M1.(a) Consider experiments 1 and 2: [B constant]

[A] increases × 3: rate increases by 3^2 therefore 2nd order with respect to A

1

Consider experiments 2 and 3:

[A] increases × 2: rate should increase × 2^2 but only increases × 2

Therefore, halving [B] halves rate and so 1st order with respect to B

1

Rate equation: rate = $k[A]^2[B]$

1

(b) rate = k $[C]^2[D]$ therefore k = rate / $[C]^2[D]$

1

$$k = \frac{7.2\times10^{-4}}{\left(1.9\times10^{-2}\right)^2 \times \left(3.5\times10^{-2}\right)} = 57.0$$

Allow consequential marking on incorrect transcription

1

$mol^{-2}\ dm^{+6}\ s^{-1}$

Any order

1

(c) rate = $57.0 \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2} = 3.99 \times 10^{-3}$ (mol dm^{-3} s^{-1})

OR

Their $k \times (3.6 \times 10^{-2})^2 \times 5.4 \times 10^{-2}$

1

(d) Reaction occurs when molecules have $E \geq E_a$

1

Doubling T by 10 °C causes <u>many</u> more molecules to have this *E*

1

Whereas doubling [**E**] only doubles the number with this *E*

1

(e) $E_a = RT(\ln A - \ln k) / 1000$

Mark is for rearrangement of equation and factor of 1000 used correctly to convert J into kJ

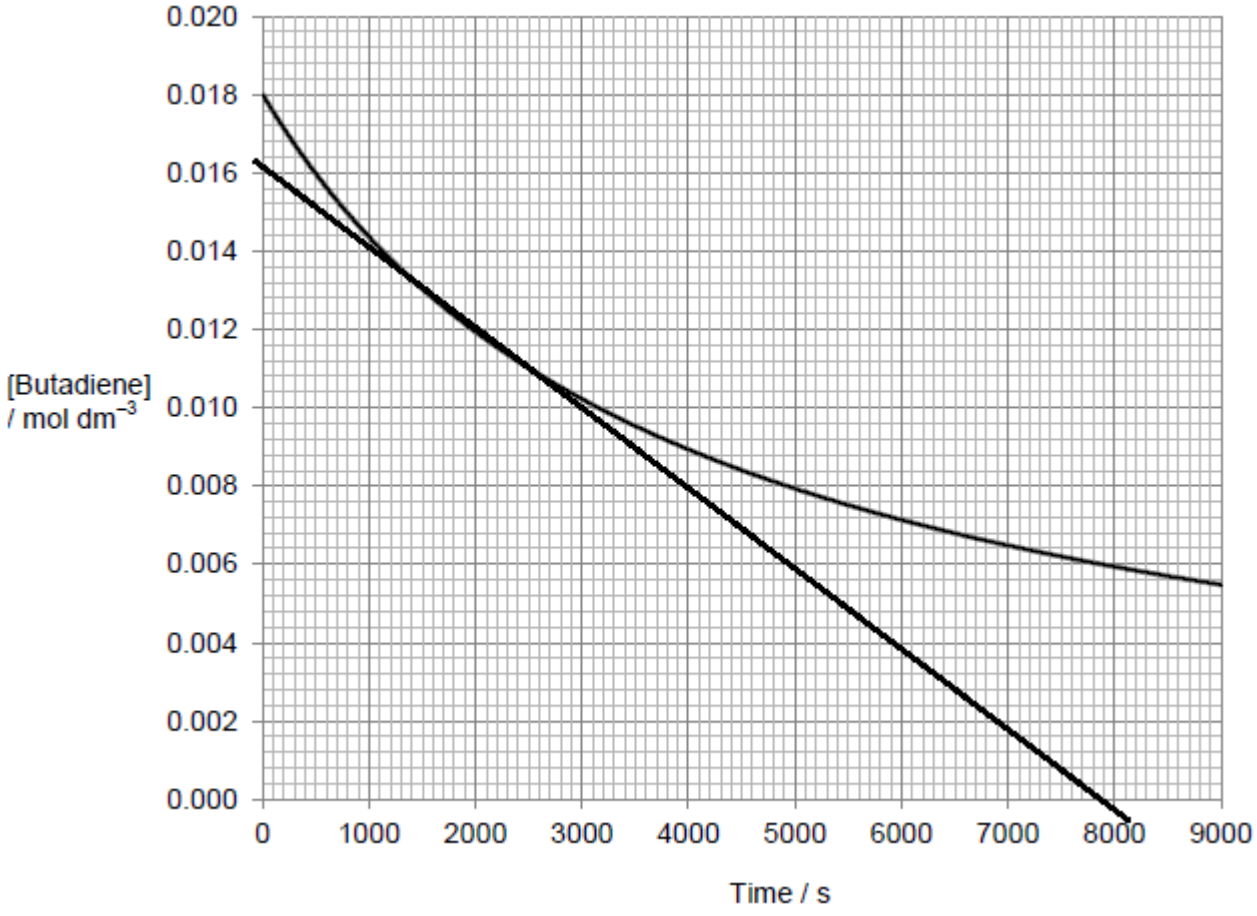
1

$E_a = 8.31 \times 300\ (23.97 - (-5.03)) / 1000 = 72.3$ (kJ mol^{-1})

1

[12]

M2.(a) Gradient drawn on graph



Line must touch the curve at 0.012 but must not cross the curve.

1

(b) Stage 1: Rate of reaction when concentration = 0.0120 mol dm^{-3}

From the tangent

Change in [butadiene] = –0.0160 – 0 and change in time = 7800 – 0

Extended response

1

Gradient = –(0.0160 – 0) / (7800 – 0) = –2.05 × 10^{-6}

Rate = 2.05 × 10^{-6} (mol dm^{-3} s^{-1})

1

Stage 2: Comparison of rates and concentrations

Initial rate / rate at 0.0120 = (4.57 × 10^{-6}) / (2.05 × 10^{-6}) = 2.23

Marking points in stage 2 can be in either order

1

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

1

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 2nd with respect to butadiene

1

[6]

M3. (a) (i) propyl methanoate

must be correct spelling

1

(ii) rate = $k[X][OH^-]$

allow $HCOOCH_2CH_2CH_3$ (or close) for X

allow ( ) but penalise missing minus

1

(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

1

= 0.10(12) 2sf minimum

1 for conseq answer

1

$mol^{-1}\ dm^3\ s^{-1}$

1 for conseq units

any order

1

(iv) $2.1(3) \times 10^{-5}$

or $2.1(2) \times 10^{-5}$ *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) 1.3×10^{-4} (1.28×10^{-4})

allow (1.26×10^{-4}) to (1.3×10^{-4}) *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

For example, if orders given are 1st in X and second in 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 k × $(0.012)(0.0175)^2$ = their k ×(3.7×10^{-6})
(allow answer to 2sf)
** in (v) for rate = their k × $(0.012)(0.105)^2$ = their k ×(1.32×10^{-4})
(allow answer to 2sf)

The numbers will of course vary for different orders.

(vi) Lowered

if wrong, no further mark

1

fewer particles/collisions have energy > E_a
OR
fewer have sufficient (activation) energy (to react)

not just fewer successful collisions

1

(b) Step 2

1

(this step with previous) involves one mol/molecule/particle
A and two Bs

or 1:2 ratio or same amounts (of reactants) as in rate equation

if wrong, no further mark

1

[11]

M4. (a) (i) $k = \frac{6.2 \times 10^{-6}}{(2.9 \times 10^{-2})^2 \times 2.3 \times 10^{-2}}$

mark is for insertion of numbers into a correctly rearranged rate equ, k = etc

AE (-1) for copying numbers wrongly or swapping two numbers

1

= 0.32 (min 2sfs)

1

mol^{-2} dm^6 s^{-1} Units must be conseq to their *k*

Any order

If k calculation wrong, allow units conseq to their k

1

(ii) 4.95×10^{-5} to 4.97×10^{-5} or 5.0×10^{-5} (min 2 sfs)

(ignore units)

rate = their k × 1.547 × 10^{-4}

1

(b) Step 2

If wrong no further mark

1

One H_2 (and two NO) (appear in rate equation)
or species (in step 2) in ratio/proportion as in the rate equation

1

[6]

M5.(a) (i) 2 or two or second or $[E]^2$

1

(ii) 1 or one or first or $[F]^1$ or [F]

1

(b) (i) $k = \dfrac{8.6\times10^{-4}}{(3.8\times10^{-2})^2\times(2.6\times10^{-2})}$

mark is for insertion of numbers into a correctly rearranged rate equ , k = etc.
AE (−1) for copying numbers wrongly or swapping two numbers.

1

= 22.9 (Allow 22.9 − 24 after correct rounding)

1

$\underline{mol^{-2}dm^{+6}\ s^{\&8722;1}}$

Any order.

1

(ii) $6.8(2)\times10^{-3}$ $(mol\ dm^{\&8722;3}s^{-1})$
OR if their k is wrong, award the mark consequentially
a quick check can be achieved by using
$\underline{\text{their answer}}$ = 2.9768×10^{-4} Allow $2.9 - 3.1\times10^{-4}$ for the mark
their *k*

Allow 6.8×10^{-3} to 6.9×10^{-3}
Ignore units.

1

[6]

M6.(a) (i) $k = \dfrac{8.4\times10^{-5}}{(4.2\times10^{-2})^2\times2.6\times10^{-2}}$ ***OR*** $\dfrac{8.4\times10^{-5}}{(1.76\times10^{-3})\times2.6\times10^{-2}}$

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

= 1.8(3)

1

$mol^{-2}\ dm^{+6}\ s^{-1}$

Any order

If k calculation wrong, allow units consequential to their k = expression

1

(ii) 5.67×10^{-4} (mol dm^{-3} s^{-1}) ***OR*** their $k \times 3.1 \times 10^{-4}$

Allow 5.57×10^{-4} to 5.7×10^{-4}

1

(b) (i) 2 or second or $[D]^2$

1

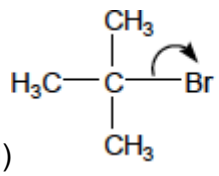
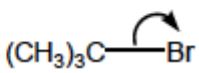
(ii) 0 or zero or $[E]^0$

1

(c) (i) Step 1 or equation as shown

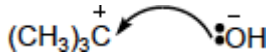
Penalise Step 2 but mark on

1

(ii)  or 

Ignore correct partial charges, penalise full / incorrect partial charges

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



allow: OH^- (must show lp)

If S_N2 mechanism shown then no mark (penalise involvement of $:OH^-$ in step 1)

Ignore anything after correct step 1

1

[8]

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

Allow 2sf

1

Exp 3 0.1(0)

1

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 × k

*Exp 3 **[Q]** = 0.015/k*

*Exp 4 **[P]** = 0.116/√k*

1

(b) $K = \dfrac{1.8 \times 10^{-3}}{(0.20)^2 \times 0.30}$

mark is for insertion of numbers into a correctly rearranged rate equ , k = etc

1

= 0.15 (min 2sfs) (allow $\frac{3}{20}$)

if upside down, score only units mark

AE (–1) for copying numbers wrongly or swapping two numbers

1

$mol^{-2}\ dm^{+6}\ s^{-1}$

Any order

If k calculation wrong, allow units conseq to their k

1

(c) G

1

[7]