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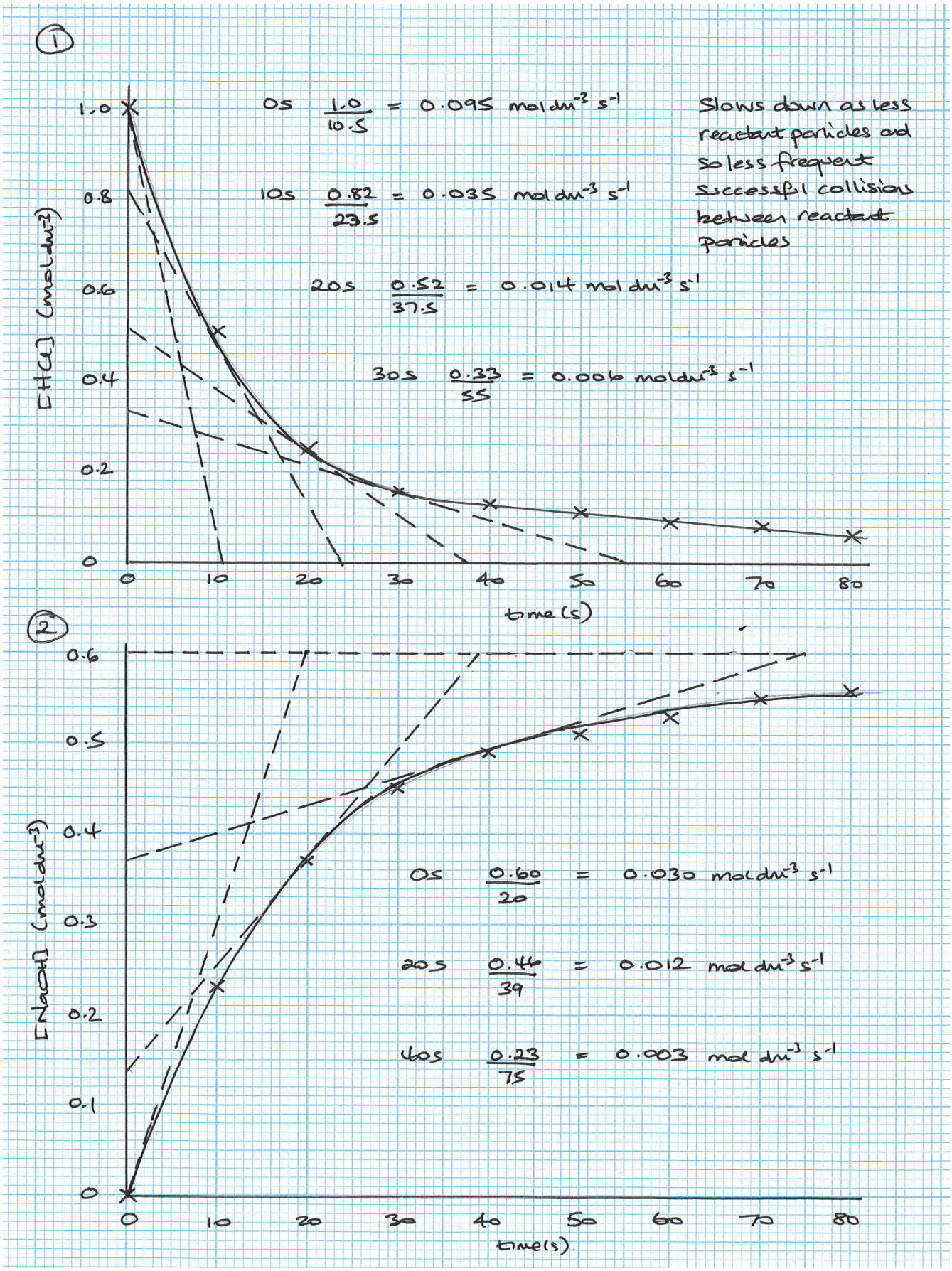
KINETICS

TASK 1 – Finding rates using gradients



TASK 2 – What orders mean

1 Consider this reaction: A + B + C → D

The rate equation is: 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 → R T acts as catalyst

The rate equation is: 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]	$k = \frac{\text{rate}}{[A]}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}}$	s^{-1}
2)	rate = k [C] [H]	$k = \frac{\text{rate}}{[C][H]}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}^2}$	$mol^{-1}\ dm^3\ s^{-1}$
3)	rate = k [S]^2	$k = \frac{\text{rate}}{[S]^2}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}^2}$	$mol^{-1}\ dm^3\ s^{-1}$
4)	rate = k [J]^2 [H]^2	$k = \frac{\text{rate}}{[J]^2[S]^2}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}^4}$	$mol^{-3}\ dm^9\ s^{-1}$
5)	rate = k [T]	$k = \frac{\text{rate}}{[T]}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}}$	s^{-1}
6)	rate = k [S] [E] [G]^2	$k = \frac{\text{rate}}{[S][E][G]^2}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}^4}$	$mol^{-3}\ dm^9\ s^{-1}$
7)	rate = k [D]^2 [C]	$k = \frac{\text{rate}}{[D]^2[C]}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}^3}$	$mol^{-2}\ dm^6\ s^{-1}$
8)	rate = k [A] [B] [C]	$k = \frac{\text{rate}}{[A][B][C]}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}^3}$	$mol^{-2}\ dm^6\ s^{-1}$
9)	rate = k [J] [G]	$k = \frac{\text{rate}}{[J][G]}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}^2}$	$mol^{-1}\ dm^3\ s^{-1}$
10)	rate = k [H^+] [Br^-]	$k = \frac{\text{rate}}{[H^+][Br^-]}$	$k = \frac{\text{(mol dm}^{-3}\text{) s}^{-1}}{\text{(mol dm}^{-3}\text{)}^2}$	$mol^{-1}\ dm^3\ s^{-1}$

TASK 4 – Finding rate equations using initial rates data

a) rate = $k[A]^2$ $k = \frac{rate}{[A]^2} = \frac{10}{3^2}$ = 1.11 $mol^{-1}\ dm^3\ s^{-1}$

b) rate = $k[D][E]$ $k = \frac{rate}{[D][E]} = \frac{5}{0.1^2}$ = 500 $mol^{-1}\ dm^3\ s^{-1}$

c) rate = $k[H^+]^2[J]$ $k = \frac{rate}{[H^+]^2[J]} = \frac{12}{(0.5^2 \times 0.2)}$ = 240 $mol^{-2}\ dm^6\ s^{-1}$

d) rate = $k[T]$ $k = \frac{rate}{[T]} = \frac{300}{0.2}$ = 1500 s^{-1}

e) rate = $k[H^+][Q]$ $k = \frac{rate}{[H^+][Q]} = \frac{8}{(0.01 \times 0.2)}$ = 4000 $mol^{-1}\ dm^3\ s^{-1}$

f) rate = $k[W]^2$ $k = \frac{rate}{[W]^2} = \frac{0.016}{0.02^2}$ = 40 $mol^{-1}\ dm^3\ s^{-1}$

g) rate = $k[M]^2$ $k = \frac{rate}{[M]^2} = \frac{0.15}{0.1^2}$ = 15 $mol^{-1}\ dm^3\ s^{-1}$

h) rate = $k[HI]^2$ $k = \frac{rate}{[HI]^2} = \frac{0.41}{1.64^2}$ = 0.152 $mol^{-1}\ dm^3\ s^{-1}$

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$^+$][CH$_3$COCH$_3$]

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

TASK 6a – Rate determining step 1

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 6b – Rate determining step 2

1 a i rate = k $[CH_3CH_2CH_2Br][OH^-]$
ii 2nd order
b i rate = k $[(CH_3)_3CBr]$
ii 1st order
2 a rate = k $[Q]^2$
b rate = k $[Q]^2[P]$
c rate = k $[Q]^2[P]$

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

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

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

$= 2.17 \times 10^{-8} \text{ mol}^{-1} \text{ dm}^6 \text{ s}^{-1}$

At 40°C: $k = Ae^{-\frac{E_a}{RT}}$

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

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

$= 1.55 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^6 \text{ s}^{-1}$

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

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

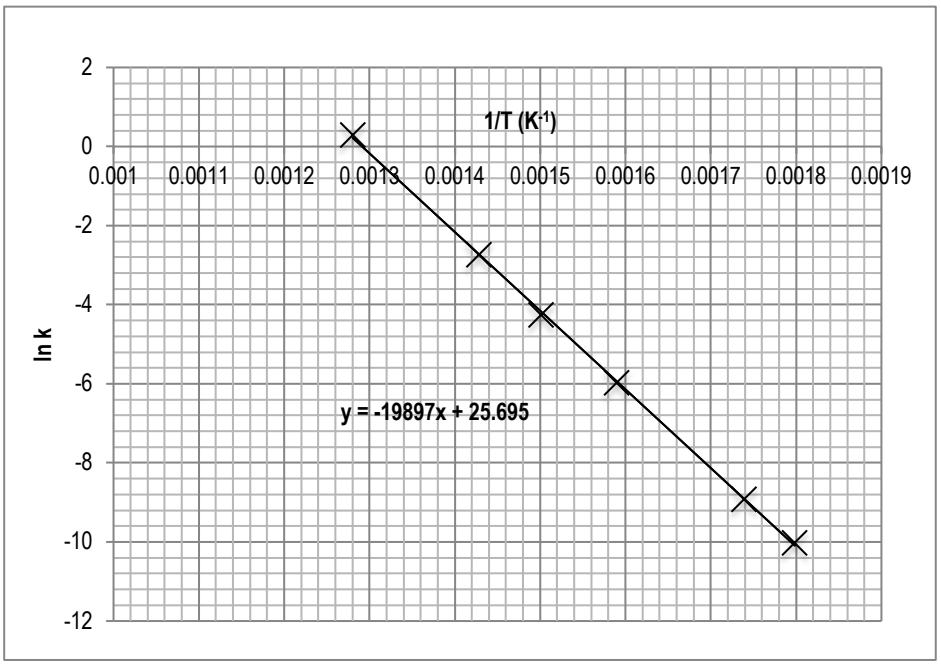
$= 6.92 \times 10^6 \times 1.70 \times 10^{-9}$

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

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

5

Temperature (K)	556	575	629	666	700	781
k (mol^{-1} dm^3 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



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

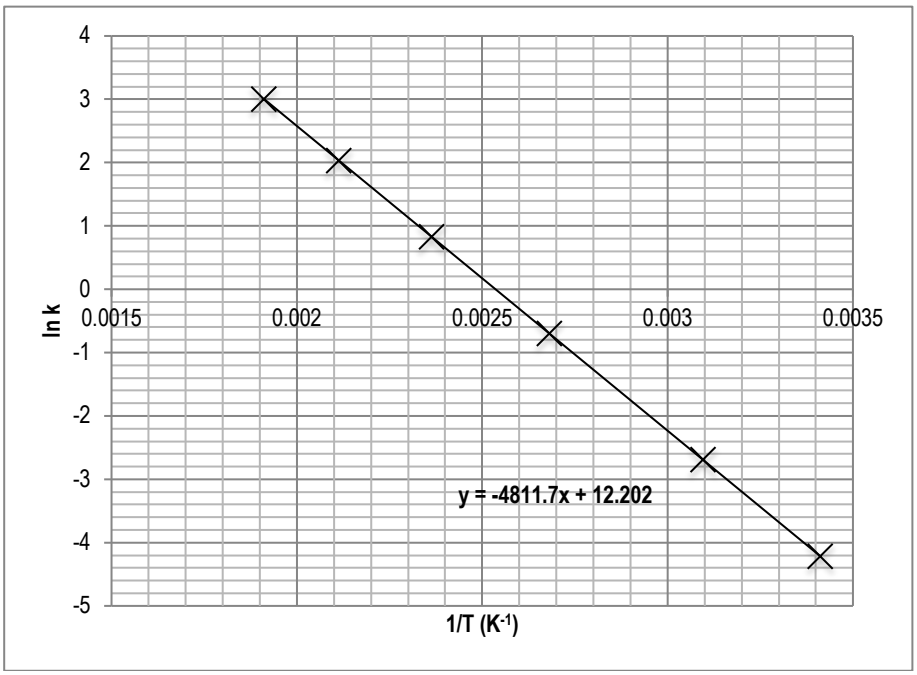
E_a = 19897 x 8.31

= 165000 J mol^{-1}

= 165 kJ mol^{-1}

6

Temperature (°C)	20	50	100	150	200	250
k (mol^{-1} dm^3 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



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

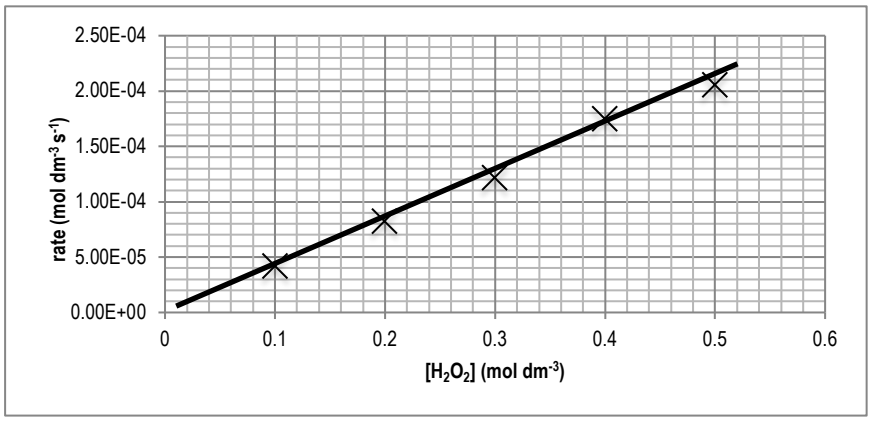
E_a = 4812 x 8.31

= 39988 J mol^{-1}

= 40.0 kJ mol^{-1}

TASK 8 – Plotting concentration-rate graphs to determine orders

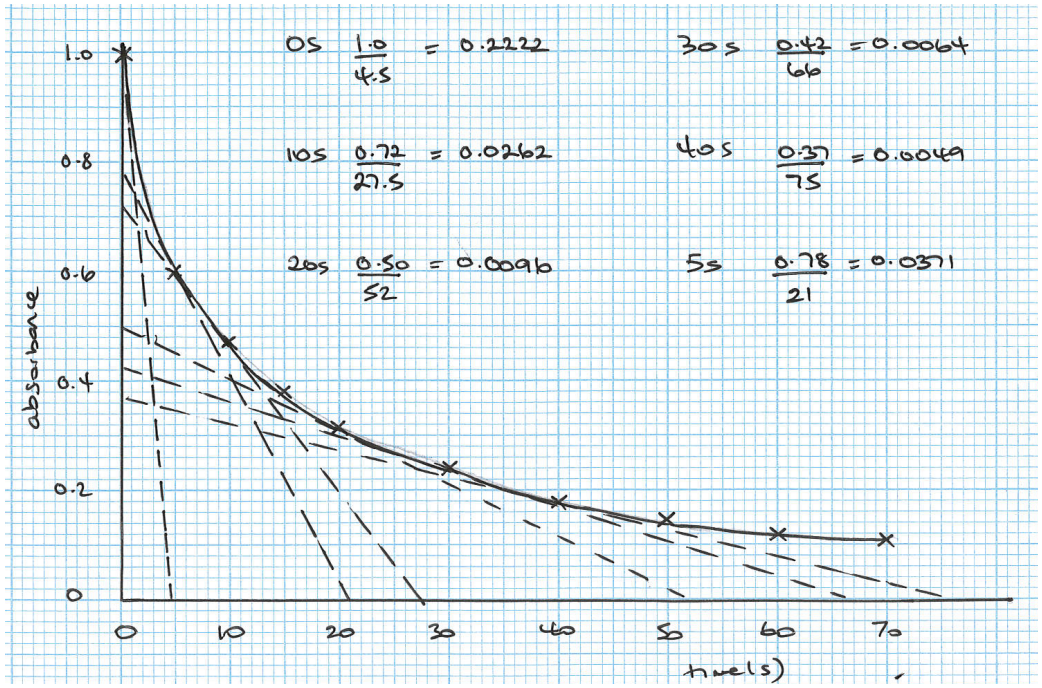
1

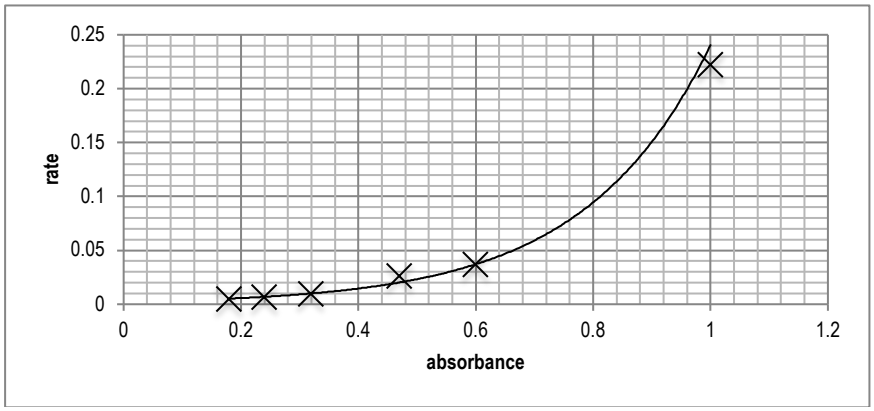


Reaction is:
first order wrt $[H_2O_2]$

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

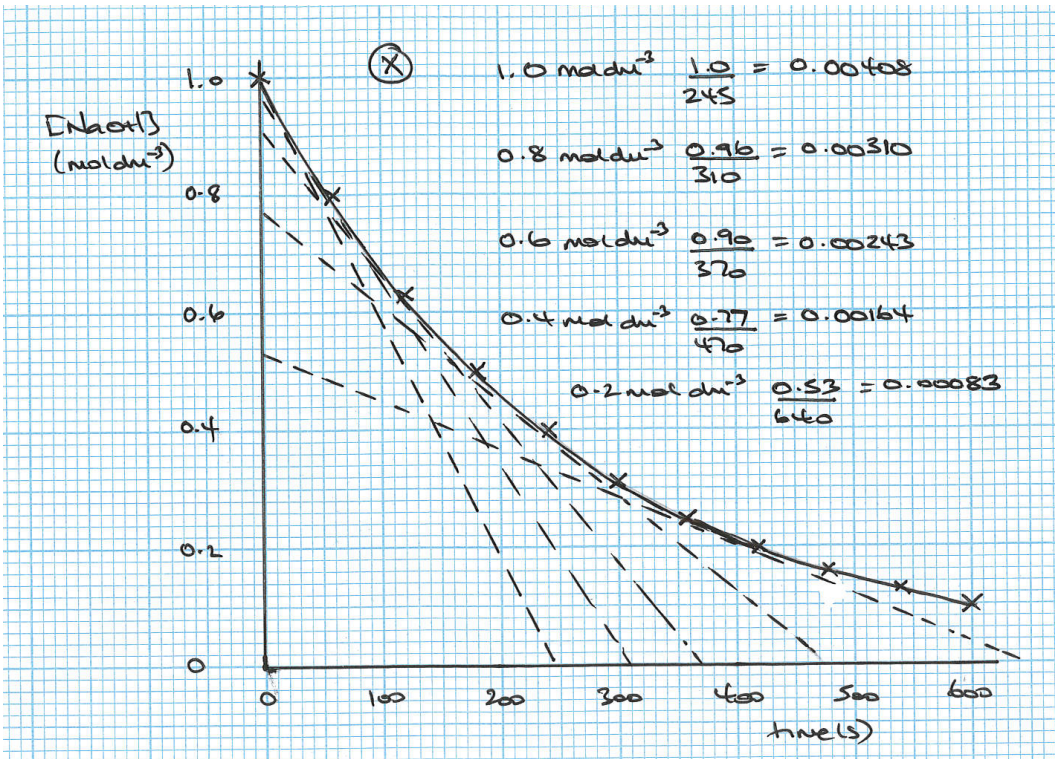


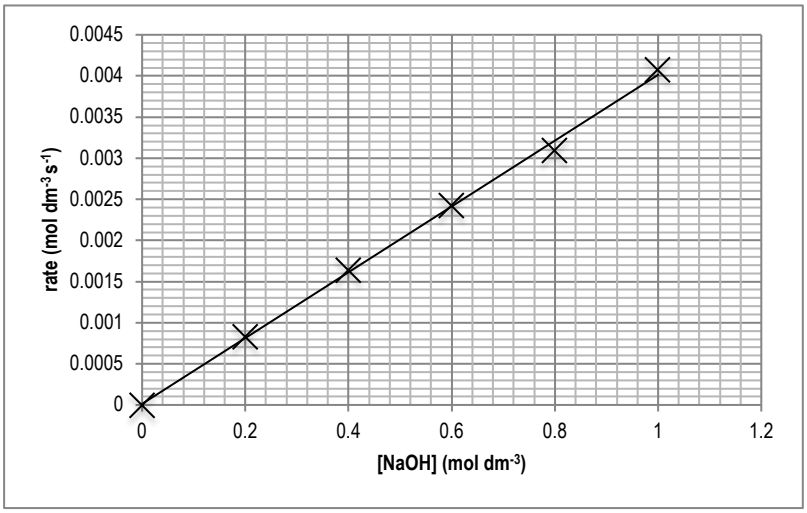


Reaction is:
second order wrt [M]

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

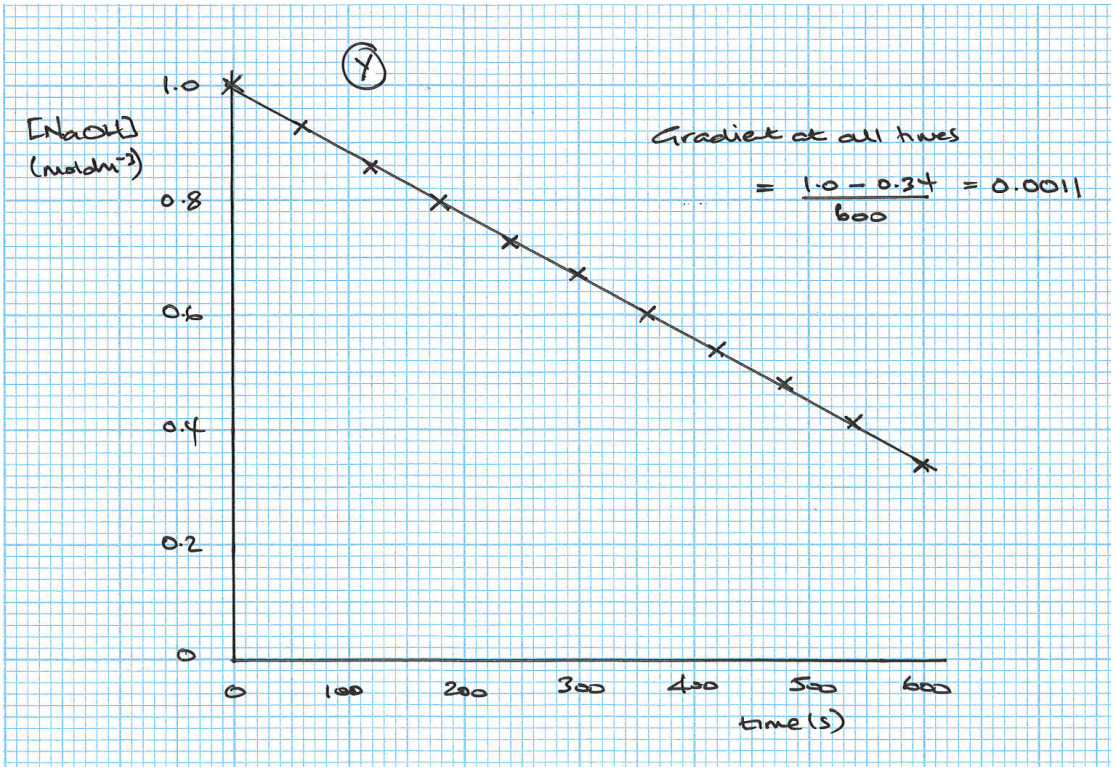


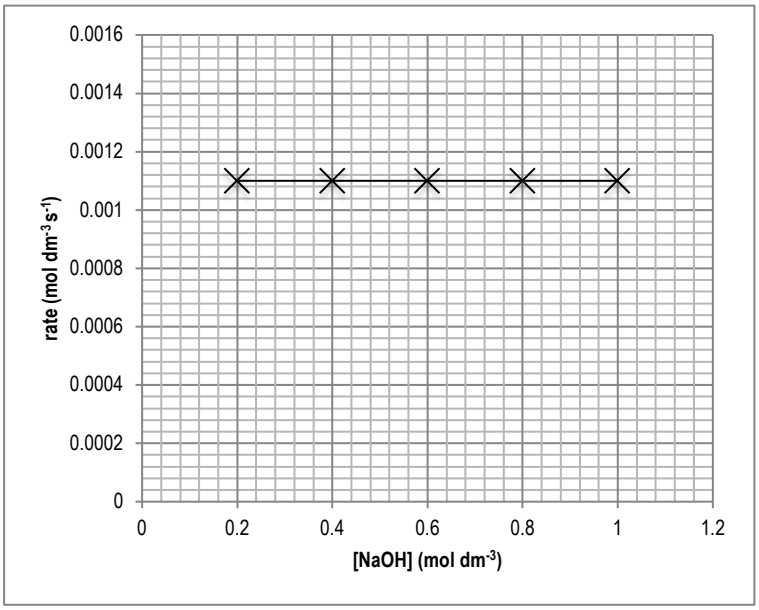


Reaction is:
first order wrt [NaOH]

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]