## Equilibria, Energetics and Elements How Fast? / 71

1. (i) $\mathrm{O}_{3}$ : Exp 2 has 4 times $\left[\mathrm{H}_{2}\right]$ as $\operatorname{Exp} 1$
and rate increases by 4 (1),
so order $=1$ with respect to $\mathrm{O}_{3}(\mathbf{1})$
$\mathrm{C}_{2} \mathrm{H}_{4}$ : Exp 3 has $2 \times\left[\mathrm{C}_{2} \mathrm{H}_{4}\right]$ and $2 \times\left[\mathrm{O}_{3}\right]$ as $\operatorname{Exp} 2$;
and rate has increased by 4 (1),
so order $=1$ with respect to $\mathrm{C}_{2} \mathrm{H}_{4}$ (1)
rate $=k\left[\mathrm{O}_{3}\right]\left[\mathrm{C}_{2} \mathrm{H}_{4}\right](\mathbf{1})$
(ii) use of $k=$ rate $/\left[\mathrm{O}_{3}\right]\left[\mathrm{C}_{2} \mathrm{H}_{4}\right]=1.0 \times 10^{-12} /\left(0.5 \times 10^{-7} \times 1.0 \times 10^{-8}\right)$
to obtain a calculated value (1)
$k=2 \times 10^{3}$ (1)
units: $\mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1} \mathbf{( 1 )} \quad 3$
(iii) $\quad$ rate $=1.0 \times 10^{-12} / 4=2.5 \times 10^{-13}\left(\mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right)(\mathbf{1}) \quad 1$
(iv) rate increases and $k$ increases (1) 1
2. $\quad 11 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{O}_{3}(\mathrm{~g}) /$
$\mathrm{O}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{O}_{3}(\mathrm{~g})(\mathbf{1})$
NO is a catalyst (1) as it is (used up in step 1 and) regenerated in step 2/ not used up in the overall reaction(1)
allow 1 mark for ' $\mathrm{O} / \mathrm{NO}_{2}$ with explanation of regeneration.'
3. (i) $\mathrm{H}_{2}$ : $\operatorname{Exp} 2$ has 2.5 times $\left[\mathrm{H}_{2}\right]$ as $\operatorname{Exp} 1$
and rate increases by 2.5 (1),
so order $=1$ with respect to $\mathrm{H}_{2}$ (1)
$\mathrm{NO}: \operatorname{Exp} 3$ has $3 x[\mathrm{NO}]$ as $\operatorname{Exp} 2 ;$
and rate has increased by $9=3^{2}$ (1),
so order $=2$ with respect to NO (1)
QWC At least two complete sentences where the meaning is clear. 1
(ii) $\quad$ rate $=\mathrm{k}[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right](1) \quad 1$
(iii) $\mathrm{k}=\frac{\text { rate }}{[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]} / \frac{2.6}{0.10^{2} \times 0.20}$ (1)
$=1300$ (1) units: $\mathrm{dm}^{6} \mathrm{~mol}^{-2} \mathrm{~s}^{-1}$ (1)
allow 1 mark for $7.69 \times 10^{-4}$ or $1.3 \times 10^{\mathrm{x}}(\mathrm{x}$ not 3$)$
4. (i) $\quad 1 \frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{O}_{3}(\mathrm{~g}) /$
$\mathrm{O}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{O}_{3}(\mathrm{~g})(\mathbf{1})$
NO is a catalyst (1) as it is (used up in step 1 and) regenerated in step 2/
not used up in the overall reaction(1)
allow 1 mark for ' $\mathrm{O} / \mathrm{NO}_{2}$ with explanation of regeneration.'
(ii) $\quad$ Rate $=k[\mathrm{NO}]\left[\mathrm{O}_{3}\right]$ (1)

Species in rate equation match those reactants in the slow step / rate determining step (1)
5. (a) (i) $\begin{aligned} & \text { Curve downwards starting at } \mathrm{t}=0 \checkmark \\ & \\ & \\ & \\ & \\ & \text { (don't worry about hitting the } x \text { axis) }\end{aligned}$
(ii) Tangent shown at start $\checkmark \quad 1$
(iii) Half-life is constant 1

OR: draw tangents and then plot a 2 nd graph of tangent or rate against concentration, which is a straight line through the origin.
(iv) Straight line through origin

(b) 4 times [KI], rate increases by $4 \checkmark$ so order $=1$ with respect to KI $\checkmark$ independent marks
(c) (i) $\quad$ rate $/ \mathrm{r}=k\left[\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{Br}_{2}\right][\mathrm{KI}] \checkmark$ or ecf from (b)
(ii) $k=\frac{\text { rate }}{\left[\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{Br}_{2}\right][\mathrm{KI}]} / \frac{0.027}{0.50 \times 0.18} \checkmark$
$=0.3(0) \checkmark \quad$ units: $\mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$
units dependent on rate equation in (i).
Mark independently.
6. From graph, constant half-life (1)

Therefore $1^{\text {st }}$ order w.r.t. $\left[\mathrm{CH}_{3} \mathrm{COCH}_{3}\right]$ (1)
From table, rate doubles when $\left[\mathrm{H}^{+}\right]$doubles (1)
Therefore $1^{\text {st }}$ order w.r.t. $\left[\mathrm{H}^{+}\right]$(1)
From table, rate stays same when $\left[\mathrm{I}_{2}\right]$ doubles (1)
Therefore zero order w.r.t. [ $\mathrm{I}_{2}$ ] (1)
Order with no justification does not score.
rate $=k\left[\mathrm{H}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COCH}_{3}\right](\mathbf{1})$
(from all three pieces of evidence)

$$
\begin{aligned}
& k=\frac{\text { rate }}{\left[\mathrm{H}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COCH}_{3}\right]} / \frac{2.1 \times 10^{-9}}{0.02 \times 1.5 \times 10^{-3}} \\
& =7.0 \times 10^{-5}(\mathbf{1}) \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1} \mathbf{( 1 )} \\
& \text { accept } 7 \times 10^{-5}
\end{aligned}
$$

rate determining step involves species in rate equation (1)
two steps that add up to give the overall equation (1)
The left hand side of a step that contains the species in rate-determining step (1)
i.e., for marking points 2 and 3:
$\mathrm{CH}_{3} \mathrm{COCH}_{3}+\mathrm{H}^{+} \rightarrow\left[\mathrm{CH}_{3} \mathrm{COHCH}_{3}\right]^{+}$
$\left[\mathrm{CH}_{3} \mathrm{COHCH}_{3}{ }^{+}\right]+\mathrm{I}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{I}+\mathrm{HI}+\mathrm{H}^{+}$
organises relevant information clearly and coherently,
using specialist vocabulary where appropriate
Use of the following four words/phrases:
constant, half-life, order, doubles/x2 (1) 1
7. (i) The slowest step (1)
(ii) $\quad 2 \mathrm{NO}_{2} \rightarrow \mathrm{NO}+\mathrm{NO}_{3}(1)$ $\mathrm{NO}_{3}+\mathrm{CO} \rightarrow \mathrm{NO}_{2}+\mathrm{CO}_{2}(\mathbf{1})$
(or similar stage involving intermediates)
8. HCl and $\mathrm{CH}_{3} \mathrm{COOH}$ have same number of moles/
release same number of moles $\mathrm{H}^{+}$/
1 mole of each acid produce $1 / 2 \mathrm{~mol}$ of $\mathrm{H}_{2}$ (1)
$\left[\mathrm{H}^{+}\right]$in $\mathrm{CH}_{3} \mathrm{COOH}<\left[\mathrm{H}^{+}\right]$in $\mathrm{HCl} /$
$\mathrm{CH}_{3} \mathrm{COOH}$ is a weaker acid than HCl (ora) (1)
$\mathrm{Mg}+2 \mathrm{HCl} \rightarrow \mathrm{MgCl}_{2}+\mathrm{H}_{2}(\mathbf{1})$
$\mathrm{Mg}+2 \mathrm{CH}_{3} \mathrm{COOH} \rightarrow\left(\mathrm{CH}_{3} \mathrm{COO}\right)_{2} \mathrm{Mg}+\mathrm{H}_{2}(\mathbf{1})$
or
$\mathrm{Mg}+2 \mathrm{H}^{+} \rightarrow \mathrm{Mg}^{2+}+\mathrm{H}_{2}(\mathbf{1})(\mathbf{1})$

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9. (i) constant half-life (1) 1
(ii) rate $=\mathrm{k}\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ (1)

Common error will be to use ' 2 ' from equation.
(iii) curve downwards getting less steep (1)
curve goes through $1200,0.30 ; 2400,0.15 ; 3600,0.075(1) 2$
(iv) tangent shown on graph at $\mathrm{t}=1200 \mathrm{~s}(\mathbf{1}) 1$
(v) $\quad 3.7(2) \times 10^{-4} \mathbf{( 1 )} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}$ (1) ecf possible from (ii) using $\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]^{\mathrm{x}}$ ( $2^{\text {nd }}$ order answer: 2.2(3) $\times 10^{-4}$ )
10. (i) slow step (1) 1
(ii) $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CH}_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow\left(\mathrm{CH}_{3}\right)_{3} \mathrm{COH}$ (1) $\quad 1$
(iii) $\mathrm{H}^{+}$is a catalyst (1)
$\mathrm{H}^{+}$used in first step and formed in second step/ regenerated/ not used up (1)
(iv) rate $=\mathrm{k}\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{CH}_{2}\right]\left[\mathrm{H}^{+}\right]$(1)
common error will be use of $\mathrm{H}_{2} \mathrm{O}$ instead of $\mathrm{H}^{+} \quad 1$

