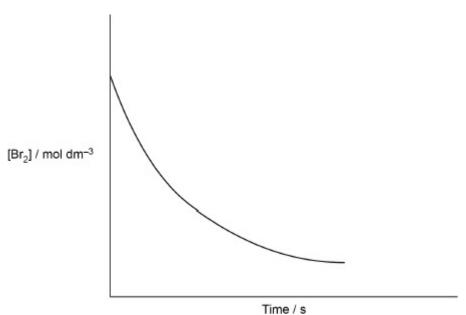
# Mark schemes

# Q1.

(a) Curve e.g.



Curve with decreasing gradient

(b) **M1** For  $[OH^-] = 7.50 \times 10^{-2}$ 

**M2** For rate =  $2.75 \times 10^{-11}$ 

M3 k = 
$$\frac{\text{rate}}{[\text{CH}_3 \text{ COCH}_3][\text{OH}^-]}$$

M3 For rearranging rate equation

OR

$$k = \frac{2.75 \times 10^{-11}}{(1.5 \times 10^{-2}) \times (2.5 \times 10^{-2})}$$

For inserting correct numbers in rearranged equation

**M4** k = 
$$7.3(3) \times 10^{-8}$$

**M5** Units =  $mol^{-1}dm^3s^{-1}$ 

If rearrangement upside down lose M3 but can score M4 for  $1.36 \times 10^7$  as ECF M5 for mol dm<sup>-3</sup> s as ECF

- M1 Arrow from C-H bond to C-C
- M2 Arrow from C=O bond to O
- M3 Arrow from lone pair on O to C-O bond
- **M4** Arrow from Br-Br bond to Br

  Dipoles must be correct if shown for M4
- (d) Step 1 includes  $CH_3COCH_3$  and  $OH^-$  and these are also in the rate equation OR

Step 1 contains all the species in the rate equation

 $Br_2$  not in step 1 <u>and</u> not in rate equation so it has to be step 1

[11]

## **Q2**.

(a) **M1** (Instead of leaving the flask open) to avoid acid/solution/liquid escaping

OR

to avoid (acid/solution/liquid) splashing/spraying/spitting (out).

Ignore evaporation/spilling/to let gas escape/to

avoid loss of product/reactant/impurities getting in

M2 (Instead of inserting a bung) to allow gas/CO<sub>2</sub> to escape Ignore pressure would build up Ignore air

NOT other wrongly identified gas(es)

(b) So that surface area/mass/amount stays (approx./effectively) constant

Ignore concentration stays constant

Ignore volume

Ignore so HCl is the limiting factor

Ignore so rate is only affected by [HCl] (as in Q)

(c) M1  $m_t$ /mass of CO<sub>2</sub> produced in time t is proportional to the (amount/concentration of) HCl that has reacted (at time t)

Alternative answer:

**M2**  $m_{\text{total}}$ /total mass of CO<sub>2</sub> produced is proportional to the total (amount/concentration of) HCl that has reacted/was present initially

(therefore  $m_{total}$  -  $m_t$  is proportional to (amount/conc of) HCl present at time t)

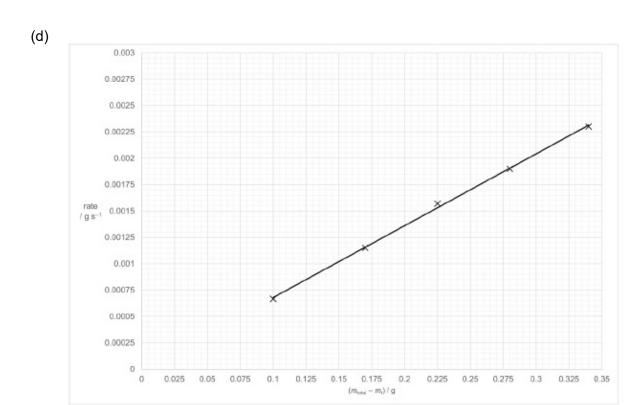
Allow 'Equal to'/'represents' for proportional to Allow m<sub>total</sub> is proportional to HCl 'added'

 $M1 \ m_{total}$  -  $m_t$  is equal/proportional to (mass/amount of)  $CO_2$  still to be produced

M2 (Mass/amount of) CO<sub>2</sub> still to be produced is proportional to (amount/concentration of) HCl still to react

2

2



- M1 Scales designed so that plotted points (and origin if shown) occupy >50% along each axis and axes labelled including units NOT if either/both scale reversed but allow ecf M2 and M3.
- **M2** Plotted points (all within half a small square)
- M3 Suitable straight line (should be within one square of all points except potentially the middle one)

M3 ECF for best fit line (points above and below) from their plotted points

(e) Straight line **AND** through origin

Allow 'constant gradient' for straight line Ignore (directly) proportional

(f) Any two from:

- Volume of gas / CO<sub>2</sub>
- pH
- Concentration of HCI/acid/H<sup>+</sup>
- Conductivity

NOT temperature

NOT 'volume' or 'concentration' unqualified

NOT time for CaCO<sub>3</sub> to 'dissolve'/disappear (as in excess)

Ignore mass loss

Ignore amount of CO2

1

3

Q3.

(a) 1.75 × 10<sup>-3</sup> AND -6.46 Allow 0.00175 NOT other sig figs (e.g. 1.7 x 10<sup>-3</sup>, -6.5) NOT 1.74 x 10<sup>-3</sup>

(b) **M1** Unit of k (is  $s^{-1}$ )

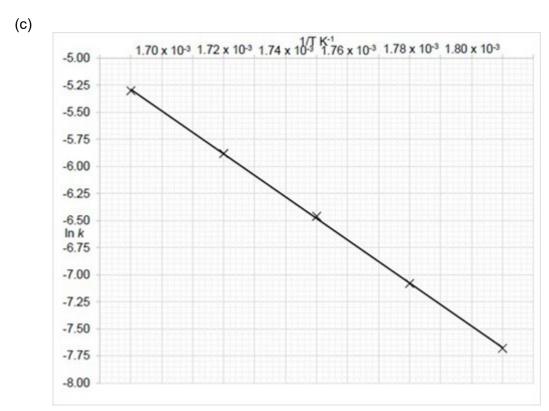
Mark independently

M1 Allow  $s^{-1}$  or  $k / s^{-1}$  or k in  $s^{-1}$ NOT just k

M2 (Order) 1/first

2

1



- M1 Points plotted (all within half a square) (ECF from (a) for 3rd point including if no values in the table)
- M2 Best fit straight line (line within one square of each point) (best fit line points above and below based on their plotted points)

(d) **M1** Gradient (expected value = -19900)

Answer of (+)161 to (+)170 gets 3/3
Allow range from -19400 to -20400 from correct plotting and best fit line
ECF from any straight line

M2 
$$-\frac{E_a}{R}$$
 = gradient

can be implied by calculation shown e.g.  $E_a = -M1 \times 8.31$  gets M2

M3 
$$E_a = \frac{-M1 \times 8.31}{1000} = (+)165 \text{ (kJ mol}^{-1}\text{)}$$

Allow negative E<sub>a</sub> if positive gradient in M1

(e) M1 (alkene) CH<sub>2</sub>=CHCH<sub>3</sub>

M2 (carbonyl) (CH<sub>3</sub>)<sub>2</sub>CO / CH<sub>3</sub>COCH<sub>3</sub>

Allow any correct structural representations

C=C must be shown

Allow C(CH<sub>3</sub>)<sub>2</sub>O

If correct two structures are given but the wrong way round, then scores 1 mark

[10]

2

3

Q4.

(a) M1 Relative rate = 1.00

$$M2[B] = 0.16$$

M3 Relative rate = 1.35

(b) M1 Step 2

M2 (By the end of step 2) 1  $\times$  H<sup>+</sup> and 2  $\times$  B have been used Allow slowest step

2

3

[5]

## Q5.

(a)  $C_nH_{2n-2}O$ 

Allow  $C_nH_{2n}CO$  or  $(CH_2)_nCO$  or  $C_nH_{2(n-1)}O$ 

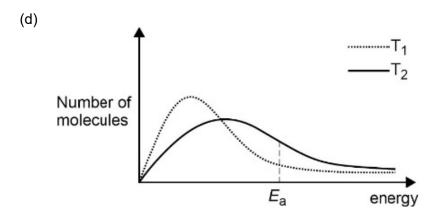
Allow other C-O bond breaking for M1

(c) M1  $\frac{k}{A} = e^{-Ea/R^2}$ 

 $M2 8.302 = \frac{34500}{8.31 \times T}$ 

M3 T = 500 K

OR via  $\ln k = \ln A - \frac{Ea}{RT}$  or shown with numbers



M5 At T₂ (many) more particles have E≥Ea

M1 x axis labelled correctly (kinetic not required)

AND y axis labelled correctly allow particles

M2 Ea labelled on x axis

M3 Distribution correct shape for T<sub>1</sub>

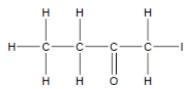
M4 Peak at T<sub>2</sub> lower with max shifted right and only crosses once

5

3

## Q6.

(a)



Apply list principle for more than one structure given

**M1** 

1-iodobutan-2-one

Allow 1-iodo-2-butanone

**M2** 

Rate

(b)  $[CH_3CH_2COCH_3][H^+] = k$ 

Rearranged expression Or with numbers

M1

 $k = 4.(04) \times 10^{-5}$  or 0.00004(04)

If upside down =  $24752 \text{ mol dm}^{-3} \text{ s}$ If multiply =  $5.20 \times 10^{-4} \text{ mol}^3 \text{ dm}^{-9} \text{ s}^-$ 

**M2** 

mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>

**M3** 

(c)  $3.6(25) \times 10^{-5}$  (mol dm<sup>-3</sup> s<sup>-1</sup>)

Allow  $3.59 \times 10^{-5}$  to  $3.63 \times 10^{-5}$ 

1

(d) Brown colour removed

Goes colourless

Allow (orange) brown to colourless

Allow purple to colourless

1

(e) As T increases rate (1/t) increases OR time for completion decreases

M1

Exponentially

OR

By a greater/ increasing factor

Or rate increases more and more as temp increases ie description of exponential increase

M2

Many more particles have  $E \ge E_a$ 

NOT just higher collision frequency NOT just more successful collisions

М3

(f) Time = 
$$\frac{1}{0.03}$$
 = 33 s

1

(g) 
$$\ln(1.55 \times 10^{-5}/1.70 \times 10^{-4}) = \frac{E_a}{R} \left(\frac{1}{333} - \frac{1}{303}\right)$$
Insertion of correct values

**M**1

$$-2.39 = \frac{E_a}{R}(-2.97 \times 10^{-4})$$
Evaluate LHS and fraction on RHS

M2

$$\frac{2.39 \times 8.31}{2.97 \times 10^{-4}} = E_a$$

Re-arrange for  $E_a$ 

**M3** 

66937

Evaluate

M4

66.9 kJ mol<sup>-1</sup>

convert to kJ mol-1

M5

If only  $k_1$  and  $k_2$  reversed this gives a negative answer for  $E_a$  Lose M1 and M5

If AE in M2 allow ECF

Allow ECF from M4 to M5 for a correct unit conversion

Allow range 66.3 - 67.1

# (h) Nucleophilic Addition

# M 3 arrow from double bond to 0 (dependent on at attempt at M2) O CN M 4 for intermediate with –ve on O

M2 arrow from lone pair to C of C = O

M1M2M3M4M5

ALLOW negative charge anywhere on cyanide But attacking lone pair must be on C Do not award M3 without attempt of M2 Allow M2 for attack to a positive carbon following breaking of C=O

Penalise covalent KCN in M2

M3 ignore partial charges unless wrong

Penalise M3 for incorrect connection between CN and C

NB Allow fully displayed or other structural formulae

[21]

1

1

1

1

1

1

$\sim$	_
( )	/
w	

(a) **M1** High**er/est** concentration of / more H<sub>2</sub>O<sub>2</sub> / particles / molecules / reactants

M2 More frequent successful collisions

### Alternative approach

**M1** Lower/est concentration of / fewer particles / molecules / reactants as time goes on

**M2** Less frequent successful collisions (look for both ideas even if separated)

Ignore 'chance' / 'probability'

(b) M1 Suitable tangent drawn

**M1** Tangent must be drawn with ruler and touch line at 0.05 mol dm<sup>-3</sup> (± 1 square) and not cross the curve (if white seen between lines it crosses)

**M2** -0.00120 to -0.00155 (mol dm<sup>-3</sup> s<sup>-1</sup>)

M2 Ignore units

**Allow** ecf from unsuitable tangent i.e if M1 not awarded

**Ignore** sign of gradient

(c) M1  $[H_2O_2]_{initial} = 0.083 \text{ mol dm}^{-3}$ 

Allow 0.082 - 0.084

**M2**  $[H_2O_2]_t = 0.0664 \text{ (mol dm}^{-3})$ 

**Allow** 0.0656 - 0.0672 (scores 2/2)

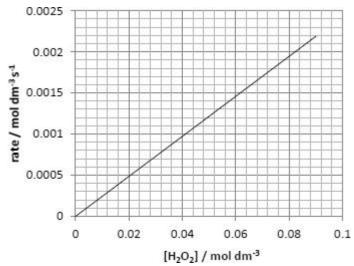
2SF minimum

**Allow** ecf from **M1** (M2 = M1  $\times$  0.8)

## (d) M1 Points plotted

M1 allow each point (± 1/2 square)

## M2 best fit straight line drawn



**M2** line should be drawn with a ruler and cover the five points given going within 1 square of each point, no doubles no kinks. The line does not need to be extended to the origin

**Allow** reasonable best fit line if points plotted incorrectly

## (e) M1 1st order

**M2** straight line graph through the origin

**Ignore** rate is (directly) proportional to  $[H_2O_2]$  **Allow** constant gradient line through the origin **Allow** use of data from line to show e.g. x2 conc = x2 rate

**Allow** if M1 missing **Not** if M1 wrong

[10]