g) \rightarrow N_2\,(g) + 2H_2O\,(g)$$

Rate data for this reaction is shown below.

Experiment	[NO] / mol dm^{-3}	[H_2] / mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.001	0.004	0.002
2	0.002	0.004	0.008
3	0.004	0.001	0.016

What is the *molecularity* of the reaction?

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(1 mark)

(b) Draw a sketch graphs of:

i) Rate against concentration of NO.

[1]

ii) Rate against concentration of H_2

[1]

.....

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(2 marks)

(c) Suggest a possible mechanism for the reaction.

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(2 marks)

(d) Suggest a Lewis structure for N_2O_2 and draw the shape of the molecule.

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(2 marks)

4 (a) The rate of reaction between manganate(VII) ions and oxalate ions, $C_2O_4^{2-}$, can be investigated by measuring how the concentration of manganate(VII) varies with time.

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

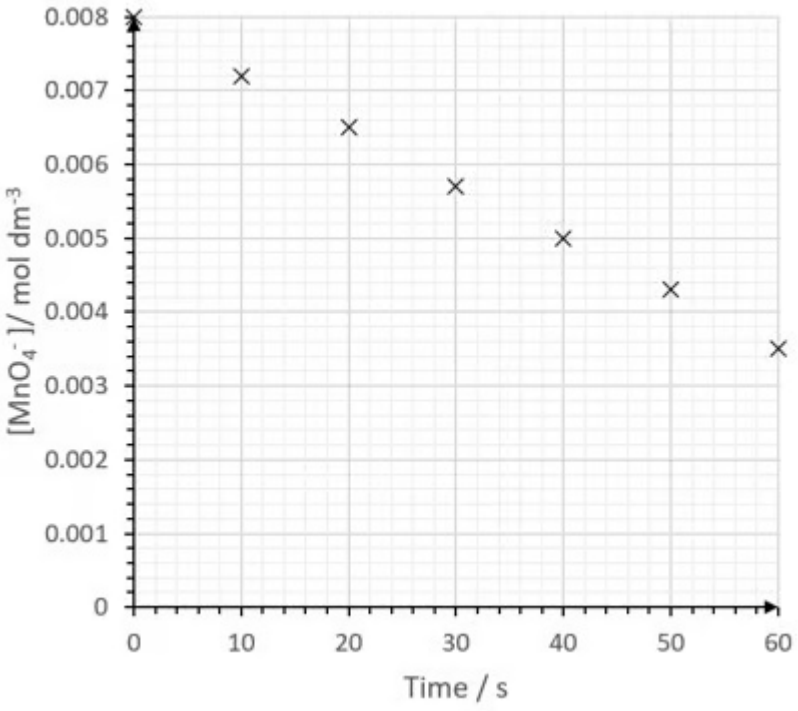
The rate is first order with respect to oxalate ions and the general rate equation for the reaction is:

$$\text{rate} = k\,[MnO_4^-]^p[C_2O_4^{2-}]^q[H^+]^r$$

i) Suggest how the change in manganate(VII) concentration can be measured.

[1]

ii) A student investigated how the concentration of manganate(VII) affected the rate of reaction and produced the following results. The oxalate ions and acid were in excess.



Determine the rate of reaction.

[2]

(3 marks)

(b) The student used an acid concentration of 1.0 mol dm^{-3}. She then varied it, keeping the other concentrations constant. She measured the rate of reaction and found the following results:

$[H^+]$/ mol dm^{-3}	Relative rate of reaction
0.5	0.0025
0.25	0.0013
0.01	0.0005

Identify the relationship between the relative rate of reaction and H^+, and hence determine the order of reaction with respect to H^+ ions.

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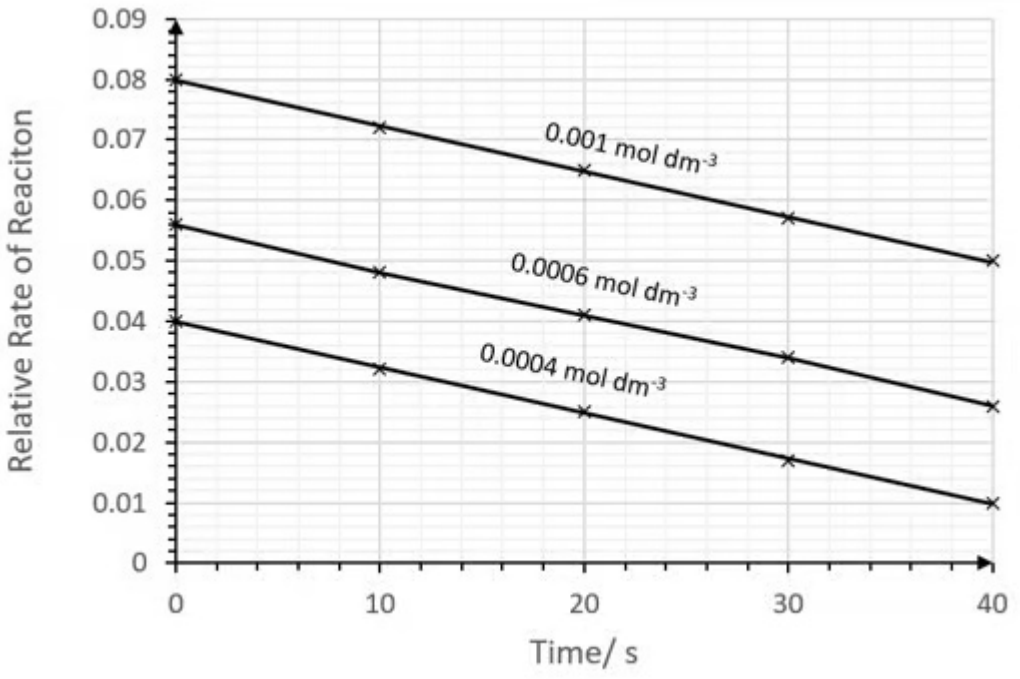
(2 marks)

(c) The student varied the concentration of $[MnO_4^-]$ and plotted the rate against time at three different concentrations:



i) Deduce, with a reason, the order of reaction with respect to MnO_4^-.

[2]

ii) Write the rate expression for the reaction.

[1]

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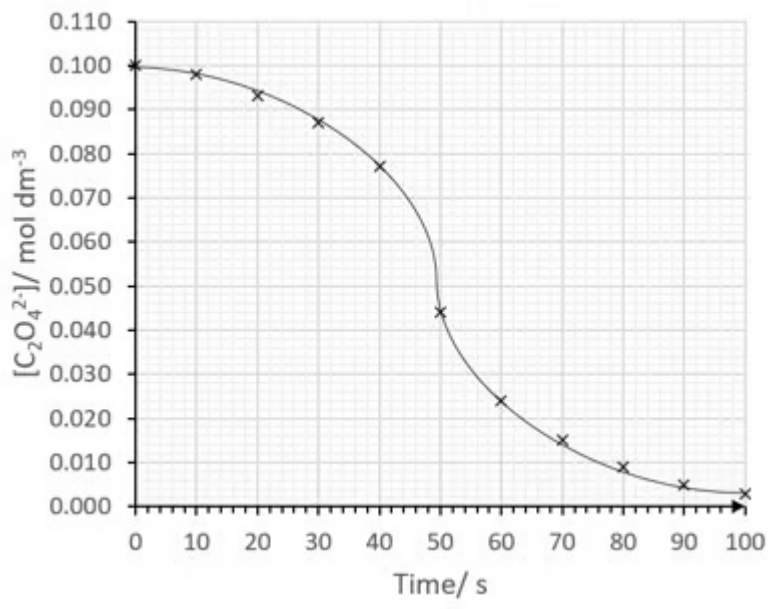
(3 marks)

(d) The student then measured the reaction time for different concentrations of $C_2O_4^{2-}$ and obtained a curve as follows:



Comment on the shape of the graph.

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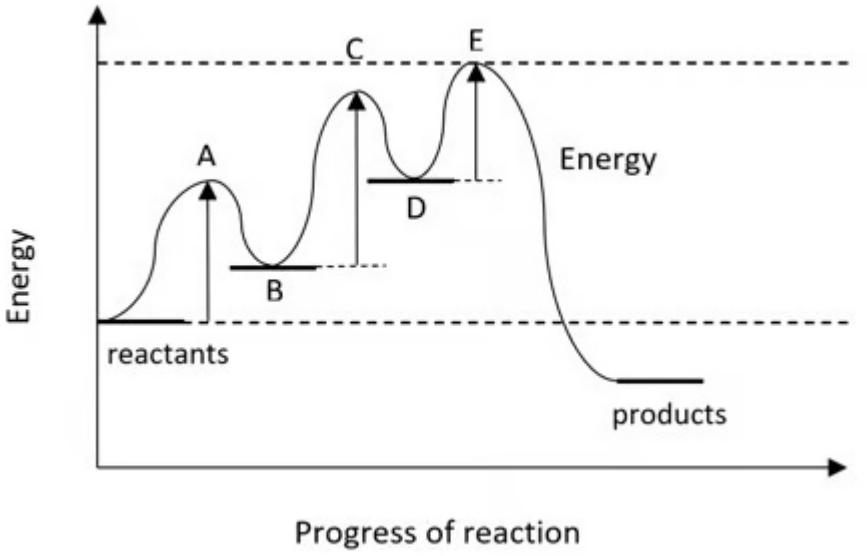
(2 marks)

5 (a) A reaction proceeds by a three step mechanism. The energy profile for the reaction is shown below:



Explain the difference between points A, C, E and B, D on the profile.

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(4 marks)

(b) Deduce which step is the rate determining step of the reaction, giving a reason.

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(2 marks)