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 $\mathrm{C}_{2} \mathrm{H}_{4}(\mathbf{1})$
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: $\mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}(\mathbf{1})$
(iii) rate $=1.0 \times 10^{-12} / 4=2.5 \times 10^{-13}\left(\mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}\right)(\mathbf{1})$
(iv) rate increases and $k$ increases (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) $\mathrm{H}^{+} /$proton donor (1)
(ii) partially dissociates/ionises (1) 1
4. $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
acid 1 base 2 base 1 acid 2 (1)
1
5. (i) $K_{\mathrm{a}}=\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}(\mathrm{aq})\right]\left[\mathrm{H}^{+}(\mathrm{aq})\right] /\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})\right]$ (1)
(ii) $M_{\mathrm{r}} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}=94(\mathbf{1})$
$\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})\right] 4.7 / 94=0.050 \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
$1.3 \times 10^{-10} \approx\left[\mathrm{H}^{+}(\mathrm{aq})\right]^{2} / 0.050 \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$ (‘$=’$ sign is acceptable)
$\left[\mathrm{H}^{+}\right]=\sqrt{ }\left\{\left(1.3 \times 10^{-10}\right) \times(0.050)\right\}=2.55 \times 10^{-6} \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
$\mathrm{pH}=-\log [\mathrm{H}+]=-\log 2.55 \times 10^{-6}=5.59(\mathbf{1})$
3 marks: $\left[\mathrm{H}^{+}\right]$; pH expression ; calc of pH from $\left[\mathrm{H}^{+}\right]$
6. $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=1.99 \times 10^{-9} \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
$\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}(\mathrm{aq})\right]=K_{\mathrm{a}}\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})\right] /\left[\mathrm{H}^{+}(\mathrm{aq})\right](\mathbf{1})$
$\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}(\mathrm{aq})\right]=0.13 \mathrm{~mol} \mathrm{dm}^{-3}(\mathbf{1})$
Calculation should use half the original concentration of phenol to find the concentration of sodium phenoxide in the buffer. This should then be doubled back up again.
Do not penalise an approach that uses the original concentration of phenol in the expression above.
7. (a) rate of forward reaction = rate of reverse reaction (1)
concentrations of reactants and products are constant but they are constantly interchanging (1)
(b) (i) $K_{\mathrm{c}}=\left[\mathrm{CH}_{3} \mathrm{OH}\right] /[\mathrm{CO}]\left[\mathrm{H}_{2}\right]^{2}(\mathbf{1})$
(ii) use of $K_{\mathrm{c}}=\left[\mathrm{CH}_{3} \mathrm{OH}\right] /[\mathrm{CO}]\left[\mathrm{H}_{2}\right]^{2}$ and moles to
obtain a calculated value (1)
convert moles to concentration by +2 : $[\mathrm{CO}]=3.10 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$; $\left[\mathrm{H}_{2}\right]=2.60 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3} ;\left[\mathrm{CH}_{3} \mathrm{OH}\right]=2.40 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
$K_{\mathrm{c}}=\left[2.60 \times 10^{-5}\right] /\left[3.10 \times 10^{-3}\right]\left[2.40 \times 10^{-2}\right]^{2}=14.6 / 14.56(1)$
If moles not converted to concentration, calculated $K_{\mathrm{c}}$ value $=3.64$ (scores 1st and 3rd marks)
units: $\mathrm{dm}^{6} \mathrm{~mol}^{-2}$ (1)
(c) (i) fewer moles of gas on right hand side (1) 1
(ii) None (1)
(d) (i) moved to left hand side/reactants increase/less products (1)
(ii) $\Delta H$ negative because high temperature favours the endothermic direction (1)
(e) (i) $\mathrm{CH}_{3} \mathrm{OH}+1 \frac{1}{2} \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}(1) \quad 1$
(ii) adds oxygen/oxygenated (1) 1
8. (i) $\mathrm{H}_{2}$ : Exp 2 has 2.5 times $\left[\mathrm{H}_{2}\right]$ as Exp 1
and rate increases by 2.5 (1),
so order $=1$ with respect to $\mathrm{H}_{2}(1)$
NO: Exp 3 has 3 x [NO] as Exp 2;
and rate has increased by $9=3^{2} \mathbf{( 1 )}$,
so order $=2$ with respect to NO (1)
QWC At least two complete sentences where the meaning is clear.
(ii) rate $=\mathrm{k}[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]$ (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$) \quad 3$
9. (i) $\quad 1 \frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{O}_{3}(\mathrm{~g}) /$
$\mathrm{O}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{O}_{3}(\mathrm{~g})(1)$
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)
10. (a) $K_{\mathrm{c}}=\frac{\left[\mathrm{PCl}_{3}\right]\left[\mathrm{Cl}_{2}\right]}{\left[\mathrm{PCl}_{5}\right]}$ (1)
(b) (i) $\mathrm{PCl}_{5}>0.3 \mathrm{~mol} \mathrm{dm}^{-3} ; \mathrm{PCl}_{3}$ and $\mathrm{Cl}_{2}<0.3 \mathrm{~mol} \mathrm{dm}^{-3}$ (1)
(ii) At start, system is out of equilibrium with too much $\mathrm{PCl}_{3}$ and $\mathrm{Cl}_{2}$ and not enough $\mathrm{PCL}_{5}$ /

$$
\frac{0.3 \times 0.3}{0.3}=0.3 \text { is greater than } K_{\mathrm{c}}=0.245 \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}
$$

(c) (i) $K_{\mathrm{C}}$ does not change as temperature is the same (1)
(ii) Fewer moles on left hand side (1)
system moves to the left to compensate for increase in pressure by producing less molecules (1)
(d) (i) $\quad K_{\mathrm{C}}$ decreases (as more reactants than products)(1)
(ii) Forward reaction is exothermic/ reverse reaction is endothermic (1)
equilibrium $\rightarrow$ left to oppose increase in energy/
because $K_{\mathrm{c}}$ decreases (1)
11. (a) (i) Ionic product (1) 1
(ii) $K_{\mathrm{w}}=\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$ (1) state symbols not needed
(b) moles of $\mathrm{HCl}=\frac{5 \times 10^{-3} \times 21.35}{1000}=1.067 \times 10^{-4} \mathrm{~mol}(\mathbf{1})$
moles of $\mathrm{Ca}(\mathrm{OH})_{2}=\frac{1.067 \times 10^{4}}{2}=5.34 \times 10^{-5} \mathrm{~mol}$ (1)
concentration of $\mathrm{Ca}(\mathrm{OH})_{2}=40 \times 5.34 \times 10^{-5}$

$$
=2.136 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}
$$

2 marks for $4.27 \times 10^{-3} / 8.54 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$
(no factor of 4)
(c) $\left[\mathrm{OH}^{-}\right]=2 \times 2.7 \times 10^{-3}=5.4 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$ (1)
$\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{K_{\mathrm{w}}}{\left[\mathrm{OH}^{-}(\mathrm{aq})\right]}=\frac{1.0 \times 10^{-14}}{5.4 \times 10^{-3}}=1.85 \times 10^{-12} \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( \mathbf { 1 } )}$
$\mathrm{pH}=-\log \left(1.85 \times 10^{-12}\right)=11.73 / 11.7$ (1)
ecf is possible for pH mark providing that the $\left[\mathrm{H}^{+}\right]$
value has been derived from $K_{\mathrm{w}} /\left[\mathrm{OH}^{-}\right]$
If pOH method is used, $\mathrm{pOH}=2.27$. would get $1^{\text {st }}$ mark, $\mathrm{pH}=14-2.27=11.73$ gets $2^{\text {nd }}$ mark.
Commonest mistake will be to not double $\mathrm{OH}^{-}$and to use $2.7 \times 10^{-3}$
This gives ecf answer of $11.43 / 11.4$, worth 2 marks.
$\mathrm{pH}=11.13$ from dividing by 2 : worth 2 marks
(d) 8 (1)
12. (a) $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}+2 \mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{Ca}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}+2 \mathrm{CaSO}_{4}$ (1)
(b) $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{HPO}_{4}{ }^{2-}(\mathrm{aq}) /$
$\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{aq}) \rightleftharpoons 2 \mathrm{H}^{+}(\mathrm{aq})+\mathrm{PO}_{4}{ }^{3-}(\mathrm{aq})(\mathbf{1})$
(or equivalent with $\mathrm{H}_{2} \mathrm{O}$ forming $\mathrm{H}_{3} \mathrm{O}^{+}$)
(c) (i) $\mathrm{HPO}_{4}{ }^{2-}$ (1)
(ii) $\mathrm{H}_{3} \mathrm{PO}_{4} \mathbf{( 1 )} 1$
(iii) $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$produced $\mathrm{Ca}\left(\mathrm{H}_{2} \mathrm{PO}_{4}\right)_{2}$ or on LHS of an attempted equilibrium equation (1)
2 equations/equilibria to shown action of buffer (1)(1) from:
$\mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}^{+} \rightleftharpoons \mathrm{H}_{3} \mathrm{PO}_{4} /$
$\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HPO}_{4}^{2-}$
$\mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{OH}^{-} \rightleftharpoons \mathrm{H}_{2} \mathrm{O}+\mathrm{HPO}_{4}{ }^{2-} /$
$\mathrm{H}^{+}+\mathrm{OH}^{-} \rightleftharpoons \mathrm{H}_{2} \mathrm{O}$
13. Correct equation for a metal (1)

Correct equation for a carbonate (1)
Correct equation for a base (1)
14. (a) partial dissociation: $\mathrm{HCOOH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HCOO}^{-}$(1)
(b) (i) $\mathrm{pH}=-\log \left(1.55 \times 10^{-3}\right)=2.81 / 2.8$ (1)
$\left[\mathrm{H}^{+}\right]$deals with negative indices over a very wide range/ pH makes numbers manageable /removes very small numbers (1)
(ii) $K_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]}{[\mathrm{HCOOH}(\mathrm{aq})]}$ (1) (state symbols not needed)
(iii) $K_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]^{2}}{[\mathrm{HCOOH}(\mathrm{aq})]}=\frac{\left(1.55 \times 10^{-3}\right)^{2}}{0.015}$ (1)
$=1.60 \times 10^{-4}\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)(\mathbf{1})$
$\mathrm{p} K_{\mathrm{a}}=-\log K_{\mathrm{a}}=-\log \left(1.60 \times 10^{-4}\right)=3.80(\mathbf{1})$
(iv) Percentage dissociating $=\frac{\left(1.55 \times 10^{-3}\right) \times 100}{0.015}=10.3 \% /$ 10\% (1)
(working not required)
15. (i) $\mathrm{HCOOH}+\mathrm{NaOH} \rightarrow \mathrm{HCOONa}+\mathrm{H}_{2} \mathrm{O}$ (1)
state symbols not needed
(ii) $\mathrm{n}(\mathrm{HCOOH})=0.0150 \times 25.00 / 1000=3.75 \times 10^{-4}$ (1)
volume of $\mathrm{NaOH}(\mathrm{aq})$ that reacts is $30 \mathrm{~cm}^{3}$ (1)
so $[\mathrm{NaOH}]=3.75 \times 10^{-4} \times 1000 / 30=0.0125 \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
(iii) $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$ (1)
$\mathrm{pH}=-\log \left(1 \times 10^{-14} / 0.0125\right)=12.10 / 12.1(\mathbf{1})$ (calc 12.09691001)
(iv) metacresol purple (1)
pH range coincides with pH change during sharp rise OR
pH 6-10 /coincides with equivalence point/end point (1)
16. (a) $K_{\mathrm{c}}=\frac{[\mathrm{HI}]^{2}}{\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]}$ (1)
(b) $\begin{array}{llll}\text { (i) } & \mathrm{H}_{2} & \mathrm{I}_{2} & \mathrm{HI}\end{array}$
$0.30 \quad 0.20$
0
0.14
0.04
0.32
(1) (1)
(ii) $\quad K_{\mathrm{C}}=\frac{0.32^{2}}{0.14 \times 0.04}=18.28571429$ (1) $=18$ (to 2 sig figs) (1) no units (1) (or ecf based on answers to (i) and/or (a))
(c) $K_{\mathrm{c}}$ is constant (1)

Composition of mixture is the same (1)
17. (i) $\mathrm{I}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g}) \rightarrow 2 \mathrm{HI}(\mathrm{aq})+\mathrm{S}(\mathrm{s})$
species and balance (1)
state symbols: accept (s) for $\mathrm{I}_{2}$; (aq) for $\mathrm{H}_{2} \mathrm{~S}$ (1)
(ii) amount $\mathrm{I}_{2}$ reacted $=1.89 \mathrm{~mol} / \mathrm{HI}$ formed $=3.44 \mathrm{~mol}(\mathbf{1})$ theoretical amount HI produced $=3.78 \mathrm{~mol} / 484 \mathrm{~g} \mathrm{(1)}$
$\%$ yield $=\frac{3.44 \times 100}{3.78}$ or $\frac{440 \times 100}{484}=91.0 \%(\mathbf{1})$
(iii) $[\mathrm{HI}]=\frac{3.44 \times 1000}{750}=4.58 / 4.59 \mathrm{~mol} \mathrm{dm}^{-3}(\mathbf{1})$
$\mathrm{pH}=-\log 4.59=-0.66(\mathbf{1})$

$$
2
$$

18. 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 [ $\mathrm{I}_{2}$ ] 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)

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

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)
19. (a) (i) (+)1 (1)
(ii)


Look for atoms bonded together.
AND other lone pairs.
(b) (i) $\mathrm{C}_{13} \mathrm{H}_{18} \mathrm{O}_{2}$ (1)
(ii) any chemical that reacts to produce gas:
e.g. carbonate and $\mathrm{CO}_{2}(\mathbf{1})$
accept: metal more reactive than Pb and $\mathrm{H}_{2}$
balanced equation to match chemical added (1)
(c) $\quad M_{\mathrm{r}}$ (Lidocaine) $=236(\mathbf{1})$

Moles Novocaine $=100 \times 10^{-3} / 236=4.24 \times 10^{-4} \mathbf{( 1 )}$
Concentration of Novocaine $=4.24 \times 10^{-4} \times(1000 / 5)$
$=0.0847 / 0.0848 / 0.085 \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
(d) mass $\mathrm{C}=12 \times \frac{3.74}{44.0}=1.02 \mathrm{~g} /$
moles $\mathrm{CO}_{2}=\frac{3.74}{44}=0.085 \mathrm{~mol}(\mathbf{1})$
mass $\mathrm{H}=\frac{2}{18} \times 0.918=0.102 \mathrm{~g} /$
moles $\mathrm{H}_{2} \mathrm{O}=\frac{0.918}{18}=0.051 \mathrm{~mol}(\mathbf{1})$
ratio $\mathrm{C}: \mathrm{H}=\frac{1.02}{12}: \frac{0.102}{1}=0.0850: 0.102=5: 6 / 10: 12 /$
ratio $\mathrm{CO}_{2}: \mathrm{H}_{2} \mathrm{O}=5: 3 / 10: 6$ (1)
mass $\mathrm{O}=1.394-(1.020+0.102)=0.272 \mathrm{~g}$
/ using 1.394 g eugenol and $M_{\mathrm{r}}=164$, shows that 1
molecule contains 2 atoms of O (1)
2
$\therefore$ molecular formula $=\mathrm{C}_{10} \mathrm{H}_{12} \mathrm{O}_{2}(\mathbf{1}) \quad 1$
20. (a) (change in) concentration/mass/volume with time
(b) (i) $\mathrm{O}_{2}$ :

Exp 2 has $4 \times\left[\mathrm{O}_{2}\right]$ as Exp. 1: rate increases by 4 (1), so order $=1$ with respect to $\mathrm{O}_{2}(\mathbf{1})$

NO:
Exp 3 has $3 \times[\mathrm{NO}]$ as Exp. 3: rate has increases by 9 (1), so order $=2$ with respect to NO (1)
(ii) rate $=k\left[\mathrm{O}_{2}\right][\mathrm{NO}]^{2}(\mathbf{1})$
(iii) $k=\frac{\text { rate }}{\left[\mathrm{O}_{2}\right][\mathrm{NO}]^{2}}=\frac{7.10}{0.0010 \times 0.0010^{2}}=7.10 \times 10^{9}$ (1)
units: $\mathrm{dm}^{6} \mathrm{~mol}^{-2} \mathrm{~s}^{-1}$ (1)
21. (i) The slowest step (1) 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)
22. (a) strength of acid/extent of dissociation/ionisation (1)
(b) (i) $\mathrm{H}_{2} \mathrm{SO}_{3}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{HSO}_{3}^{-}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COOH}_{2}{ }^{+}(\mathrm{aq})$ acid 1 base 2 (1) base $1 \quad$ acid 2 (1)

1 mark for labels on each side of equation
(ii) $\mathrm{CH}_{3} \mathrm{COOH}$ is the stronger acid/
$K_{\mathrm{a}} \mathrm{CH}_{3} \mathrm{COOH}$ is greater/
$\mathrm{CH}_{3} \mathrm{COOH}$ is more acidic ORA (1)

$$
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}_{2}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})(\mathbf{1}) \quad 2
$$

(c) For $\mathrm{HCl}, \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$(1) (or with values). Could be awarded below $=-\log 0.045=1.35$ (1) (accept 1.3)

For $\mathrm{CH}_{3} \mathrm{COOH},\left[\mathrm{H}^{+}\right]=\sqrt{ }\left(\mathrm{K}_{\mathrm{a}} \times\left[\mathrm{CH}_{3} \mathrm{COOH}\right]\right) /$
$\checkmark\left(1.70 \times 10^{-5} \times 0.045\right)(\mathbf{1})$
$\left[\mathrm{H}^{+}\right]=8.75 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
$\mathrm{pH}=-\log 8.75 \times 10^{-4}=3.058 / 3.06(\mathbf{1})($ accept 3.1) 5
23. 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 $\mathrm{H}_{2}(\mathbf{1})$
$\left[\mathrm{H}^{+}\right]$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
$\mathrm{Mg}+2 \mathrm{H}^{+} \rightarrow \mathrm{Mg}^{2+}+\mathrm{H}_{2} \mathbf{( 1 ) ( \mathbf { 1 } )} 4$
24. amount of NaOH in titration $=0.175 \times 22.05 / 1000$
or $3.86 \times 10^{-3} \mathbf{( 1 )}$ (calc: $3.85875 \times 10^{-3}$ )
amount of $\mathbf{A}$ in $25.0 \mathrm{~cm}^{3}=0.5 \times \mathrm{mol} \mathrm{NaOH}$
or $1.93 \times 10^{-3} \mathbf{( 1 )}$ (calc: $1.929375 \times 10^{-3}$ )
amount of $\mathbf{A}$ in $250 \mathrm{~cm}^{3}=10 \times 1.93 \times 10^{-3}$ or $1.93 \times 10^{-2} \mathbf{( 1 )}$
$1.93 \times 10^{-2} \mathrm{~mol} \mathbf{A}$ has a mass of 2.82 g
molar mass of $\mathbf{A}=2.82 / 1.93 \times 10^{-2}=146 \mathrm{~g} \mathrm{~mol}^{-1}(\mathbf{1})$
(or $M_{r}$ of $\mathbf{A}$ is 146)
Therefore $\mathbf{A}$ is adipic acid / $\mathrm{HOOC}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{COOH}$ (1)
25. (a) $\quad K_{\mathrm{p}}=\frac{\mathrm{p}\left(\mathrm{SO}_{3}\right)^{2}}{\mathrm{p}\left(\mathrm{SO}_{2}\right)^{2} \times \mathrm{p}\left(\mathrm{O}_{2}\right)}$ (1)(1)

1 mark for correct powers but wrong way up.

1 mark for square brackets
(b) An increase in pressure moves equilibrium to the right because there are less gaseous moles on the right hand side (1) Increased pressures are expensive to generate/safety problems with walls of containers/enables gases to flow (1)
$K_{\mathrm{p}}$ gets less with increasing temperature (1)
$\mathrm{SO}_{2}$ and $\mathrm{O}_{2}$ increase/ $\mathrm{SO}_{3}$ decreases (1)
Equilibrium $\rightarrow$ left to oppose increase in temperature (1)
Forward reaction is exothermic or $\Delta \mathrm{H}$ is - ve /reverse reaction is endothermic or $\Delta \mathrm{H}$ is +ve because $K_{\mathrm{p}}$ gets less with increasing temperature (1)
QoWC: organises relevant information clearly and coherently, using specialist vocabulary where appropriate (1)
(c) $3.0 \times 10^{2}=\frac{\mathrm{p}\left(\mathrm{SO}_{3}\right)^{2}}{10^{2} \times 50}(\mathbf{1})$
$\mathrm{p}\left(\mathrm{SO}_{3}\right)=\sqrt{ }\left(3.0 \times 10^{2} \times 10^{2} \times 50\right)=1225 \mathrm{kPa}(\mathbf{1})$
$\%\left(\mathrm{SO}_{3}\right)=100 \times 1225 /(1225+10+50)=95 \%(\mathbf{1})$
(d) (i) $2 \mathrm{ZnS}+3 \mathrm{O}_{2} \rightarrow 2 \mathrm{ZnO}+2 \mathrm{SO}_{2}$ (1)(1)
$\mathrm{ZnS}, \mathrm{O}_{2}$ as reactants and $\mathrm{SO}_{2}$ as a product: 1st mark.
ZnO and balance: $2^{\text {nd }}$ mark
(ii) ZnS is more available than S . (1) 1
26. (a) (i) $\mathrm{O}_{3}: 1$
and $\mathrm{C}_{2} \mathrm{H}_{4}(\mathbf{1}) \quad 1$
(ii) 2 (1) 1
(iii) rate $=\mathrm{k}\left[\mathrm{O}_{3}\right]\left[\mathrm{C}_{2} \mathrm{H}_{4}\right](\mathbf{1}) \quad 1$
(b) (i) measure gradient/tangent (1)
at $t=0 /$ start of reaction (1)
(ii) $\mathrm{k}=\frac{\text { rate }}{\left[\mathrm{O}_{2}\right]\left[\mathrm{C}_{2} \mathrm{H}_{4}\right]}$ (1) $\mathrm{k}=\frac{1.0 \times 10^{-12}}{0.5 \times 10^{-7} \times 1.0 \times 10^{-8}}=2 \times 10^{3} \mathbf{( 1 )} \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1} \mathbf{( 1 )} \quad 3$
(iii) $2 \mathrm{~mol} \mathrm{CH}_{2} \mathrm{O}$ forms for every $0.5 \mathrm{~mol} \mathrm{O}_{2}$ / stoichiometry of $\mathrm{CH}_{2} \mathrm{O}: \mathrm{O}_{2}$ is not $1: 1$ (1)
(iv) rate increases (1) k increases (1)
27. (i) each atom has two unpaired electrons (1) 1
(ii) 2 oxygen atoms bonded by double bond (1)
third oxygen bonded by a covalent bond and outer shells correct (1)
For $2^{\text {nd }}$ mark, all O atoms must have an octet.
A triangular molecule would have 3 single covalent bonds for $1^{\text {st }}$ mark but the origin of each electron must be clear for $2^{\text {nd }}$ mark
(iii) amount of $\mathrm{O}_{3}$ in $150 \mathrm{~kg}=150 \times 10^{3} / 48=3.13 \times 10^{3} \mathrm{~mol}(\mathbf{1})$
amount of Cl radicals in $1 \mathrm{~g}=1 / 35.5=2.82 \times 10^{-2} \mathrm{~mol}(\mathbf{1})$
1 mol Cl destroys $3.13 \times 10^{3} / 2.82 \times 10^{-2}=1.11 \times 10^{5} \mathrm{~mol} \mathrm{O}_{3}$
1 Cl radical destroys $1.11 \times 10^{5} \mathrm{O}_{3}$ molecules (1)
(calculator: 110937)
28. (i) proton donor (1) 1
(ii) partially dissociates (1) 1
29. $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ acid $1 \quad$ base 2 (1) base $1 \quad$ acid 2 (1) 1 mark for each acid-base pair
30. (i) $K_{\mathrm{a}}=\frac{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}\right]}$
(ii) concentration $=38 / 94 \mathbf{( 1 )}=0.40 \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
(first mark for $M_{r}$ of phenol - incorrect answer here will give ecf for remainder of question)

$$
1.3 \times 10^{-10} \approx \frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]^{2}}{0.40}
$$

( $‘=$ ’ sign is acceptable)
$\left[\mathrm{H}^{+}\right]=\sqrt{ }\left\{\left(1.3 \times 10^{-10}\right) \times(0.40)\right\}=7.2 \times 10^{-6} \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$ $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log 7.2 \times 10^{-6}=5.14(\mathbf{1})$

3 marks: $\left[\mathrm{H}^{+}\right]$(1); pH expression (1); calc of pH from $\left[\mathrm{H}^{+}\right]$(1)

## Common errors:

Without square root, answer = $10.28 \mathbf{( 1 ) ( 1 ) ( 0 )}$
Use of 38 as molar concentration does not score $1^{\text {st }} 2$ marks.
This gives an answer of 4.15 for 3 marks (1)(1)(1)
31.

/ NaOH / Na (1)
weak acid/base pair mixture formed (1)
On structure, 1 mark for O Na on either or both phenol groups.
32. moles HCl in $23.2 \mathrm{~cm}^{3}=0.200 \times 23.2 / 1000=4.64 \times 10^{-3} \mathbf{( 1 )}$
moles $\mathbf{B}$ in $25 \mathrm{~cm}^{3}=$ moles $\mathrm{HCl}=4.64 \times 10^{-3} \mathbf{( 1 )}$
moles $\mathbf{B}$ in $250 \mathrm{~cm}^{3}=4.64 \times 10^{-3} \times 10=4.64 \times 10^{-2}$ (1)
$4.64 \times 10^{-2} \mathrm{~mol} \mathbf{B}$ has a mass of 4.32 g
molar mass of $\mathbf{B}=4.32 / 4.64 \times 10^{-2}=93 \mathrm{~g} \mathrm{~mol}^{-1}(\mathbf{1})$
$93-16=77$ (1)
Therefore $\mathbf{B}$ is phenylamine / $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}$ (1)
There may be other valid structures that are amines. These can be credited provided that everything adds up to 93.
Answer could be a primary, secondary or tertiary amines.
33. (a) (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)
(iv) tangent shown on graph at $\mathrm{t}=1200 \mathrm{~s}$ (1)
(v) $\quad 3.7(2) \times 10^{-4}$ (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: $2.2(3) \times 10^{-4}$ )
(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)
(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 $\mathrm{H}^{+}$
35. (a) High Pressure

Equilibrium $\rightarrow$ right as fewer moles on right hand side and the shift reduces number of molecules/compensates for increasing pressure (1)
Rate increases/ more collisions (1)

## High temperature

Equilibrium $\rightarrow$ left as equilibrium goes to the left to compensate for increased temperature/absorbs the energy/in endothermic direction (ora) (1)
Rate increases/ more successful collisions (1)

## Other effect

High pressures expensive/ high temperatures expensive /high pressures cause safety problems (1)1

QWC: One correct statement followed by correct explanation (1) 1
(b)
(i) CO
$\mathrm{H}_{2}$
$\mathrm{CH}_{3} \mathrm{OH}$
1.0
2.0
1.8 (1)
0.0
0.9
$0.9 / 2.8$ or 0.321 or $0.32 / 0.3 \quad 1.8 / 2.8$ or 0.643 or
0.1 (1) $0.64 / 0.6 \quad 0.1 / 2.8$ or 0.036 or 0.04 $3.21(\mathrm{MPa}) \quad 6.43(\mathrm{MPa}) \quad 0.36(\mathrm{MPa})$

In $3^{\text {rd }}$ and $4^{\text {th }}$ rows, ecf from previous row
(ii) $\mathrm{K}_{\mathrm{p}}=\frac{\mathrm{p}\left(\mathrm{CH}_{3} \mathrm{OH}\right)}{\mathrm{p}(\mathrm{CO}) \times \mathrm{p}\left(\mathrm{H}_{2}\right)^{2}}$ (1)(1)

1 mark for $K_{\mathrm{c}}$ / use of any [ ] /inverted/power missing.
(iii) $\quad K_{p}$ stays the same (1)

Equilibrium position moves to the right/yield increases (1) in response to increase in reactants (1)
$K_{\mathrm{p}}=\frac{0.261}{3.70 \times 5.10^{2}}=2.71 \times 10^{-3} \mathbf{( 1 )} \mathrm{MPa}^{-2} \mathbf{( 1 )}$
(iv) calc value $2.7120546 \times 10^{-3}$; answer and/or units ecf from (ii) 2
(c) $\mathrm{CH}_{3} \mathrm{OH}+1.5 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}(\mathbf{1})$ 1
36. (i) completely dissociates/ionised (1) proton donor (1)
(ii) $\mathrm{NO}_{3}{ }^{-}(\mathbf{1}) \quad 1$
37. (i) $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right] /-\log (0.015)(\mathbf{1})=1.82 / 1.8(\mathbf{1})($ Not 2$)$
(ii) $\left[\mathrm{H}^{+}\right]=0.0075 \mathrm{~mol} \mathrm{dm}{ }^{-3}$
$\mathrm{pH}=-\log (0.0075)=2.12 / 2.1(\mathbf{1})$
38. (i) $K_{\mathrm{w}}=\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$ (1)
state symbols not needed
(ii) $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=10^{-\mathrm{pH}}=10^{-13.54}=2.88 / 2.9 \times 10^{-14} \mathrm{~mol} \mathrm{dm}^{-3}$ (1)
$[\mathrm{NaOH}] /\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=\frac{K_{\mathrm{w}}}{\left[\mathrm{H}^{+}(\mathrm{aq})\right]}=\frac{1.0 \times 10^{-14}}{2.88 \times 10^{-14}}$
$=0.347 / 0.35 \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
39. (i) a solution that minimises/resists/opposes pH changes (1)
(ii) The buffer must contain both $\mathrm{CH}_{3} \mathrm{COOH}$ and $\mathrm{CH}_{3} \mathrm{COONa}$ /
$\mathrm{CH}_{3} \mathrm{COO}^{-}$/weak acid and conjugate base(*) (1)
Solution A is a mixture of $\mathrm{CH}_{3} \mathrm{COOH}\left({ }^{*}\right)$ and $\mathrm{CH}_{3} \mathrm{COONa}\left({ }^{*}\right)$ /
/ has an excess of acid /is acidic (1)
Solution B, contains only $\mathrm{CH}_{3} \mathrm{COONa}$ / only $\mathrm{CH}_{3} \mathrm{COO}^{-}$ /only the salt/ is neutral (1)
$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{CH}_{3} \mathrm{COONa}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) /$ acid/alkali has been neutralised/
$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ and NaOH react together (1) 4
40. $\quad\left[\mathrm{H}^{+}\right]$increases (1)
$\mathrm{H}_{2} \mathrm{O}$ ionises more /
for $\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}^{+}+\mathrm{OH}^{-}$, equilibrium moves to the right (1) 2
exo/endo is 'noise'

