M1.(a) Consider experiments 1 and 2: [B constant]
$[A]$ increases $\times 3$ : rate increases by $3^{2}$ therefore 2 nd order with respect to $A$

Consider experiments 2 and 3 :
[A] increases $\times 2$ : rate should increase $\times 2^{2}$ but only increases $\times 2$
Therefore, halving $[B]$ halves rate and so 1st order with respect to $B$

Rate equation: rate $=k[\mathrm{~A}]^{2}[\mathrm{~B}]$
(b) rate $=k[C]^{2}[D]$ therefore $k=$ rate $/[C]^{2}[D]$
$k=\frac{7.2 \times 10^{-4}}{\left(1.9 \times 10^{-2}\right)^{2} \times\left(3.5 \times 10^{-2}\right)}=57.0$

Allow consequential marking on incorrect transcription
$\mathrm{mol}^{-2} \mathrm{dm}^{+6} \mathrm{~s}^{-1}$
Any order
(c) rate $=57.0 \times\left(3.6 \times 10^{-2}\right)^{2} \times 5.4 \times 10^{-2}=3.99 \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right)$

OR
Their $k \times\left(3.6 \times 10^{-2}\right)^{2} \times 5.4 \times 10^{-2}$
(d) Reaction occurs when molecules have $E \geq E_{a}$

Doubling T by $10^{\circ} \mathrm{C}$ causes many more molecules to have this $E$

Whereas doubling [ $\mathbf{E}$ ] only doubles the number with this $E$
(e) $\quad E_{\mathrm{a}}=R T(\ln A-\ln k) / 1000$

Mark is for rearrangement of equation and factor of 1000 used correctly to convert J into kJ
$E_{\mathrm{a}}=8.31 \times 300(23.97-(-5.03)) / 1000=72.3\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$

M2.(a) Gradient drawn on graph


Line must touch the curve at 0.012 but must not cross the curve.
(b) Stage 1: Rate of reaction when concentration $=0.0120 \mathrm{~mol} \mathrm{dm}^{-3}$

From the tangent
Change in [butadiene] $=-0.0160-0$ and change in time $=7800-0$
Extended response

Gradient $=-(0.0160-0) /(7800-0)=-2.05 \times 10^{-6}$
Rate $=2.05 \times 10^{-6}\left(\mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right)$

Stage 2: Comparison of rates and concentrations
Initial rate / rate at $0.0120=\left(4.57 \times 10^{-6}\right) /\left(2.05 \times 10^{-6}\right)=2.23$

Inital concentration / concentration at point where tangent drawn $=0.018$ / $0.012=1.5$

Stage 3: Deduction of order
If order is 2 , rate should increase by factor of $(1.5)^{2}=2.25$ this is approximately equal to 2.23 therefore order is 2 nd with respect to butadiene
(ii) rate $=k[X]\left[\mathrm{OH}^{-}\right]$
allow $\mathrm{HCOOCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}$ (or close) for $X$ allow () but penalise missing minus
(iii) $k=\frac{8.5 \times 10^{-5}}{(0.024)(0.035)}$

In (a)(iii), if wrong orders allow mark is for insertion of numbers in correct expression for $k$ If expression for $k$ is upside down, only score units conseq to their expression
$=0.10$ (12) $\quad$ 2sf minimum
1 for conseq answer
$\mathrm{mol}^{-1} \mathrm{dm}^{3} \mathrm{~s}^{-1}$
1 for conseq units
any order
(iv) $2.1(3) \times 10^{-5}$
or $2.1(2) \times 10^{-5} \quad$ ignore units
allow 2 sf
NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong $k$

See * below
1
(v) $1.3 \times 10^{-4}\left(1.28 \times 10^{-4}\right)$
allow $\left(1.26 \times 10^{-4}\right)$ to $\left(1.3 \times 10^{-4}\right) \quad$ ignore units
allow 2 sf
NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong $k$

See ** below

For example, if orders given are 1 st in X and second in $\mathrm{OH}^{-}$
[The mark in a(ii) and also first mark in a(iii) have already been lost]
So allow mark *in (iv) for rate $=$ their $\mathrm{k} \times(0.012)(0.0175)^{2}=$ their $\mathrm{k} \times\left(3.7 \times 10^{-6}\right)$
(allow answer to 2sf)
${ }^{* *}$ in $(v)$ for rate $=$ their $\mathrm{k} \times(0.012)(0.105)^{2}=$ their $\mathrm{k} \times\left(1.32 \times 10^{-4}\right)$
(allow answer to 2sf)
The numbers will of course vary for different orders.
(vi) Lowered
if wrong, no further mark
fewer particles/collisions have energy $>\mathrm{E}_{\mathrm{a}}$
OR
fewer have sufficient (activation) energy (to react)
not just fewer successful collisions
(b) Step 2
(this step with previous) involves one $\mathrm{mol} / \mathrm{molecule} /$ particle A and two Bs
or 1:2 ratio or same amounts (of reactants) as in rate equation if wrong, no further mark

M4.
(a) (i) $k=\frac{0.2 \times 10}{\left(2.9 \times 10^{-2}\right)^{2} \times 2.3 \times 10^{-2}}$
mark is for insertion of numbers into a correctly rearranged rate equ, $k=$ etc AE (-1) for copying numbers wrongly or swapping two numbers
$=0.32(\mathrm{~min} 2 \mathrm{sfs})$
1
$\mathrm{mol}^{-2} \mathrm{dm6} \mathrm{~s} \mathrm{~s}^{-1}$ Units must be conseq to their $k$
Any order
If $k$ calculation wrong, allow units conseq to their $k$
1
(ii) $4.95 \times 10^{-5}$ to $4.97 \times 10^{-5}$ or $5.0 \times 10^{-5}(\mathrm{~min} 2 \mathrm{sfs})$
(ignore units)
rate $=$ their $k \times 1.547 \times 10^{4}$
(b) Step 2

If wrong no further mark

One $\mathrm{H}_{2}$ (and two NO) (appear in rate equation) or species (in step 2) in ratio/proportion as in the rate equation
(ii) 1 or one or first or [F] or [F]
(b) (i) $\quad k=\frac{8.6 \times 10^{-4}}{\left(3.8 \times 10^{-2}\right)^{2} \times\left(2.6 \times 10^{-2}\right)}$
mark is for insertion of numbers into a correctly rearranged rate equ , $k=$ etc. AE (-1) for copying numbers wrongly or swapping two numbers.
$=22.9$ (Allow $22.9-24$ after correct rounding)
(ii) $\quad 6.8(2) \times 10^{-3}\left(\mathrm{~mol} \mathrm{dm}^{887223} \mathrm{~s}^{-1}\right)$

OR if their k is wrong, award the mark consequentially a quick check can be achieved by using their answer $=2.9768 \times 10^{-4}$ Allow $2.9-3.1 \times 10^{-4}$ for the mark their $k$

Allow $6.8 \times 10^{-3}$ to $6.9 \times 10^{-3}$
Ignore units.

Mark is for insertion of numbers into a correctly rearranged rate equ , $k=$ etc.
If upside down, score only units mark from their $k$
AE (-1) for copying numbers wrongly or swapping two numbers
$=1.8(3)$
(b) (i) 2 or second or [D] ${ }^{2}$
(ii) 0 or zero or [E] ${ }^{\circ}$
(c) (i) Step 1 or equation as shown

Penalise Step 2 but mark on


Ignore correct partial charges, penalise full / incorrect partial charges

If Step 2 given above, can score the mark here for

allow: $\mathrm{OH}^{-}$(must show Ip)
If $S_{N} 2$ mechanism shown then no mark (penalise involvement of : $\mathrm{OH}^{-}$in step 1)
Ignore anything after correct step 1

M7.(a) Exp 2 14.(4) $\times 10^{-3}$ OR $1.4(4) \times 10^{-2}$ or 0.014
Allow 2sf

Exp 3 0.1(0)

Exp 4 0.3(0)
If three wrong answers, check their value of $k$ in 1(b).
They can score all 3 if they have used their (incorrect) value of $k$. see below.
Exp 2 rate $=0.096 \times k$
Exp 3 [Q] $=0.015 / k$
Exp $4[P]=0.116 / \sqrt{ } k$
(b) $K=\frac{1.8 \times 10^{-3}}{(0.20)^{2} \times 0.30}$
mark is for insertion of numbers into a correctly rearranged rate equ, $k=$ etc
$=0.15(\mathrm{~min} 2 \mathrm{sfs}) \quad$ (allow $\frac{3}{20}$ )
if upside down, score only units mark
AE (-1) for copying numbers wrongly or swapping two numbers
$\mathrm{mol}^{-2} \mathrm{dm}^{+6} \mathrm{~S}^{-1}$
Any order
If $k$ calculation wrong, allow units conseq to their $k$
(c) G

