1. (i) Experiments 1 & 2, [R–CH_2–Cl] × 3, Rate × 3 **(1)**

$\therefore$ 1st order w.r.t. [R–CH_2–Cl] **(1)**

Experiments 1 & 3, [R–CH_2–Cl] and [OH^-] × 2, rate × 4 **(1)**

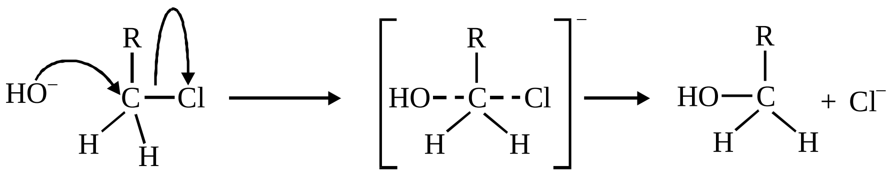
$\therefore$ 1st order w.r.t. [OH^-] **(1)** 4

(ii) Rate = k [R–CH_2–Cl] [OH^-] consequential on (i) 1

(iii) $k = \dfrac{\text{rate}}{[RCH_2Cl][OH^-]} = \dfrac{4.0\times10^{-4}\,\text{mol dm}^{-3}\text{s}^{-1}}{0.050\times0.10\,\text{mol}^2\text{dm}^{-6}} =$ 0.080 **(1)** $\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$ **(1)**

2

(iv) (S_N2)



(1) **(1)** **(1)**

3

Note *S_N1: allow if first order **deduced** from parts **(1)** and (ii) for **full** marks.*

[10]

2. (a) (i) $Kp = \dfrac{P_{SO2}^{\ 2} \times P_{O2}}{P_{SO3}^{\ 2}}$ **(1)**

[ ] no mark
( ) OK 1

(ii)

	$2SO_3$	→	$2SO_2$	+ O_2	
Mols at start	2		0	0	
mols at equ	0.5		1.5	0.75	**(1)**

Mark by process

1 mark for working out mole fraction

1 mark for × 10

1 mark for correct substitution in K_p and answer

1 mark for unit

i.e. $P_{SO2} = \frac{1.5}{2.75} \times 10 = 5.46$

$P_{O2} = \frac{0.7}{2.75} \times 10 = 2.73$

$P_{SO3} = \frac{0.5}{2.75} \times 10 = 1.83$

n.b. could show mole fraction for all 3 and <u>then</u> × 10 later to give partial pressure.

Kp = $(5.46)^2 \times (2.73) / (1.83)^2$ = 24.5 **(1)** atm **(1)** 5

(b) (i) No effect **(1)** 1

(ii) No effect **(1)** 1

[8]

3. (a) (i) Working to show first order with respect to $[S_2O_8^{2}]$ **(1)**

Working to show first order with respect to $[I^-]$ **(1)**
overall equation **(1)** 3
Consequential

(ii) Sum of power of the concentration terms (for thio and iodide) in rate equation / number of each species involved up to and including or, in, the rate–determining step in the reaction mechanism / Sum of the partial / individual orders / general equation of the form $[\text{thio}]^m[\text{iodide}]^n$ overall order = m + n **(1)** 1

(iii) 36 **(1)** $dm^3 mol^{-1} s^{-1}$ **(1)** 2
Consequential on part (i)

(iv) Rate equation depends on mechanism / rate equation only involves those species in the rate determining step / slowest step **(1)** 1

(b) (i) Colorimetry / conductivity / remove samples and titrate with (standard) sodium thiosulphate solution **(1)** 1

(ii) Constant temperature **(1)** 1

(iii) Colorimeter / conductivity **adv** that monitoring is continuous / does not need removal of samples
or
disadv of titration is problems with timing **(1)** 1

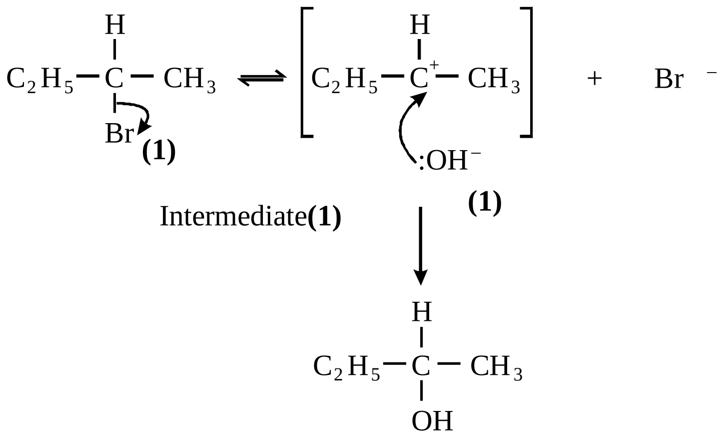
[10]

4. (a) (i)

- Rate of reaction - Rate of decrease / change in concentration of reactants **(1)**
- Overall order of a reaction - sum of the powers to which concentration terms are raised in the overall rate equation **(1)** 2

(ii) (The stoichiometric equation includes all the reactants) the rate equation only includes those species involved in the rate determining step / rate depends on mechanism **(1)** 1

(b) (i)



3

(ii)

- The reaction goes through a planar intermediate and this can be attacked from either side **(1)**
- producing an equal mixture of the two optical isomers /racemic mixture / 50-50 mixture **(1)** 2

(iii)

- Double conc. bromo compound rate double $\propto$ power 1 **(1)**
- Treble conc of bromo compound and double cone OH rate only up three times thus not dependant on conc of OH **(1)**

Rate = rate constant [bromoalkane] **(1)**
Must show use of data 3

(c) After given time remove sample **(1)**
neutralise with nitric acid / quench / stop by adding specified reagent **(1)** 3
add silver nitrate and observe extent of ppt.
/ as above and titrate solution with silver nitrate / titrate with specified reagent **(1)**
Allow 1 mark for continuous method based on conductivity or pH

[14]

5. (a) (i) $200 \times 0.05 / 330 = 30.3 \times 10^{-3} = 3.03 \times 10^{-2}$ **(1)** 1

(ii) graph linear axes at a sensible scale **(1)**
all points correct **(1)**
sensible smooth curve **(1)**
calculate 2 rates correctly (2)
1.25×10^{-6} (1.0-1.5) 5
2.5×10^{-5} (2.0 – 4. 0)

(b) (i) 0.0300 – 0.0150 = 800
0.0150 – 0.00750 = 900
0.0080 – 0.0040 = 800
Any 2 half life correctly calculated **(1)**
constant half life = 800 **(1)** 3
first order **(1)**

(ii)
- second reaction faster than first **at beginning (1)**
- first speeds up when product present **(1)** 2

(c) (i) Presence of potassium (ions) or K^+ 1

(ii) Add NaOH to solution **until in excess (1)**
Buff / cream / beige ppt. (turning brown) shows manganese(II) **(1)** 2

[14]

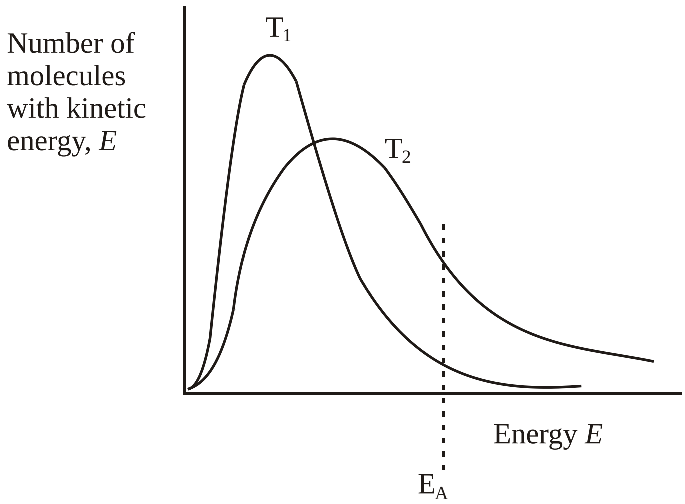
6. (a) Measure (volume/ amount of gas) with a **gas syringe** / inverted burette
OR Loss in mass with (top pan) **balance**
OR Described titrimetric method **(1)**
..........at regular time intervals **(1)** 2

(b) (i) Rate is proportional to (hydrogen peroxide) concentration
OR Index of (hydrogen peroxide) concentration in rate equation is 1 1

(ii) Rate = **k**$_{(1)}$[H_2O_2((aq))] 1

(iii) Measure/ calculate/ find several/two hal-lives **(1)**
(Check) half–lives are constant **(1)** 2

(c) (i)



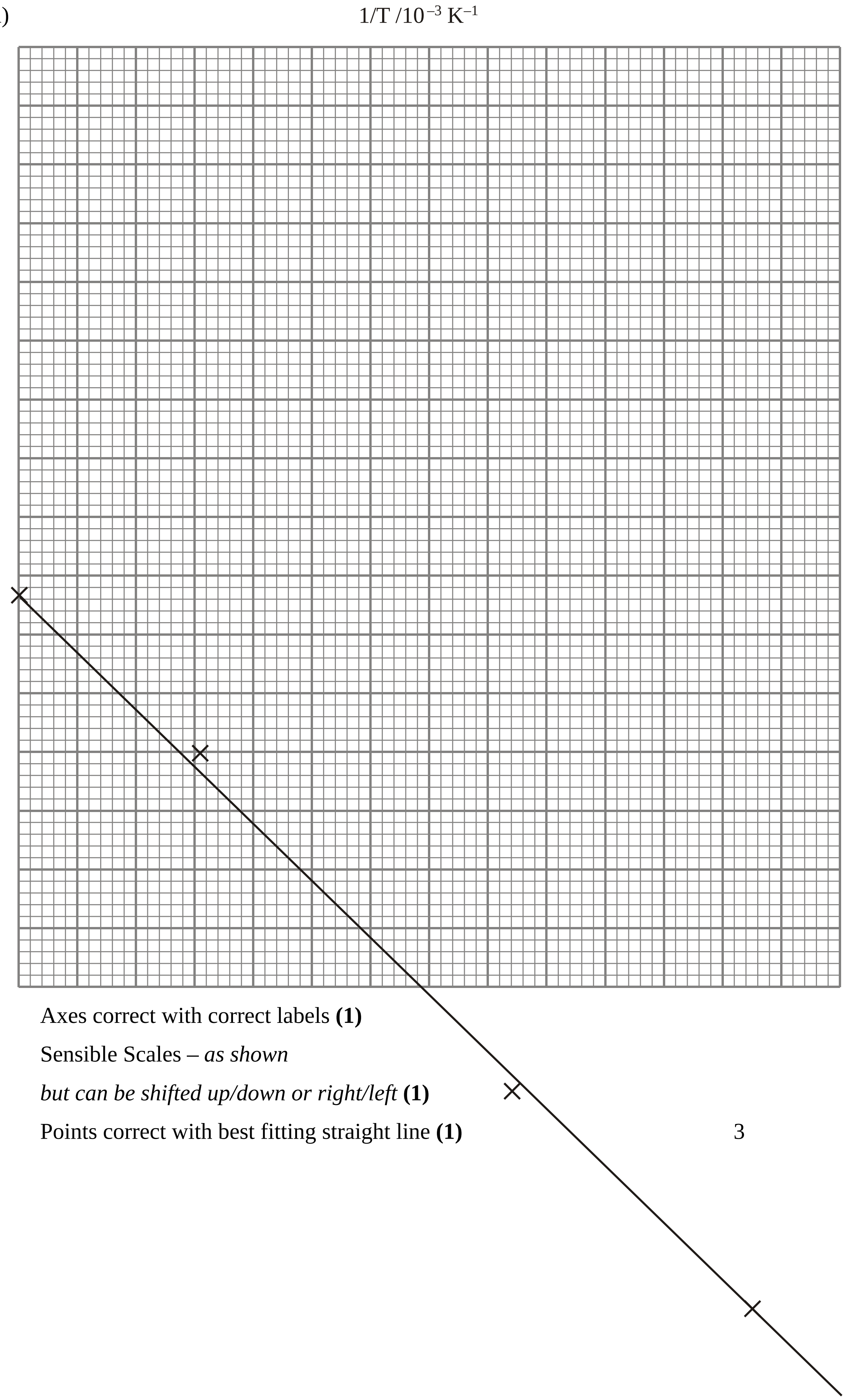
General shape of T_1 graph **(1)**

General shape of T_2 graph: higher temperature peak lower
and moved to the right **(1)**

Check that graphs start at zero – penalise once
Check that graphs do not meet energy axis – penalise once.

(Many) more molecules with energy in excess of E_A/ E_{min} / a certain value **(1)**
Can be shown (as shading) on the diagram
Activation energy shown **(1)** 4

(ii)



Axes correct with correct labels **(1)**

Sensible Scales – *as shown*

but can be shifted up/down or right/left **(1)**

Points correct with best fitting straight line **(1)** 3

(iii) Gradient = –9700 (allow –9200 to –10200) **(1)**
$\frac{E_a}{R}$ = – gradient / E_a = –8.31 × gradient **(1)**

[16]

= +81 kJ mol^{-1} / +81000 J mol^{-1} *ALLOW* 76 to 86
Correct answer, units, sign, 2SF **(1)** 3

7. (a) rate = k[A][B] **(1)** *or any other where m+n = 2*
rate = $k[A]^2$ **(1)**
rate = $k[B]^2$ **(1)** 3

(b) (i) Working to show first order with respect to H_2 **(1)**
Working to show second order with respect to NO **(1)**
Overall rate equation (must be consequential)
rate k $[H_2]$ $[NO]^2$ **(1)** 3

(ii) 0.02 = k $(1.0)^2(1.0)$ or correct use of either of the other two rows of data
k = 0.02 /1.0 = 0.02 **(1)**
$mol^{-2}dm^6s^{-1}$ **(1)** 2

Consequential on (b)(i)

(c)
- Molecules move faster/have more kinetic energy **(1)**
- More molecules / collisions have at least E_{act} **(1)**
- Greater proportion/fraction of collisions are successful OR more **of** the collisions are successful **(1)** 3

(d) k increases 1

(e)
- Catalyst provides an alternative route **(1)**
- With a lower activation energy *(consequential on first mark)* **(1)**
- Rate increases because more collisions have enough energy to overcome the lower activation energy **(1)**
[Accept argument based on Arrhenius equation for third mark] 3

[15]

8.	(a)	(i)	The reaction produces ions (H^+ and Br^-) / the number of ions increases	1
		(ii)	To enable the halogenoalkane to mix with water / to dissolve / to increase solubility	1
		(iii)	The rate doubles	1
		(iv)	Order 1/first order	1
		(v)	**Water** a possible reactant is present in excess	1
	(b)	(i)	$\frac{0.75}{5} = 0.15 / 0.150\ (\times 10^{-3})$ $\frac{1.5}{9} = 0.17 / 0.167\ (\times 10^{-3})$ $\frac{2.25}{14} = 0.16 / 0.161\ (\times 10^{-3})$ Method **(1)** Answers **(1)**	2
		(ii)	Rate is unaffected / very little affect	1
		(iii)	Zero	1
	(c)	(i)	Rate = $k_{(1)}\ [C_5H_{11}Br]$	1
		(ii)	$C_5H_{11}Br \xrightarrow{slow} C_5H_{11}^+ + Br^-$ **(1)** $C_5H_{11}^+ + OH^- \xrightarrow{fast} C_5H_{11}OH$ **(1)** No speeds ***(1 max)*** Can be stated in words	2

[12]

9.	(a)	(i)	$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ species **(1)** balance **(1)**	2
		(ii)	starch **(1)** blue / blue–black to colourless **(1)**	2
	(b)		double $[I_2]$ no change so zero order **(1)** double $[Me_2CO]$ doubles rate so first order **(1)** rate = $k[Me_2CO][H^+]$ **(1)**	3

(c) (i) Power to which concentration raised in rate equation
OR
the number of that species involved up to and including the rate determining step 1

(ii) Sum of the individual reaction orders OR sum of powers 1

(d) Iodine not involved in the rate determining step **(1)**
two **(1)** *NOT* "more than 1" 2

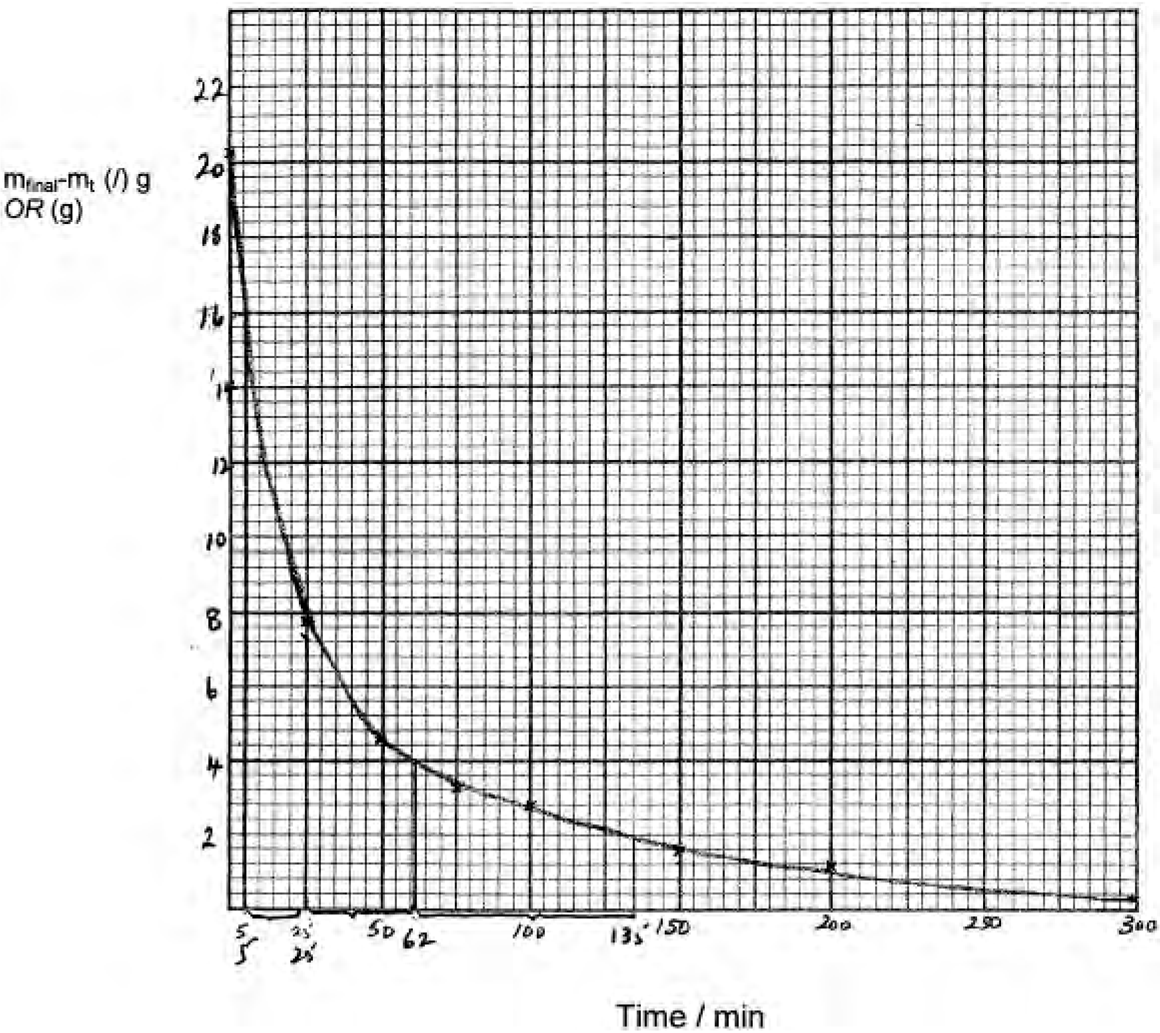
(e) $CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CH_3COONa + CHI_3 + 3NaI + 3H_2O$
CHI_3 **(1)**
other species **(1)**
balance **(1)** 3

[14]

10. (a) 1

Time	Mass urea	$m_{final} - m_t$
200	19.1	1.2
300	20	0.3

(b)



Labelled axes including units and sensible scale **(1)**
Correct plotting of points and smooth curve **(1)** 2

(c) [NH_4CNO] / ammonium cyanate concentration 1

(d) (i) Half–lives starting at t_o = 17,30 min (each ± 5 min), 60 ± 10
Starting at t= 16, half–lives are 20, 37 min (each ± 5 min), 73 ±10.
One correct **(1)**
Second and third correct half–life **(1)**
Max 1 *if no units* 2

(ii) Second order **(1)**
Because half–life is increasing / doubling / not constant **(1)** 2

(iii) Rate = k[NH_4CNO]^2 or rate = k[NH_4CNO] [H_2O] 1

(e) (i) (rds =) slow**<u>est</u>** step / stage part of the mechanism 1

(ii) Order is with respect to ammonium cyanate as water is in excess (approximately 55.5 mol of water: 0.35 mol ammonium cyanate) **(1)**
So only ammonium cyanate concentration is changing / water concentration does not change significantly **(1)** 2

[12]

11. (a) (i) Calculates or shows on graph two half–lives that are the same **(1)**
States that half–life is constant **(1)** Consequence on attempt at determining a half– life 2

(ii) **Either**
Cannot tell as water is in excess
Or
Overall order appears to be one as concentration of water does not change 1

(iii) **Either**
Calculates gradient correctly **(1)**
Divides by chosen ester concentration **(1)**
Answer and units **(1)**
Or
$kt_{1/2}$ = ln 2 **(1)**
substitutes values **(1)**
k in units of hr^{-1} **(1)** 3

(iv) At given / known times / regular intervals **(1)**
Remove samples and quench **(1)**
Titrate with (standard) sodium hydroxide solution / (standard) alkali **(1)** 3

(b) (i) Reaction with higher activation energy has smaller k 1

(ii) (Second) has a catalyst present 1

[11]

12. (a) (i) order wrt 2-bromo-2-methylpropane = 1/first **(1)**
order wrt sodium hydroxide = 0/zero **(1)** 2

(ii) rate = k $[(CH_3)_3CBr]$ $[NaOH]^0$
/ rate = k $[(CH_3)_3CBr]$ $[OH^-]^0$
/ rate = k $[(CH_3)_3 CBr]$ 1

(b) k = rate/$[(CH_3)_3CBr]$ = $(1.5\times10^{-4})/(5\times10^{-4}) = 3.0\times10^{-1}$ / 3×10^{-1} / 0.3 **(1)**
s^{-1} **(1)** 2

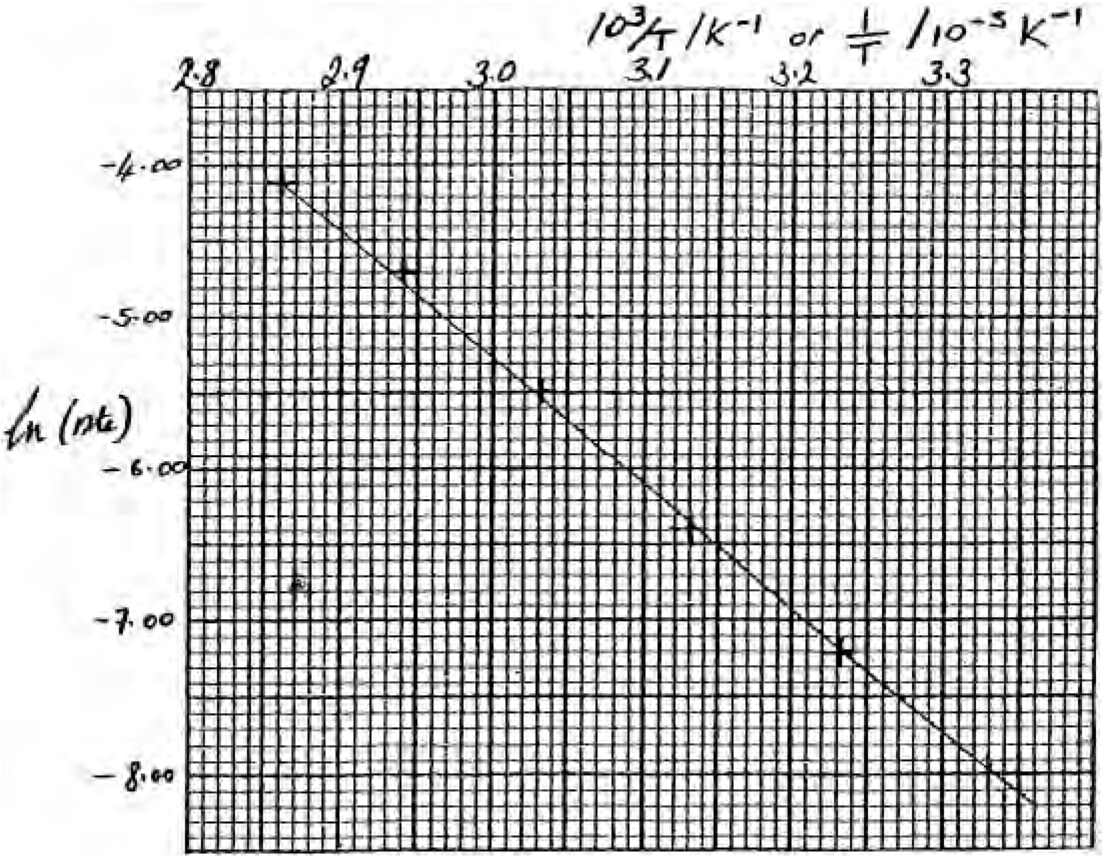
(c) Yes as only species in the rate determining step/ slowest step / equation in (c) are in rate equation. 1

(d) 1/temp ln(rate)

350K	2.86×10^{-3}	–4.10
	(1)	**(1)**

2

(e)



Axes correct way round and labelled correctly, sensible scales ie covering more than half of grid **(1)**

All points plotted accurately ignoring small errors, best fit straight line drawn **(1)**

Numbers on vertical axis should increase going upwards. 2

(f) gradient = -8.32×10^3 (K) **(1)**

ALLOW– 7800 to – 8900 (k)

E_a. = –8.31x gradient. = +69 kJ mol^{-1}/ + 69000 J mol^{-1}

ALLOW +65 to + 75 kJ mol^{-1} **(1)** 2

[12]

13. (a) Withdrawal of sample of **known** volume/ measured amount/ using **(1)**
pipette **(1)**
Quench (with ice)

Titrate with acid of **known** concentration **(1)**
OR
Use of pH meter **(1)** Calculation of $[H^+]$ **(1)**
Calculation of $[OH^-]$ using K_w expression **(1)** 3

(b) (i) Axes labelled with suitable scale [> ½ available space on both **(1)**
axes] **(1)**
All points plotted accurately and smooth curve 2

(ii) 240 s +/– 30 s ignore missing or incorrect units 1

(iii) 1st order as half-lives are constant. 1

(iv) Overall order as (initial) concentrations are equal (not volume) /
neither reactant is in excess/ equimolar/equal amounts 1

(v) Rate = $k[OH^-]/[NaOH]/[(CH_3)_3CBr]$ 1

(c) (i) S_N**1 (1)**
as only 1 reactant in rate determining step, (as 1st order **(1)**
overall)/ it is a tertiary halogenoalkane 2

(ii) $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ **(1)**
$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ **(1)**
Must be consistent with b(iii)
ALLOW S_N2 *if consistent.* 2

[13]

14. (a) (i) sum of the powers to which the **concentration** (terms) are raised in the rate equation / number of species involved up to and including the rate determining step (in the reaction mechanism)
OR
General equation with sum of partial orders explained 1

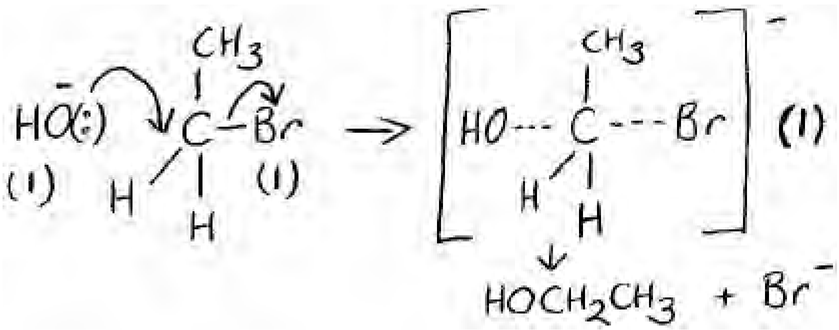
(ii) constant (of proportionality) in the rate equation / numerically = rate when all concs 1 mol dm^{-3} / correct example 1

(b) (i) Both orders 1 **(1)**
Double concentration of one while other is constant and the rate doubles
OR refer to two specific experiments **(1)** 2

(ii) rate = $k\,[CH_3I]\,[OH^-]$
consequential on (i) 1

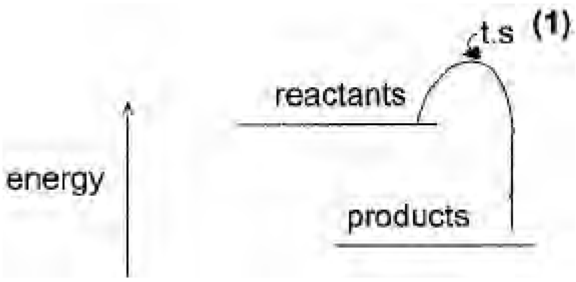
(iii) e.g. $k = \text{rate} / [CH_3I][OH^-]$
so $k = 1(.0) \times 10^{-3}$ **(1)** $mol^{-1}\ dm^{-3}\ s^{-1}$ **(1)**
Consequential on (ii) 2

(c) (i) *IGNORE shape and position of bonds*
DO NOT ALLOW OH·····C



Arrow from bond to Br must be in first step
Lone pair not essential, but if it is shown the arrow must start from it.
ALLOW arrow from negative charge
Max 1 *for completely correct S_N 1 mechanism* 3

(ii)



Energy labelled and levels of reactants and products **(1)**
If double hump can get **1 (out of 2)** for levels 2

[12]

15. (a) (i) Points plotted correctly **(1)**
Curve drawn **(1)** 2

(ii) Tangent drawn and at correct place **(1)**
Calculation of Δy and Δx **(1)**
$\Delta y \div \Delta x$ to give slope *(ignore sign of slope)* **(1)**
Accuracy of answer: accept anything between 0.01 and 0.02 **(1)** 4

(b) (i) Rate = slope (or more accurately rate = –slope)
OR
0.060 ÷ their slope (= 4 approximately) **(1)**
so, when the concentration halves, the rate goes down by a factor of 4, **(1)**
so the reaction is second order (stand alone mark) **(1)** 3

(ii) *Any **two** of*

I Rate = k $[S_2O_8^{2-}]$ $[H_3AsO_3]$
II Rate = k $[S_2O_8^{2-}]^2$
III Rate = k $[H_3AsO_3]^2$ **(2)**
[Only penalise the omission of k or wrong type of [ ] once. Rate equations must be marked consequentially on their order in (i)]

Repeat experiment using double / different initial $[S_2O_8^{2-}]$ / initial $[H_3AsO_3]$, **(1)**
but keeping the [other] unchanged **(1)**

*E.g. Any **one** of the following, as applicable to their two chosen rate equations*

If initial rate doubles rate equation **I** is correct

If initial rate quadruples with doubling $[S_2O_8^{2-}]$, rate equation **II** is correct

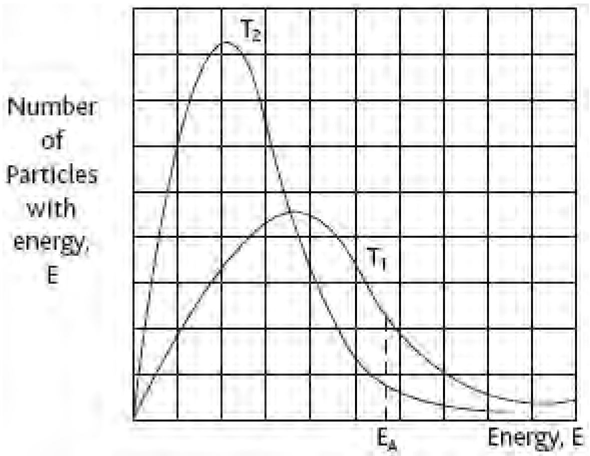
If initial rate does not alter with doubling / changing $[S_2O_8^{2-}]$, rate equation **III** is correct

If initial rate quadruples with doubling $[H_3AsO_3]$, rate equation **III** is correct

If initial rate does not alter with doubling / changing $[H_3AsO_3]$, rate equation **II** is correct. **(1)** 5

[14]

16. (a) (i)



Starts at zero and approaching *x*-axis **(1)**
Maximum greater and at lower energy**(1)** – *T_2 needs only to be just higher than T_1*
T_2 curve must go below T_1 curve approaching the x-axis 2

(ii) As the temperature increases the energy of the particles increases **(1)**

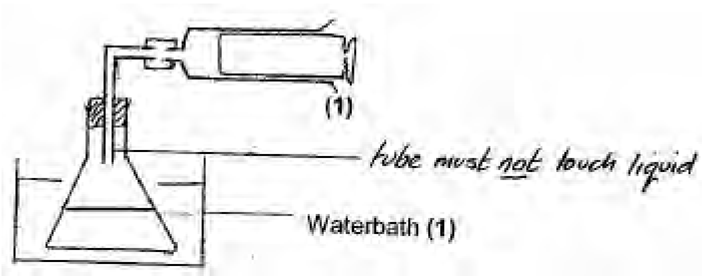
Use the diagram shading areas
OR more particles to the right hand side of E_A line **(1)**

and so more (successful) collisions/particles have energy greater / equal or greater than the activation energy **(1)**
NOT "equal" *on its own*
NOT mention of "frequency of collisions" on its own 3

(iii) A catalyst provides an alternative route with a lower activation energy/ which requires less energy **(1)**

so more collisions / particles have energy greater than the activation energy **(1)** 2

(b) (i) e.g.



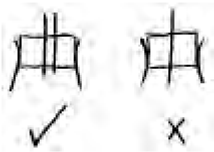
Measure the volume of gas given off in a given time / count bubbles / obscuring cross using limewater **(1)**

and then repeat over a range of temperatures **(1)**

No diagram max 3

If method shown cannot possibly work **max 1** *ie waterbath or sensible range of temperatures BUT NOT different temperatures*

Penalty
–1 for poor diagram



4

(ii) Positive

1 mol goes to 4 moles/particles (so more disorder) /increase in number of moles/particles **(1)**

products include a gas (and so more disorder) **(1)**

NOT 1 mole of compound/element goes to 4 moles of compound/element

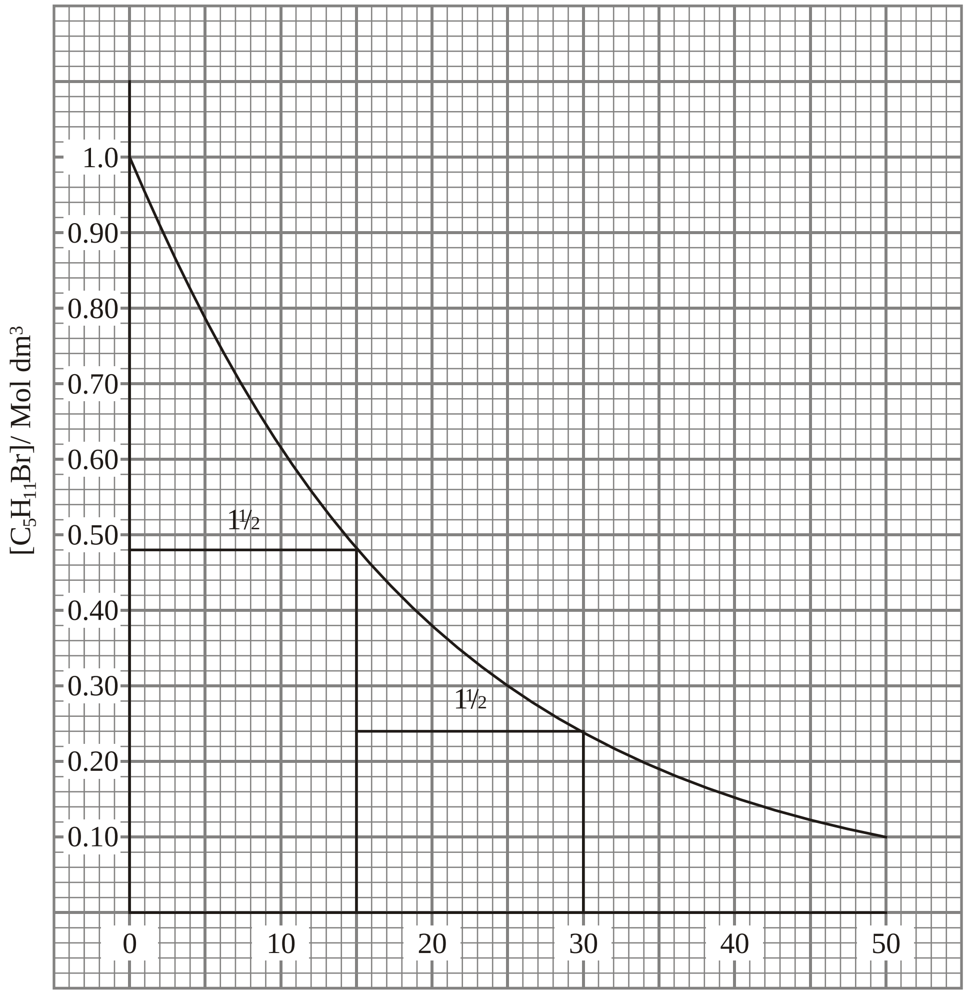
If "negative" **0 (out of 2)** 2

(iii) Positive *with some explanation* e.g. $\Delta S_{surroundings} = -\Delta H/T$ *OR* because reaction is exothermic **(1)**

ΔH is therefore negative and so $\Delta S_{surroundings}$ must be positive **(1)**
If negative given in (ii) allow TE here 2

[15]

17. (a) (i) Correct points **(1)**
Smooth curve **(1)** 2



Time/ min

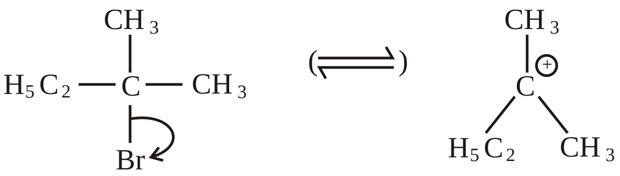
(ii) First half life 15 min (± 1 min) **(1)**
Second half life 15 min (± I min) **(1)** 2
If not shown on graph max **(1)**

(iii) 1^{st} order **(1)**
$t_{½}$ is constant **(1)** 2

(b) (i) Zero 1

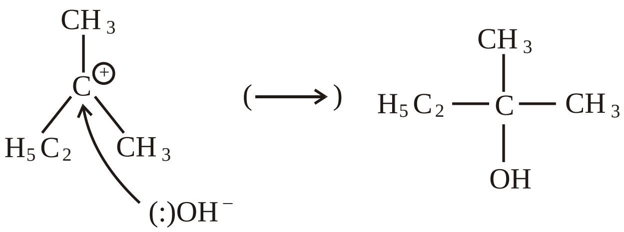
(ii) Rate = k [2-bromo-2-methylbutane] *ALLOW a formula* 1
Mark consequentially on (a) (iii) and (b) (i)

(iii)



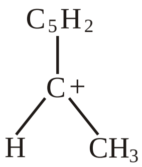
(1) (1)

(+ Br^-)



(1)

Mark consequentially on (ii) , i.e. If S_N2 mechanism given in (b) (ii), then one mark for each arrow (2) and transition state including sign ***(1)*** 3

(c) The intermediate / carbocation  is planar **(1)**

(Equal) attack from either side **(1)**
(therefore) racemic mixture (produced) **(1) Standalone mark** 3

[14]

18. (a) (i) Negative with some sensible explanation eg fewer moles of product **(1)**

3 moles of gases going to 2 moles of gases **(1)** 2
MUST mention gases or no changes in state

(ii) Positive *with some explanation* eg exothermic so surroundings gain entropy **(1)**

$\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T}$ [*OR given in words*]

OR

$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ [*OR given in words*]
as reaction goes, ΔS_{total} must be positive therefore $\Delta S_{\text{surroundings}}$ must be positive

OR

Surroundings gain energy so more ways of arranging energy **(1)** 2

(b) (i) $(\text{Kp}) = \frac{P_{NO_2}{}^2}{P_{NO}{}^2 \times P_{O_2}}$ **(1)**

*Check that it is **not** a "+" on denominator.*
ALLOW ( ) but NOT [ ] eg *ALLOW* $((P_{NO_2})^2)^2$ etc

ALLOW $(pNO_2)^2$

Atm^{-1} / Pa^{-1} / kPa^{-1} / $\text{m}^2\ \text{N}^{-1}$ **(1) –** *2nd mark dependent on 1st*
ALLOW atms^{-1} / atmospheres^{-1}
NOT atm⁻*etc*
NOT Kpa^{-1} 2

(ii) Temperature
A lower temperature is needed to get a better yield (and would cost less) because the reaction is exothermic **(1)**

but the lower temperature may slow the reaction down too much *OR reverse argument* **(1)**

Pressure
A high pressure will increase yield as only two moles on the right compared to three on the left/less moles on the right hand side **(1)**

It will also increase the rate of the reaction **(1)**

Low pressure because of cost only gets mark if higher yield at higher pressure identified

To award any of the yield marks must say why 4

(c) (i) Must be a quantity that can be measured
Eg

The pressure could be measured **(1)**
as it will decrease as the reaction proceeds because there are only two/fewer moles on the right compared to three on the left **(1)**

OR colour **(1)**
as the nitrogen(IV) oxide is brown whereas the other gases are colourless **(1)**

OR total volume **(1)**
which will decrease by one third/because there are fewer moles **(1)**

ALLOW acidity because NO_2 acidic **and** others not **(1 max)**

NOT dilatometry
NOT temperature — 2

(ii) [NO] second order **(1)**

because when conc of NO is doubled, the rate goes up four times **(1)**

$[O_2]$ first order **(1)** — 3

Then (iii), (iv) and (v) must follow consistently from (ii)

(iii) *ALLOW TE from (ii) e.g.*

rate = $k[NO]^2[O_2]$	rate = $k[NO][O_2]$	1

(iv)

third / 3	second / 2	1

(v)

8000 **(1)** $dm^6\ mol^{-2}\ s^{-1}$ **(1)**	8 **(1)** $dm^3\ mol^{-1}\ s^{-1}$ **(1)**	
Units can be given in any order		2

(d) The activation energy must be low
OR bond energies low
NOT "more successful collisions"
NOT large rate constant — 1

[20]

19. (a) Rate of decrease OR rate of change in **concentration** of reactants
OR rate of increase OR rate of change in **concentration** of products.
OR change in **concentration** of reactants with time OR change in **concentration** of products with time **(1)**
NOT just 'amount'
Sum of the **powers** to which the **concentrations** are raised in **the rate equation** OR number of species involved in (up to and including) the rate determining step OR sum of partial orders **if** illustrated with a general rate equation **(1)**
'Sum of the partial orders' alone does not score. 2

(b) (i) Both orders correct **(1)**
EITHER
Expt 1 + 3: double [A], doubles rate so order **1** **(1)**
Expt 1 + 2: double [B], four × rate so order **2** **(1)**
OR
Double [A] keeping [B] constant doubles rate so order **1** **(1)**
Double [B] keeping [A] constant four × rate so order **2** **(1)**
Omission of experiment number or keeping a concentration constant to be penalised ONCE only **(1)** 3

(ii) Rate = k [A] $[B]^2$. 1
Mark consequentially on (i)

(iii) $k = \dfrac{\text{rate}}{[A]\ [B]^2} = \dfrac{0.00200}{0.100 \times (0.100)^2}$
= 2(.00) **(1)** $mol^{-2}\ dm^6$ **min^{-1}** **(1)**

Consequential on their rate equation in (ii)
Use of experiment 2 or experiment 3 can score max **(1)** 2

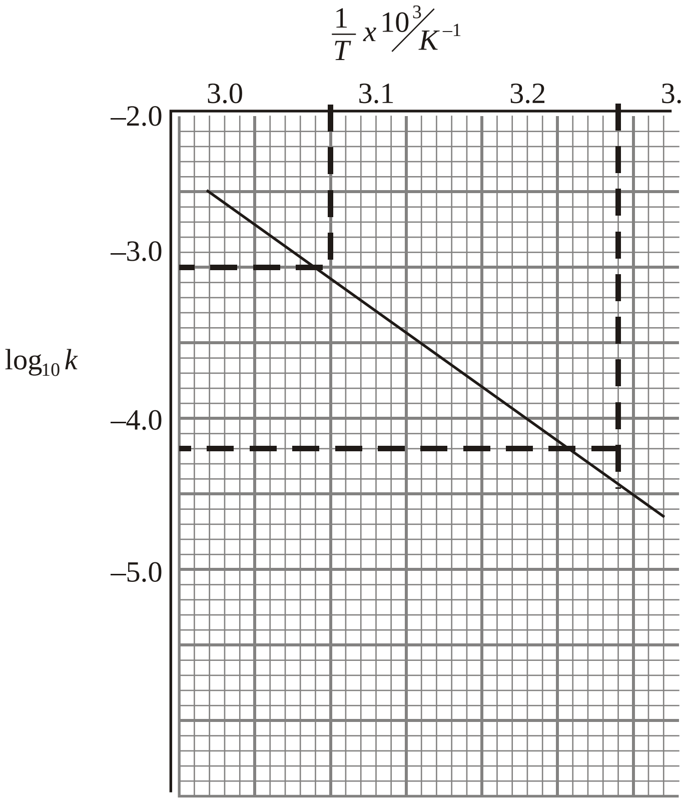
(iv) $A + B \rightarrow AB$
$AB + B \xrightarrow{rds} AB_2$ **(1)** *for first two equations*
$AB_2 + B \xrightarrow{fast} AB_3$ **(1)**

OR
$B + B \rightarrow B_2$
$A + B_2 \xrightarrow{rds} AB_2$ **(1)** *for first two equations*
$AB_2 + B \xrightarrow{fast} AB_3$ **(1)**

OR
$A + 2B \xrightarrow{slow / rds} AB_2$ **(1)**
$AB_2 + B \xrightarrow{fast} AB_3$ **(1)**

Identifying slow(est) OR rate determining step by appropriate notation **(1)**
S_N1 or S_N2 scores zero 3

(c) (i)



All points plotted accurately **(1)**
with best-fit straight line drawn **(1)** 2

(ii) Gradient eg $= \dfrac{-4.25 - (-3.10)}{0.00330 - 0.00310}$

$= \dfrac{-1.15}{0.00020}$

= –5750 (K) **(1)**

ALLOW = –5450 to -6050 (K) but MUST have a negative sign

ALLOW if gradient is left as a correct fraction such as $\dfrac{-1.15}{0.00020}$

E_a = (+)5750 × 2.30 × 8.31

= (+)110 kJ mol^{-1} / (+) 110000 J mol^{-1} **(1)**

ALLOW = (+)104 to (+)116 kJ mol^{-1} 2

IGNORE S.F.

(2nd mark consequential on gradient, but value of E_a must be in correct units)

[15]

20. (a) **Any 2**

Measure the loss in mass as a gas/carbon dioxide is given off **(1)**

Measure the concentration of the acid by titration
OR Carry out a titration with sodium hydroxide **(1)**
NOT "titration" on its own

Measure conductivity because 4 ions go to 3 ions / decrease in ions / change in number of ions **(1)**

Measure pH because acid is used up / changes / concentration changes /one reactant is acidic **(1)**

NOT dilatometry / nmr / x-ray crystallography / temperature change / colorimetry / indicator / change in mass of $CaCO_3$ — 2

(b) Initially some carbon dioxide dissolves in the solution (until the solution is saturated).
OR
Some CO_2 might escape whilst adding acid/before putting on bung — 1

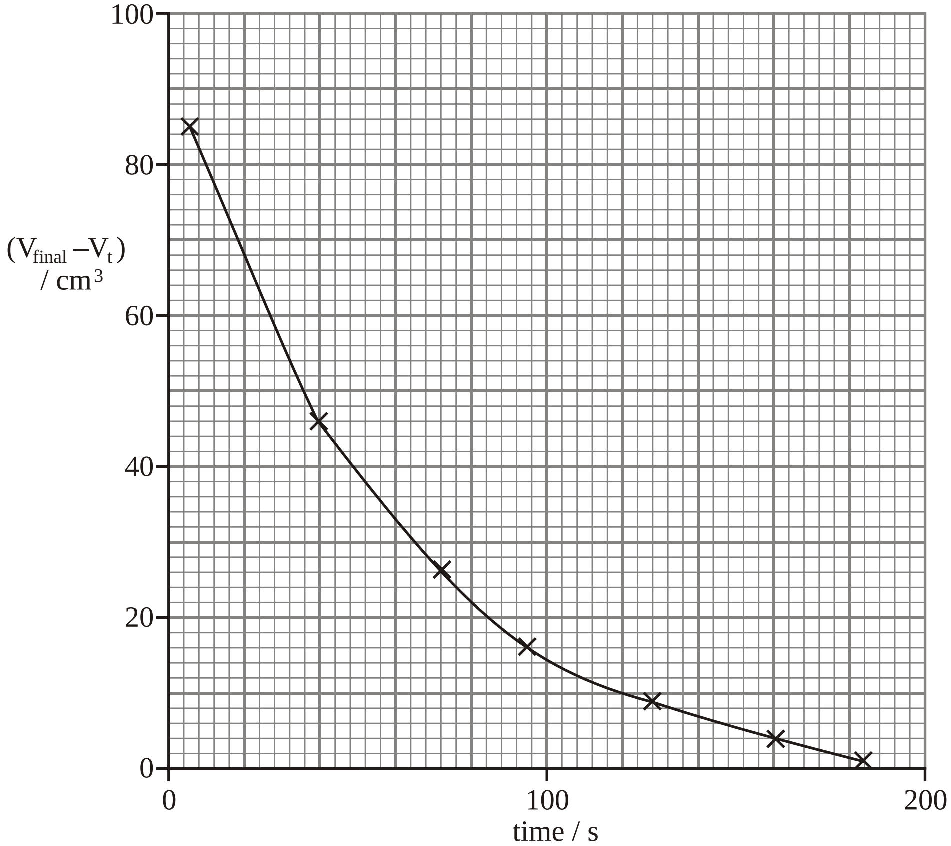
(c) (i) 88 (cm^3) — 1

(ii)

95	72	**16**	
125	79	**9**	
155	84	**4**	
185	87	**1**	1

(iii) The concentration of the hydrochloric acid / HCl
OR [HCl]
NOT concentration of reactants — 1

(iv)



ALLOW extrapolated back to between 88 and 100

points correctly plotted **(1)**
ALLOW TE for points

and reasonably smooth curve drawn **(1)** 2
NOT dot-to-dot

(v) three **successive** half-lives shown on the graph **(1)**
MUST start at defined volume NOT 0s/85 cm^3

all three values similar about 37s **(1)**
ALLOW 32-42 or show on graph
NOT 40, 80, 120

constant half-life / half-life not increasing means first order reaction **(1)**

*If only two half lives shown **max 2***
*If in (v) zero / 2^{nd} order deduced **max 1** for first part but TE allowed to parts (vi) and (vii)* 3

(vi) rate = k[HCl]
OR rate =k$[HCl]^1$
OR rate =K$[HCl]^1[CaCO_3]^0$
NOT rate = k$[V_{final}-V_t]^1$

If zero order
rate = k
OR rate = k$[HCl]^0$
If second order
rate = k $[HCl]^2$
NOT rate = k$[CaCO_3]^1[HCl]^1$ 1

(vii) s^{-1}

T.E zero order – mol dm^{-3} s^{-1}
second order – dm^3 mol^{-1} s^{-1} 1

(d) Δ**S**$_{system}$
positive + some sensible reason eg gas given off **(1)**
as a mole of a gas given off and three moles including one solid becomes three moles with no solid / gas more random than solid
OR
Gas more disordered than a solid

OR
Despite same number of moles/particles **(1)**

Δ**S**$_{total}$

positive + some reason **(1)**
eg
positive because reaction exothermic / favourable **(1)**

positive + good reason **(2)**
eg
positive because reaction is spontaneous / goes to completion / feasible
OR Δ**S**$_{surroundings}$ is positive because ΔH is negative /
reaction exothermic ∴ ΔS_{total} positive **(2)** 4
[provided ΔS_{system} shown positive earlier]

[17]

21. (a) (i) (5.0/1000) × 0.010 = 5.0 × 10^{-5} (mol) 1

(ii) ½ × 5.0 × 10^{-5} = 2.5 × 10^{-5} (mol) **(1)**
TE from (i) 1

(iii) 2.5 × 10^{-5} × (1000/40.0) = 6.25 × 10^{-4} mol dm^{-3}

6.25 × 10^{-4} / 5 = 1.25 × 10^{-4} (mol dm^{-3} s^{-1}) **(1)**
Allow T.E. 2

Accept (ii) X5: 2 marks

Accept (ii) ÷5: 1st mark

(b) (i) First 1

(ii) First **(0)**
Comparing experiments 2& 3
[I^-] doubles, so from (b)(i) rate should also double
yet rate is 6 times greater,
so extra trebling of rate must be caused by trebling of [$S_2O_8^{2-}$]
$\Rightarrow$ Rate $\propto$ [$S_2O_8^{2-}$]^1 **(1)**

Or other valid argument 1

(iii) Rate = k [$S_2O_8^{2-}$] [I^-] **(1)** 1

Accept T.E. from (i) + (ii)

(iv) k = rate / ([$S_2O_8^{2-}$] [I^-]) = 2.74×10^{-5} / (0.01×0.02)
= <u>0.137 dm3 mol^{-1} s^{-1}</u>
numerical answer **(1)** units **(1)**
Mark independently 2 **[9]**

Accept T.E. from (iii)

22. (a) (i) QWC
Both orders correct **(1)**

Expt 1 + 2: as [B] doubles rate x4 so second order (wrt B)

OR
As [B] doubles with [A] constant rate x4 so second order (wrt B) **(1)**

Expt 1 + 3: as [A] doubles rate x2 so first order (wrt A)

OR
As [A] doubles with [B] constant rate x2 so first order (wrt A) **(1)**

Omission of experiment numbers or failure to refer to constant concentration of the other reagent penalise once only 3

(ii) rate = k [A] [B]^2
Can use upper or lower case “k” 1

Must be consequential on (i)

(iii) $k = \dfrac{0.00195}{0.10 \times 0.10^2}$ = 0.195 **(1)** $mol^{-2}\ dm^6\ s^{-1}$ **(1)**

[IGNORE s.f. in answer]

[If wrong experiment chosen only unit mark available] 2

Both marks consequential on (ii), but rate equation must include k

(b) (i) QWC

Increasing T means molecules have/collide with greater energy **(1)**

so a greater **proportion** /more **of** the molecules collide with/have E ≥ Ea/the activation energy **(1)**

so a greater proportion **of the collisions** are successful
OR
more **of the collisions** are successful/more successful collisions in a given time **(1)** 3

(ii) (at least) two steps **(1)**

Simultaneous collision of three particles is unlikely
OR valid mechanism e.g.
A + B → AB fast
AB + B → AB_2 slow
OR
A + B → AB slow
AB + B → AB_2 fast **(1)** 2

Accept number more than two

(c) Value of slope = – 1.2 × 10^4

Accept any number between – 1.15 × 10^4 and – 1.25 × 10^4 inclusive

Negative sign **(1)** Value **(1)**
Multiply by –8.31 **(1)**

Divide by 1000 to give 104 (kJ mol^{-1}) **(1)**
[units not essential but penalise wrong units]

allow 95.5 – 104 consequential on slope

Correct answer with some working **(4)**
Correct answer with no working **(3)**
Penalise –1 mark if final answer is negative
IGNORE sig figs 4

[15]

23. (a) measuring the time taken **(1)**
for the potassium manganate(VII) to become colourless/go brown **(1)**

OR
measuring the time taken **(1)**
for a measured volume of CO_2 to be collected **(1)**

OR
Take sample at a given time **(1)**
(Quench and) titrate with Fe^{2+}(aq) **(1)** 2

Accept measuring the time taken for the potassium manganate(VII) to change colour = 1

Accept other suitable reducing agents

(b) (i) Glucose = 0 **(1)**

potassium manganate (VII) = 1 – because when the concentration of (potassium manganate (VII)) doubles so does the rate/because the rate in experiment 1 is double the rate in experiment 2 (and $[KMnO_4^-]$ is double but $[C_6H_{12}O_6]$ and $[H^+]$ are constant) **(1)**

hydrogen ions = 1 because order wrt $[MnO_4^-]$ = 1 so when $[MnO_4^-]$ & $[H^+]$ double, rate is quadrupled / when $[MnO_4^-]$ is quadrupled and $[H^+]$ is doubled rate goes up by a factor of 8
OWTTE **(1)** 3

(ii) rate = $k[MnO_4^-][H^+]$

OR
rate = $k[KMnO_4][H^+]$ 1

Accept correct names

Accept expressions including $[C_6H_{12}O_6]^0$

Accept TE from (b)(i)

(iii) 4×10^{-3} **(1)**

$dm^3\ mol^{-1}\ s^{-1}$ **(1)** unit mark independent of 1st mark
but must be consistent with rate equation 2

Accept units in any order
allow TE from (b)(i) & (b) (ii)

(c) (i) 3.22×10^{-3} –4.00
both needed for the mark 1

Accept 0.00322

Accept –4

(ii) labelled axes including units and sensible scale **(1)**

correct plotting of points and line of best fit **(1)** 2

Reject /10^{-3}

(iii) gradient = – 10823(K) **(1)**

$E_a = 10823 \times 8.31 = + 89939\ J\ mol^{-1}$

Accept gradient range = –11200 to –10400
Accept TE from gradient to E_a

= (+) 90 kJ mol^{-1} / (+) 90 000 J mol^{-1} **(1)** 2

Accept (+) 93 to (+) 86 kJ mol^{-1} but must be consistent with gradient

[13]

24. (a) (i) Hydroxide ions / OH^- / OH^- (aq) 1

Reject sodium hydroxide /NaOH

(ii) **A**: $\frac{8.0 \times 10^{-4}}{33}$ = $2.4(2) \times 10^{-5}$ (mol dm^{-3} s^{-1}) **(1)**

B: $\frac{8.0 \times 10^{-4}}{16}$ = $5.0(0) \times 10^{-5}$ (mol dm^{-3} s^{-1}) **(1)** 2

(iii) (Comparing **A** and **B**), rate
(approximately) doubles/time halves when concentration (of 2-bromo-2-methylpropane) doubles, so reaction is 1st order
(wrt 2-bromo-2-methylpropane) 1

Reject because [C_4H_9Br] $\propto$ rate of reaction OR there is a steady increase in rate when [C_4H_9Br] increases/is doubled

(iv) (Rate of reaction in **B** = 5.0×10^{-5} mol dm^{-3} s^{-1})
Rate of reaction in **C** = 1.2×10^{-3} /24
= 5.0×10^{-5} (mol dm^{-3} s^{-1}) **(1)**

Focus on the value 5.0×10^{-5} for 1st mark

(Comparing **B** and **C**), rate remains <u>constant</u> when concentration of NaOH changes (by 50 %), so reaction is **zero order** wrt NaOH **(1)**

Mark independently 2

*Accept rate for C calculated to be the same as that calculated for **B** in (a)(ii)*

(v) Rate = $k[CH_3C(Br)(CH_3)CH_3]^{(1)}$ $([OH^-]^0)$
Allow transferred error, but answer must be consistent with (iii) & (iv)

Look for inclusion of rate constant, k 1

Accept $[NaOH]^0$ instead of $[OH^-]^0$

Rate = $k[C_4H_9Br]^{(1)}([OH^-]^0)$

(vi) $CH_3C(Br)(CH_3)CH_3 \xrightarrow{\text{slow}} CH_3C^+(CH_3)CH_3 + Br^-$ **(1)**
Positive charge must be on carbon shown

$CH_3C^+(CH_3)CH_3 + OH^- \xrightarrow{\text{(fast)}} CH_3C(OH)(CH_3)CH_3$ **(1)**

Identification of the rate determining step/RDS **(1)**

Only allow this S_N1 mechanism if consistent with
1st order reaction in (a)(v) 3

Accept $CH_3C^+(CH_3)CH_3 + H_2O \rightarrow CH_3C(OH)(CH_3)CH_3 + H^+$

Allow S_N2 mechanism consequential on 2nd order rate equation in (a)(v):
OH– attacks C–Br forming
C–OH as C–Br breaks to form Br^-,
*Or can be shown in diagram, e.g. with transition state using dotted bonds or with curly arrows in one concerted step **(max 2)***

(b) 1-bromobutane is a primary halogenoalkane /
2-bromo-2-methylpropane is a tertiary halogenoalkane **(1)**

Primary carbonium ion intermediate cannot easily be stabilised /
tertiary carbonium ion intermediate can be stabilised **(1)**

Mark independently 2

Accept arguments based on relative activation energies of formation of primary vs tertiary carbonium ion intermediates / steric hindrance in the tertiary compound

[12]

25. (a) (i) second order **(1)**
rate proportional to the square of the (partial) pressure of NO
OR
the rate doubles as the square of the (partial) pressure of NO doubles **(1)**
Conditional on correct order 2

(ii) as (partial) pressure (of O_2) doubles rate doubles, so first order

Accept concentration of O_2 instead of (partial) pressure

OR
gradient of line is $k\,p(O_2)^x$ so if this doubles the order (w.r.t. O_2) must be 1 — 1

(iii) rate = $k\,p(NO)^2 p(O_2)$

Accept rate = $k[NO]^2[O_2]$

Reject any equation without k

Cq on orders in (i) and (ii) — 1

Accept "R" for "rate"

Accept "K" for lower case "k"

Reject rate = k
Reject $p[NO]^2p[O_2]$

(iv) $atm^{-2}\ s^{-1}$
ALLOW this mark, even if *p*[ ] used in (iii)

Cq on (iii)
[if overall second order, unit is $atm^{-1}\ s^{-1}$.
If overall first order unit is s^{-1}] — 1

Accept $mol^{-2}\ dm^6\ s^{-1}$ if concs used in (iii)

(b) (i) plot ln *k* vs 1/T **(1)**

giving straight line of gradient – *Ea/R*
OR
E_a = –gradient × R **(1)**

STAND ALONE MARKS

[2nd mark could be scored from (ii) if no reference to gradient here in (i) provided a clear expression is stated] — 2

If plot 1/T vs ln k ***and*** *gradient is $-R/E_a$* ***(2)***

If plot ln k vs 1/RT ***and*** *gradient $-E_a$* ***(2)***

Reject"log"

(ii) $E_a = 2.95 \times 10^4 \times 8.314$ **(1)**

(= 245, 145 J mol^{-1})

= 245 (kJ mol^{-1}) **(1)**

Accept 245,000 ***J*** *(mol^{-1})* ***(2)***

[Note to examiners:
give credit if candidate uses 2.95×10^{-4} or $1/2.95 \times 10^4$]

Correct answer with no working **(2)**
Answers **not** to 3 SF can only score the 1st mark

Note:
–245 (kJ mol^{-1}) **(1)** but must be 3SF
245,000 **kJ** (mol^{-1}) **(1)** but must be 3SF
–245,000 **kJ** mol^{-1} **(0)**

If 245 or –245 is given, units are **not** needed

If 245,000 is given, units are **essential**

DO **NOT** PENALISE K^{-2} OR K^{-1} **in any unit** 2

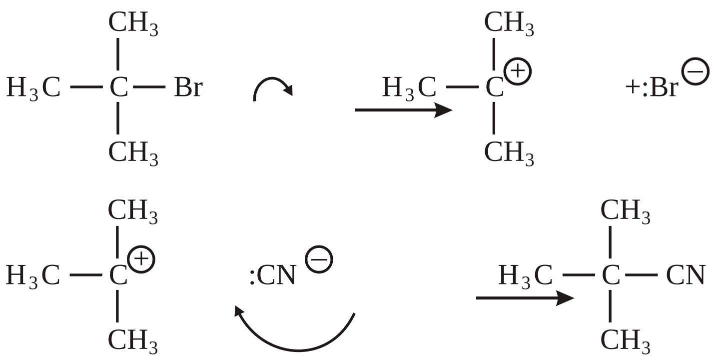
(iii) B 1

[10]

26. (i) **1st Mark**
S_N1
Or
must be (at least) two steps **(1)**

2nd Mark
only the halogenoalkane is involved in the r.d.s.
OR
CN^- is **not** involved in rds **(1)** 2

(ii)



Accept $(CH_3)_3C–Br$

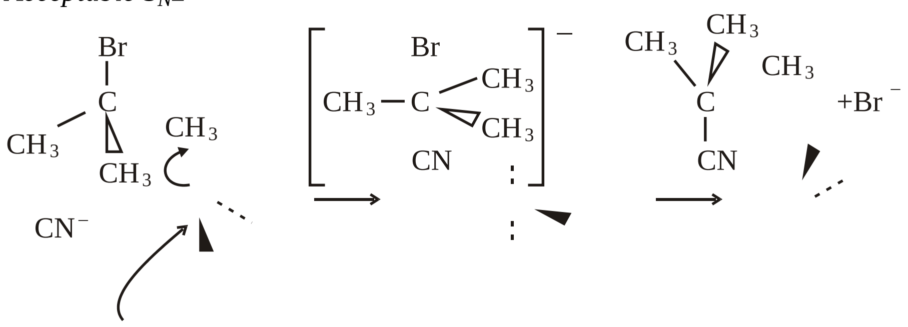
first arrow must start from bond, not the carbon atom and not end past the bromine atom **(1)**

structure of carbocation **(1)** Br^- not essential

attack by cyanide, arrow must start from C or –ve charge on C **not** N and –ve charge must be present somewhere on ion; lone pair not essential **(1)**
IGNORE any references to rates of the steps 3

*Accept completely correct S_N2 version scores **(1)***

Acceptable S_N2



[5]

27. (a) Any three from

Reject dilatometry

- Titrate with (sodium) thiosulphate to measure concentration of I_2.

  Reject I^-

- Titrate with an **alkali/base** (eg sodium hydroxide) to measure concentration of H^+/acid.

  IGNORE indicators unless inappropriate e.g. starch

- Titrate with silver ions to measure I^-
- Measure colour change (**colorimetry**) as iodine is coloured [colour changes not needed]

  Accept addition of starch to give colour

  If incorrect colours given, then no mark. Benedict's solution to give colour

- Use pH (meter) to measure H^+/acidity
- Measure conductivity as (2) **ions** on RHS

  Reject electrolysis

IGNORE any reference to quenching 3

Reject measure volume of hydrogen

(b) Add sodium (hydrogen)carbonate **(1)**

Reject alkali/base/sodium hydroxide

which neutralises/reacts with/removes the H^+ **(1)**

Accept ice/ice-cold water to slow the reaction max 1

Reject cold water

2nd mark awarded only if an alkali added 2

(c) (i) First order **(1)**

In exp 2 and exp 3 / concentrations of iodine and H^+ remain constant **(1)**

Could compare experiments 1 and 3

propanone concentration increases by 1.5 times and the rate also increases by 1.5 times **(1)** 3

(ii) Zero (order) / 0 (order) 1

Accept Zeroth (order)

(iii) Rate = $k[H^+][CH_3COCH_3]$

ALLOW TE from (i) and (ii)
IGNORE state symbols 1

Accept rate = $k[H^+][CH_3COCH_3][I_2]^0$

Accept "R" or "r" for rate

Accept "K" for "rate constant"

(iv) H^+ and CH_3COCH_3

IGNORE state symbols 1

Accept Names, [], displayed formula

ALLOW TE from rate equation in (iii)

(v) $CH_3COCH_3 + H^+ \rightarrow CH_3C^+OHCH_3$ **(1)**

"+" can appear anywhere on formula
"+" sign must appear on the product for the 1st mark

The (positive) hydrogen ion is attracted to the lone pair of electrons / δ^- on the oxygen atom (in the propanone). **(1)** 2

No TE from earlier parts

[13]

28. (a) D 1

(b) A 1

(c) B 1

(d) A 1

[4]

29. D

[1]

30. D

[1]

31. (a) $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
Accept state symbols omitted 1

(b) (i) Positive because a gas is given off **(1)**
which is more disordered and so has more entropy **(1)** 2

(ii) Positive because the reaction is exothermic **(1)**
and = $-\Delta H/T$ **(1)** 2

(iii) Positive because the reaction occurs / total entropy change
is the sum of the two positive values above. 1

(c) (i) Surface coated with magnesium oxide (which would react to
form water rather than hydrogen). 1

(ii) QWC

Initial number of moles of HCl = 20 × 1 /1000 = 0.02

Number of moles of Mg = 0.1 / 24 = 0.00417 **(1)**
number of moles of HCl which reacts is 0.00834 **(1)**

Therefore number of moles of HCl left = 0.01166 **(1)**
Ignore sig figs

so the concentration nearly halves which would significantly
reduce the rate and so make the assumption that the initial
rate is proportional to 1/time invalid / inaccurate. **(1)**

Increase the volume of acid to (at least) 50 cm^3 **(1)**
Or measure the time to produce less than the full amount of gas
Or use a smaller piece of magnesium. **(1)** 5

(iii) Energy given out = 467 000 × 0.1/24 J = 1 946 J
20 × 4.18 × ΔT = 1 946 **(1)**
$\Delta T = 23.3^{(o)}$ **(1)**

Accept units of degrees celsius or Kelvin

This temperature change would significantly increase
the rate of the reaction **(1)**
Carry out the reaction in a water bath of constant
temperature/use a larger volume of more dilute acid **(1)** 4

(iv) At 329 time 4s 1/time = 0.25 s^{-1} ln(rate) = –1.39 **(1)**

At 283 time 124s 1/time = 0.00806 s^{-1} ln(rate) = –4.82 **(1)**
[graph to be drawn]

Plot line with new gradient = – 3.43 / 0.00049
= – 7 000 **(1)**

Accept –6800 to –7200

Activation energy = + 7 000 × 8.31
= + 58.2 kJ mol^{-1} **(1)** 4

(v) QWC

Rate of reaction reduced because less surface area in contact with the acid. **(1)** 1

(vi) Any two

- Repeat the experiment at each of the temperatures
- obtain an initial rate eg by measuring the volume of gas given off before the reaction is complete.
- Other sensible suggestions. 2

(vii) The rate should be lower, since ethanoic acid is a weaker acid (compared to hydrochloric acid) and so there will be a lower concentration of hydrogen ions present. 1

[24]

32. QWC

Answer must be given in a logical order, addressing all the points using precise terminology

- Collision **frequency** increases as particles moving more quickly **(1)**
- More collisions have sufficient energy to overcome activation energy / more molecules on collision have energy ≥ activation energy **(1)**
- A greater **proportion** of collisions result in reaction **(1)**
- Collision energy has greater effect **(1)**
- Homogeneous all in same phase and heterogeneous in different phases / gas and solid **(1)**
- No need to separate products from catalyst **(1)** 6

Reject more collisions

Reject more successful collisions

[6]