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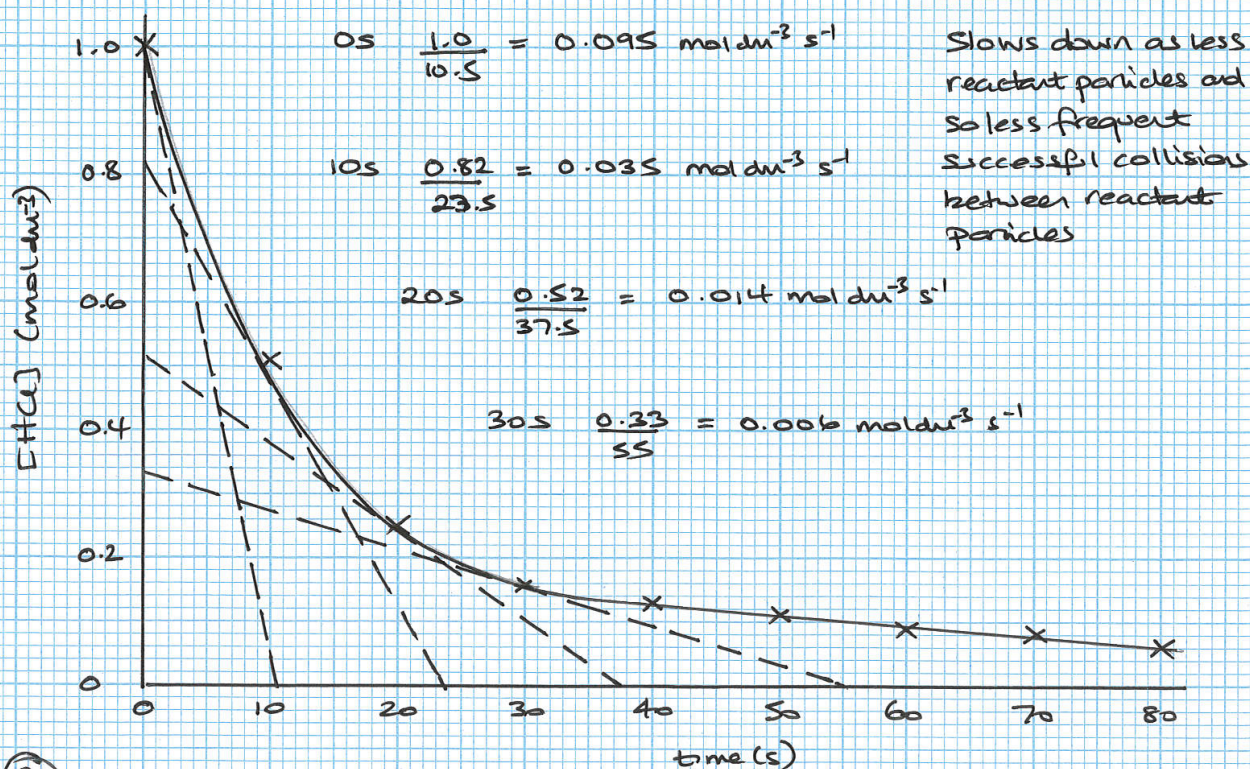


KINETICS

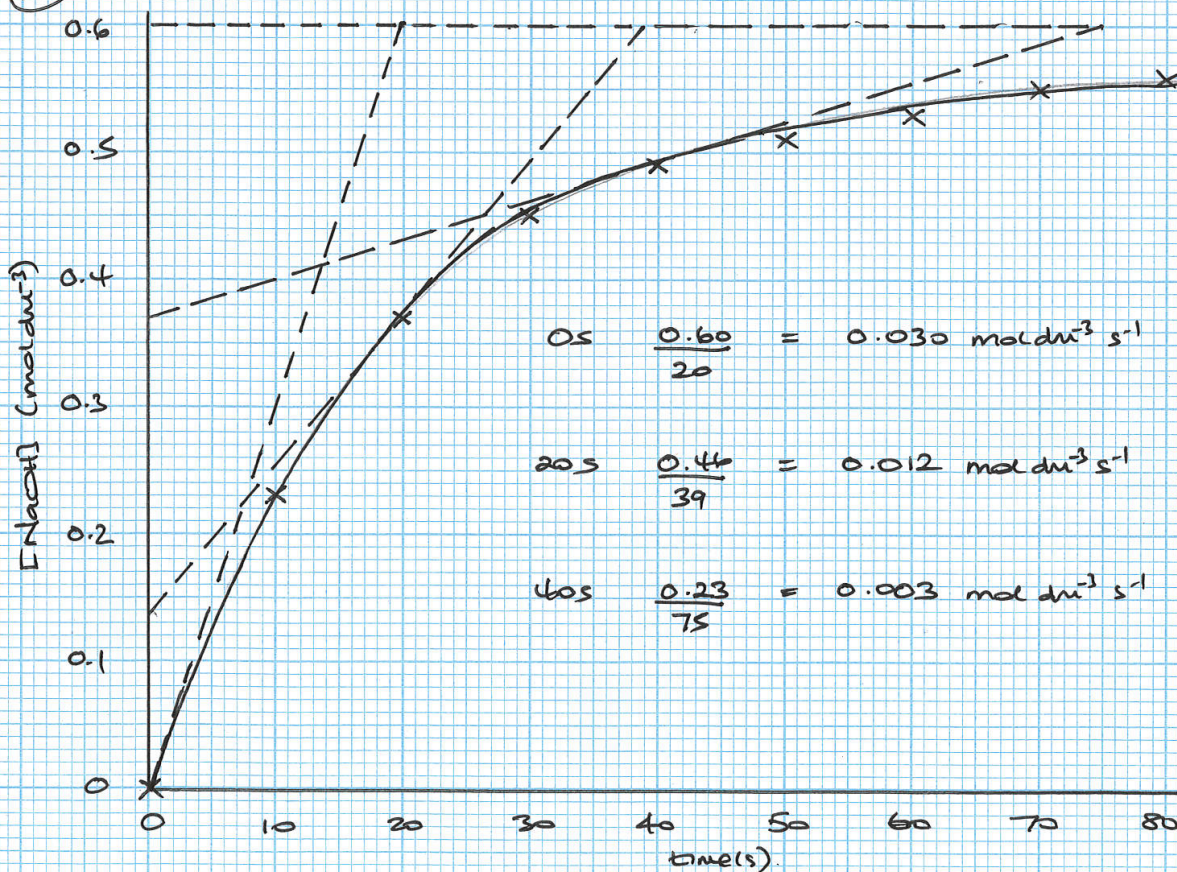


TASK 1 – Finding rates using gradients

①



②



TASK 2 – What orders mean

1 Consider this reaction: $A + B + C \rightarrow D$

The rate equation is: $\text{rate} = k [B] [C]^2$

Complete the table to show how changing the concentrations affects the rate.

Initial rate (mol dm ⁻³ s ⁻¹)	Change in concentration of reagents	Effect on rate	New initial rate (mol dm ⁻³ s ⁻¹)
2.5	[A] x 3	None	2.5
0.75	[B] x 4	x 4	3.0
12	[C] x 10	x 100	1200
0.50	[D] x 5	None	0.50
0.25	[A] ÷ 4	None	0.25
2.8	[B] ÷ 10	÷ 10	0.28
3.5	[C] ÷ 3	÷ 9	0.39
0.80	[D] ÷ 2	None	0.80
10.3	[A] x 2, [B] x 2	x 2	20.6
6.5	[B] x 2, [C] x 3	x 18	117
12.5	[A] x 2, [B] ÷ 3	÷ 3	4.17
4.8	[B] x 3, [C] ÷ 2	x ¾	3.6
12.5	[A] x 6, [B] ÷ 4, [C] x 2	None	12.5
2.9	[A] x 2, [B] x 10, [C] ÷ 1.5	x 4.44	12.89
15.5	[B] x 3, [C] x 10, [D] ÷ 10	x 300	4650

2 Consider this reaction: $P + Q \rightarrow R$ T acts as catalyst

The rate equation is: $\text{rate} = k [P]^2 [T]$

Complete the table to show how changing the concentrations affects the rate.

Initial rate (mol dm ⁻³ s ⁻¹)	Change in concentration of reagents	Effect on rate	New initial rate (mol dm ⁻³ s ⁻¹)
6.0	[P] x 2	x 4	24.0
5.0	[Q] x 5	None	5.0
10.0	[R] x 3	None	10.0
0.80	[T] x 4	x 4	3.20
8.0	[P] ÷ 3	÷ 9	0.89
12.5	[Q] ÷ 2	None	12.5
60	[R] ÷ 5	None	60
50	[T] ÷ 10	÷ 10	5.0
12	[P] x 2, [Q] x 2	x 4	48
10	[P] x 2, [T] x 3	x 12	120
40	[Q] x 2, [T] ÷ 3	÷ 3	13.3
25	[R] x 3, [T] ÷ 2	÷ 2	12.5
10	[P] x 4, [Q] ÷ 2, [T] x 2	x 32	320
20	[P] x 2, [Q] x 10, [T] ÷ 1.5	x 2.67	53.3
30	[P] x 3, [Q] x 10, [T] ÷ 10	x 0.9	27
5	[P] ÷ 2, [Q] ÷ 2, [T] ÷ 3	÷ 12	0.42
12	[P] x 2, [Q] ÷ 10, [T] x 5	x 20	240
16	[P] ÷ 3, [Q] ÷ 2.5, [T] x 3	÷ 3	5.33
8	[P] x 2.5, [Q] ÷ 4, [T] ÷ 2	x 3.125	25

TASK 3 – Finding the units of the rate constant

Work out the units for the rate constant in each of the following examples.

	Rate equation	Rearrange to give k	Working	Units for k
1)	rate = k [A]	$k = \frac{\text{rate}}{[A]}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})}$	s^{-1}
2)	rate = k [C] [H]	$k = \frac{\text{rate}}{[C][H]}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})^2}$	$\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
3)	rate = k [S] ²	$k = \frac{\text{rate}}{[S]^2}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})^2}$	$\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
4)	rate = k [J] ² [H] ²	$k = \frac{\text{rate}}{[J]^2[S]^2}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})^4}$	$\text{mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$
5)	rate = k [T]	$k = \frac{\text{rate}}{[T]}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})}$	s^{-1}
6)	rate = k [S] [E] [G] ²	$k = \frac{\text{rate}}{[S][E][G]^2}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})^4}$	$\text{mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$
7)	rate = k [D] ² [C]	$k = \frac{\text{rate}}{[D]^2[C]}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})^3}$	$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$
8)	rate = k [A] [B] [C]	$k = \frac{\text{rate}}{[A][B][C]}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})^3}$	$\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$
9)	rate = k [J] [G]	$k = \frac{\text{rate}}{[J][G]}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})^2}$	$\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
10)	rate = k [H ⁺] [Br ⁻]	$k = \frac{\text{rate}}{[H^+][Br^-]}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})^2}$	$\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

TASK 4 – Finding rate equations using initial rates data

- a) $\text{rate} = k[\text{A}]^2$ $k = \frac{\text{rate}}{[\text{A}]^2} = \frac{10}{3^2} = 1.11 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
- b) $\text{rate} = k[\text{D}][\text{E}]$ $k = \frac{\text{rate}}{[\text{D}][\text{E}]} = \frac{5}{0.1^2} = 500 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
- c) $\text{rate} = k[\text{H}^+]^2[\text{J}]$ $k = \frac{\text{rate}}{[\text{H}^+]^2[\text{J}]} = \frac{12}{(0.5^2 \times 0.2)} = 240 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$
- d) $\text{rate} = k[\text{T}]$ $k = \frac{\text{rate}}{[\text{T}]} = \frac{300}{0.2} = 1500 \text{ s}^{-1}$
- e) $\text{rate} = k[\text{H}^+][\text{Q}]$ $k = \frac{\text{rate}}{[\text{H}^+][\text{Q}]} = \frac{8}{(0.01 \times 0.2)} = 4000 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
- f) $\text{rate} = k[\text{W}]^2$ $k = \frac{\text{rate}}{[\text{W}]^2} = \frac{0.016}{0.02^2} = 40 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
- g) $\text{rate} = k[\text{M}]^2$ $k = \frac{\text{rate}}{[\text{M}]^2} = \frac{0.15}{0.1^2} = 15 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
- h) $\text{rate} = k[\text{HI}]^2$ $k = \frac{\text{rate}}{[\text{HI}]^2} = \frac{0.41}{1.64^2} = 0.152 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

TASK 5 – Using initial rates data

1

Experiment	Initial [G] (mol dm ⁻³)	Initial [H] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	0.200	0.100	0.400
2	0.200	0.050	0.200
3	0.100	0.200	0.400
4	0.050	1.000	1.000
5	0.150	0.100	0.300
6	0.800	0.050	0.800
7	0.300	0.200	1.200
8	0.250	0.080	0.400

2

Experiment	Initial [J] (mol dm ⁻³)	Initial [K] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
9	0.500	0.200	0.360
10	0.500	0.100	0.360
11	1.000	0.200	1.440
12	0.354	0.200	0.180
13	0.100	0.100	0.014

3

Experiment	Initial [L] (mol dm ⁻³)	Initial [M] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
14	0.100	0.100	0.0500
15	0.100	0.300	0.4500
16	0.100	0.173	0.1500
17	0.025	0.200	0.0500
18	0.200	0.071	0.0500

4 a) rate = k[A][B]² k = $\frac{\text{rate}}{[A][B]^2} = \frac{16}{(2 \times 2^2)} = 2.0 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

b) rate = k[E] k = $\frac{\text{rate}}{[E]} = \frac{0.80}{4} = 0.20 \text{ s}^{-1}$

c) rate = k[P][Q] k = $\frac{\text{rate}}{[P][Q]} = \frac{0.00200}{0.1 \times 0.1} = 0.20 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

d) rate = k[H⁺][CH₃COCH₃] k = $\frac{\text{rate}}{[H^+][CH_3COCH_3]} = \frac{9 \times 10^{-5}}{(0.5 \times 6.0)} = 3.0 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

TASK 6 – Rate determining step

- 1 step 1
- 2 step 2
- 3 step 1
- 4 step 1
- 5 step 2
- 6 mechanism 1 = not possible; mechanism 2 = not possible
- 7 mechanism 1 = possible; mechanism 2 = not possible
- 8 mechanism 1 = possible; mechanism 2 = possible

TASK 7 – Using the Arrhenius equation

1 a) $k = Ae^{-\frac{E_a}{RT}}$

b) $E_a = RT (\ln A - \ln k)$

c) $A = ke^{\frac{E_a}{RT}}$

d) $T = \frac{E_a}{R(\ln A - \ln k)}$

2 $\ln k = \ln A - \frac{E_a}{RT}$

$$\frac{E_a}{RT} = \ln A - \ln k$$

$$E_a = RT (\ln A - \ln k)$$

$$E_a = (8.31 \times 298) (17.40 + 4.72)$$

$$E_a = 54788 \text{ J mol}^{-1}$$

$$E_a = 54.8 \text{ kJ mol}^{-1}$$

3 At 20°C: $k = Ae^{-\frac{E_a}{RT}}$

$$= 5.18 \times 10^5 \times e^{-\frac{75000}{8.31 \times 293}}$$

$$= 5.18 \times 10^5 \times 4.19 \times 10^{-14}$$

$$= 2.17 \times 10^{-8} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

At 40°C: $k = Ae^{-\frac{E_a}{RT}}$

$$= 5.18 \times 10^5 \times e^{-\frac{75000}{8.31 \times 313}}$$

$$= 5.18 \times 10^5 \times 3.00 \times 10^{-13}$$

$$= 1.55 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

At 40°C the reaction rate is $\frac{1.55 \times 10^{-7}}{2.17 \times 10^{-8}} = 7.16$ times faster

4 No catalyst: $k = Ae^{-\frac{E_a}{RT}}$

$$= 6.92 \times 10^6 \times e^{-\frac{150000}{8.31 \times 298}}$$

$$= 6.92 \times 10^6 \times 4.94 \times 10^{-27}$$

$$= 3.42 \times 10^{-20} \text{ s}^{-1}$$

+ catalyst: $k = Ae^{-\frac{E_a}{RT}}$

$$= 6.92 \times 10^6 \times e^{-\frac{50000}{8.31 \times 298}}$$

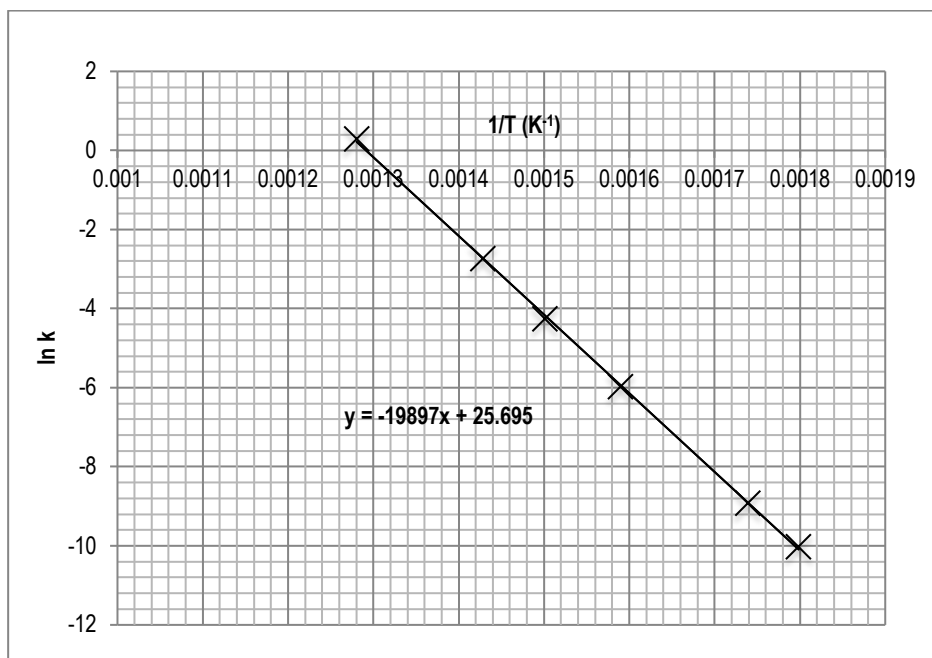
$$= 6.92 \times 10^6 \times 1.70 \times 10^{-9}$$

$$= 1.18 \times 10^{-2} \text{ s}^{-1}$$

With a catalyst the reaction rate is $\frac{1.18 \times 10^{-2}}{3.42 \times 10^{-20}} = 3.45 \times 10^{17}$ times faster

5

Temperature (K)	556	575	629	666	700	781
k ($\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)	4.45×10^{-5}	1.34×10^{-4}	2.52×10^{-3}	0.0141	0.0643	1.34
$1/T$ (K^{-1})	0.00180	0.00174	0.00159	0.00150	0.00143	0.00128
$\ln k$	-10.02	-8.92	-5.98	-4.26	-2.74	0.29

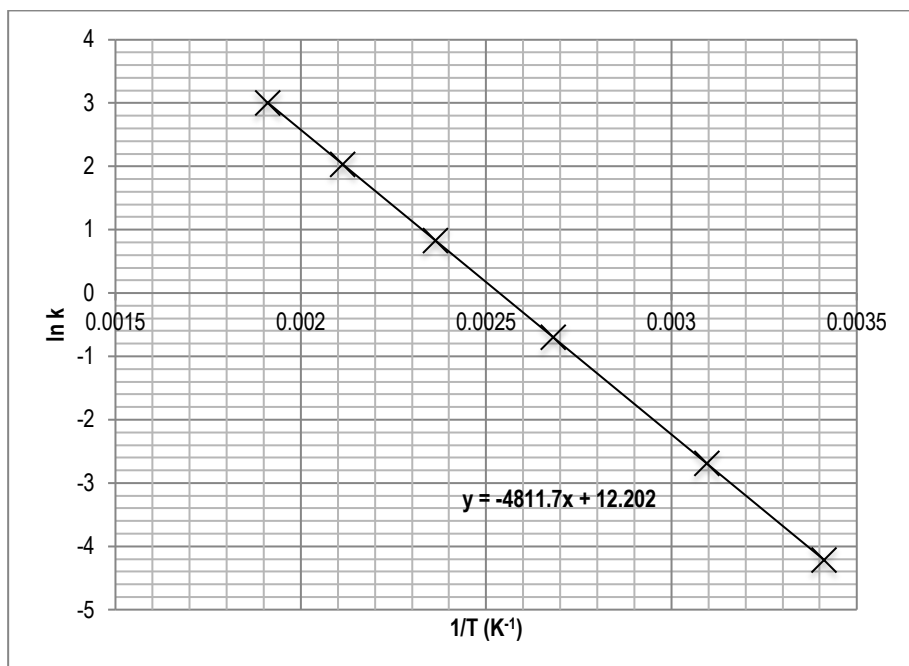


$$\text{Gradient} = -19897 = \frac{-E_a}{R}$$

$$\begin{aligned} E_a &= 19897 \times 8.31 \\ &= 165000 \text{ J mol}^{-1} \\ &= 165 \text{ kJ mol}^{-1} \end{aligned}$$

6

Temperature ($^{\circ}\text{C}$)	20	50	100	150	200	250
k ($\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)	0.0147	0.0675	0.497	2.29	7.61	20.1
$1/T$ (K^{-1})	0.00341	0.00310	0.00268	0.00236	0.00211	0.00191
$\ln k$	-4.22	-2.70	-0.70	0.83	2.03	3.00

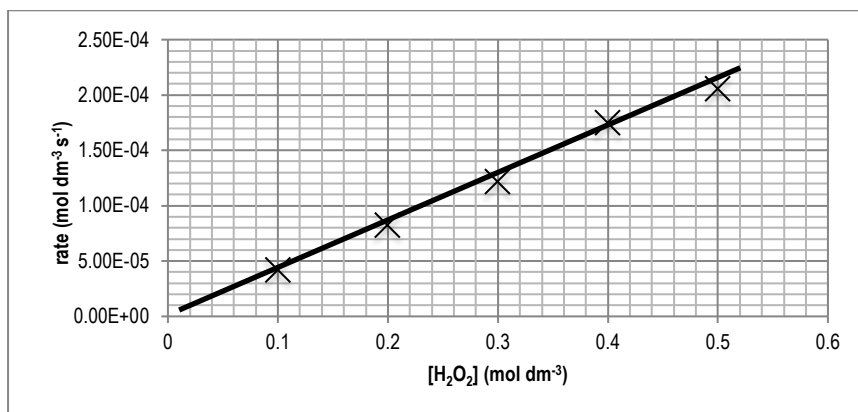


$$\text{Gradient} = -4812 = \frac{-E_a}{R}$$

$$\begin{aligned} E_a &= 4812 \times 8.31 \\ &= 39988 \text{ J mol}^{-1} \\ &= 40.0 \text{ kJ mol}^{-1} \end{aligned}$$

TASK 8 – Plotting concentration-rate graphs to determine orders

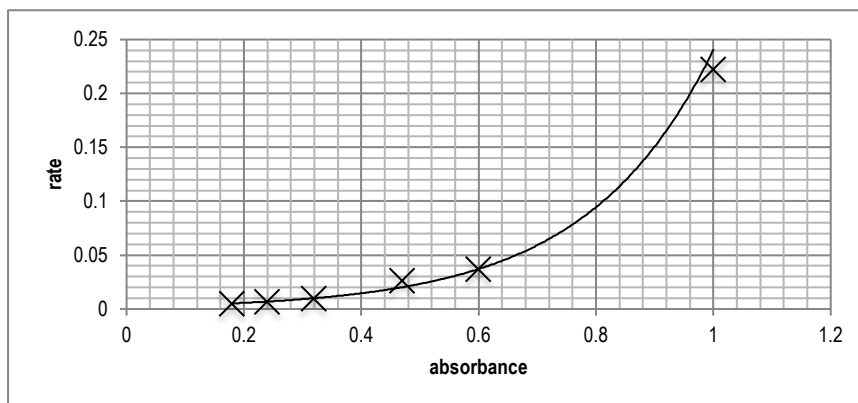
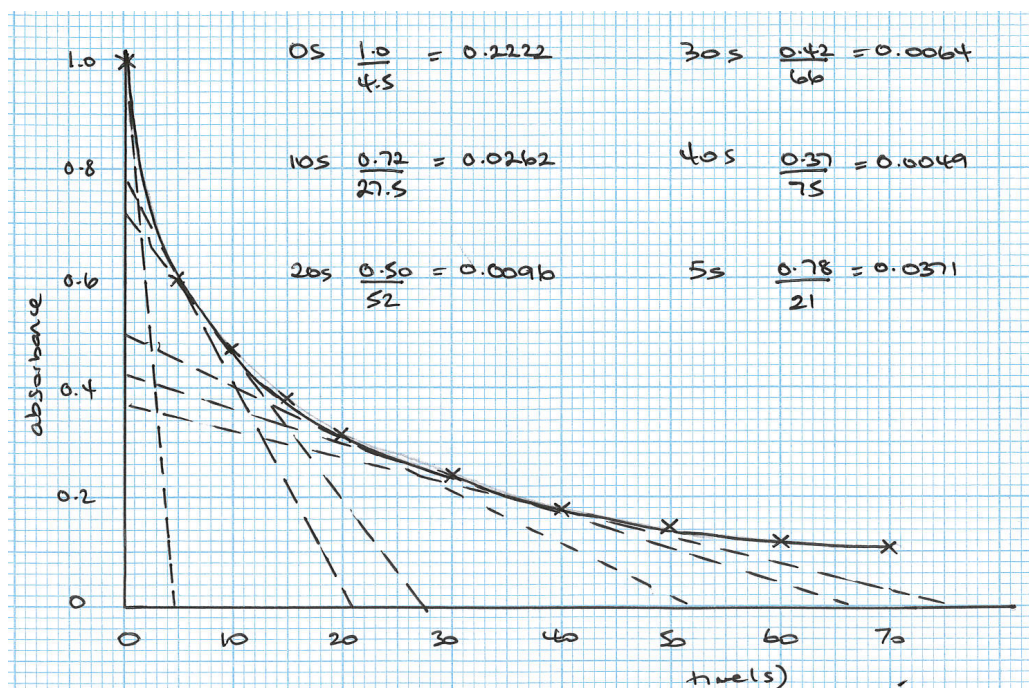
1



Reaction is:
first order wrt [H₂O₂]

2

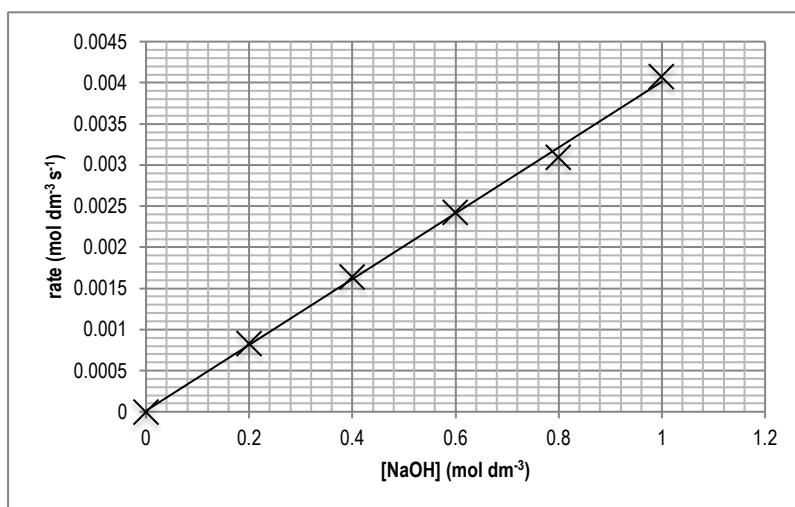
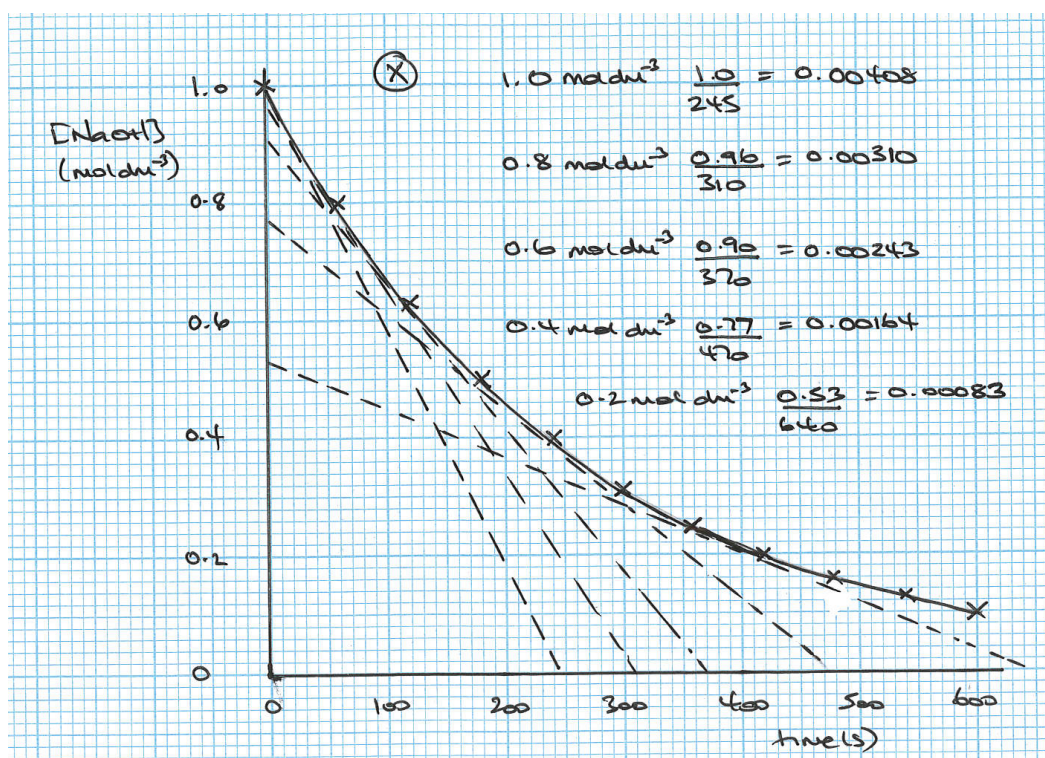
Time (s)	0	5	10	20	30	40
Absorbance	1.0	0.60	0.47	0.32	0.24	0.18
Rate (s ⁻¹)	0.2222	0.0371	0.0262	0.0096	0.0064	0.0049



Reaction is:
second order wrt [M]

3a

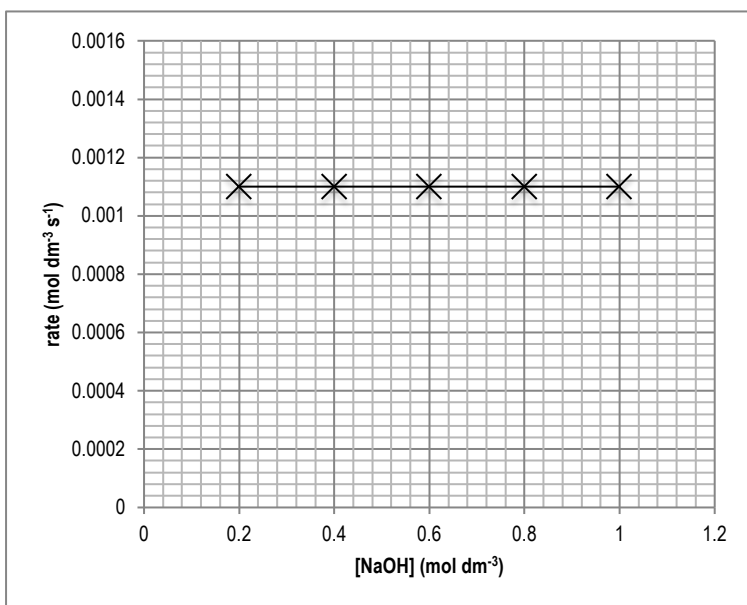
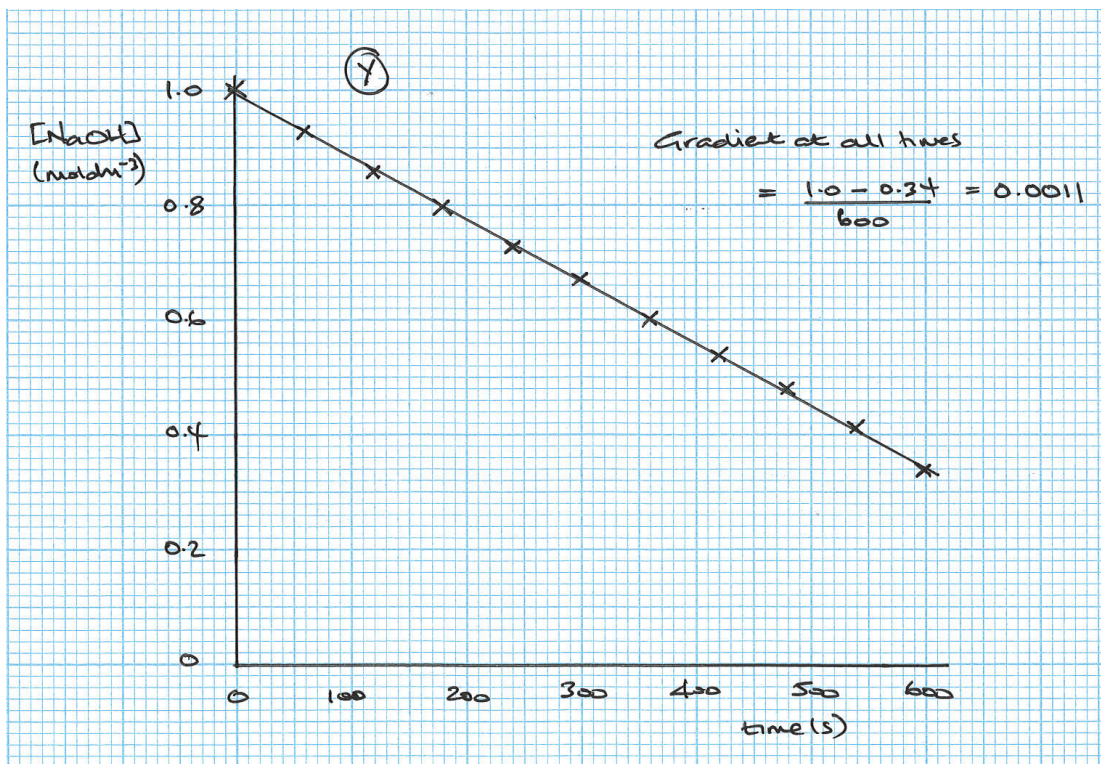
[NaOH] (mol dm ⁻³)	1.0	0.8	0.6	0.4	0.2
Rate (mol dm ⁻³ s ⁻¹)	0.00408	0.00310	0.00243	0.00164	0.00083



Reaction is:
first order wrt [NaOH]

3b

[NaOH] (mol dm ⁻³)	1.0	0.8	0.6	0.4	0.2
Rate (mol dm ⁻³ s ⁻¹)	0.0011	0.0011	0.0011	0.0011	0.0011



Reaction is:
zero order wrt [NaOH]

3c

No – the mechanisms are different because with **X** the reaction is first order with respect to [NaOH] but with **Y** it is zero order with respect to [NaOH]