ASSESSMENT and QUALIFICATIONS ALLIANCE

Mark scheme June 2003

Advanced Extension Award

Chemistry

6821

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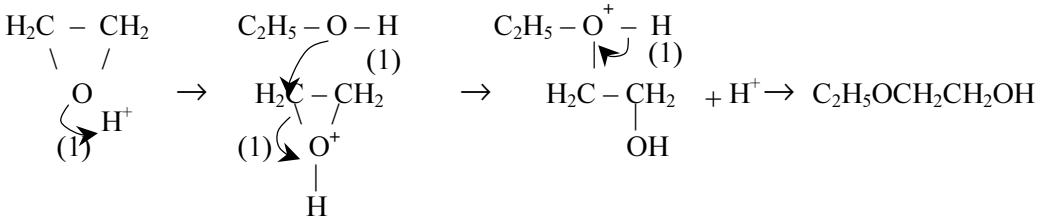
Question 1

(a) Same type of bonds broken and made or C – O and O – H (1)
Same number of bonds broken and made or C – O and O – H (1)
Strained/stressed ring (not stretched)
or repulsion between bonding electron pairs (1)
Less energy required to break bonds or more stable product or ring unstable
or more energy given out when bonds made than used when bonds broken (1)

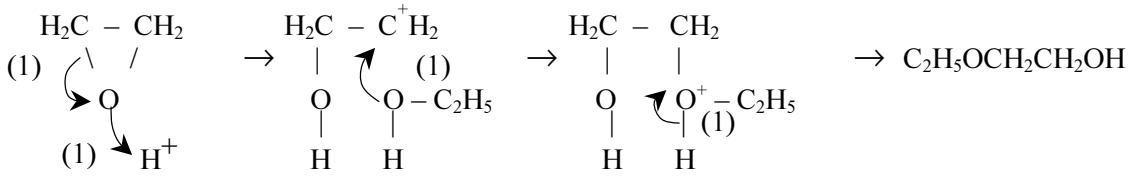
4

(b)



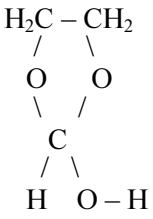
4

Or



NB *Mark four correct arrows*
Allow answers in words
Three marks can be scored if water used rather than ethanol: i.e. lose third mark

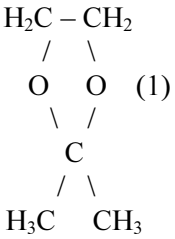
(c)



or $HCOOCH_2CH_2OH$ or $HCOOCH_2CH_2OOCH$

1

(d) Compound **X**



(1)

Products; (2) any two from
$HOCH_2CH_2OH$
$(CH_3)_2CO$ or $(CH_3)_2C(OH)_2$
$HOCH_2CH_2OC(OH)(CH_3)_2$

nmr spectrum: 2 peaks (1)

4

NB *CE = O if **X** is incorrect in part (d)*

(e) Compound **Y** $CH_3(CH_2)_3OMgCl$ (1)

Product: $CH_3(CH_2)_3OH$ or name (*not consequential to an incorrect **Y***) (1)

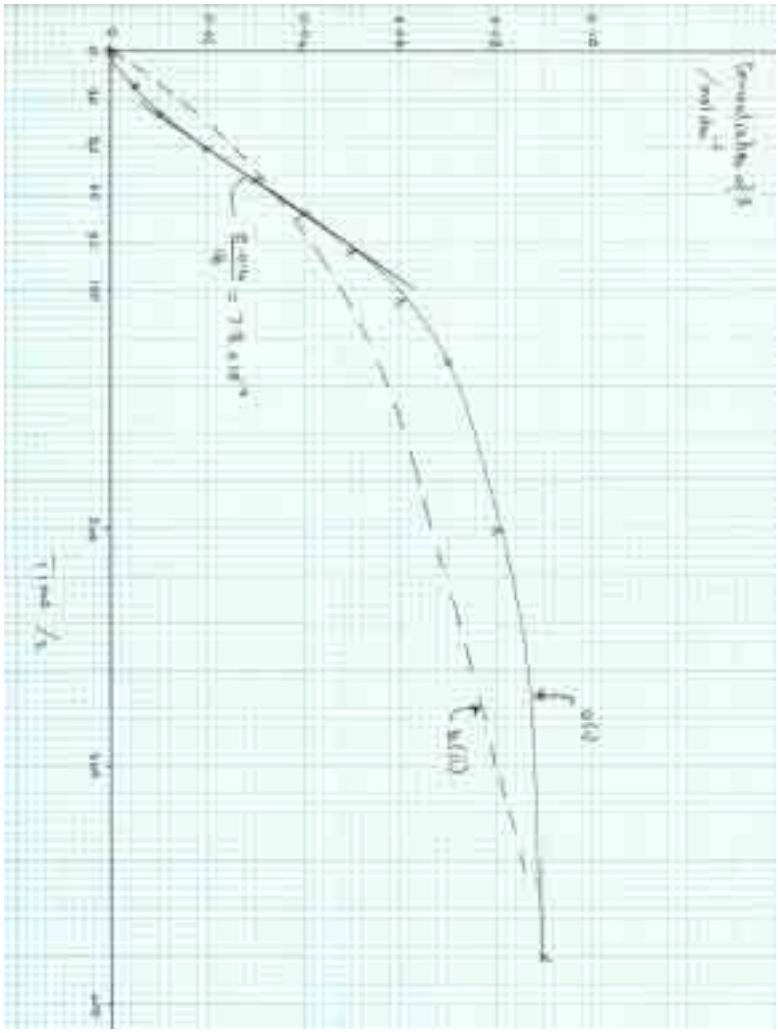
2

Question 2

(a)(i) Graph: axes labelled (and suitable scale) (1)
points plotted correctly (1)
smooth curve through all points (1)

3

NB *CE = 0 if scale non-linear*



Marks to be used on scripts

2(a)(i) Labelled Axes (both) A✓
Point P✓
Curve C✓
(a)(ii) Tangent T✓
(b)(ii) Shape S✓✓✓

Indicate errors with ✘
e.g. (a)(i) A P C
✓ ✓ ✘
(b)(ii) S ✘✓✘

(ii) Initial rate ~ $\frac{0.005}{14}$ (1) = (2.4 to 4.1) 10^{-4} (mol dm^{-3} s^{-1}) (1)

Maximum rate ~ $\frac{0.014}{18}$ = (6.7 to 8.2) 10^{-4} (mol dm^{-3} s^{-1}) (1)

NB *Method can be scored in either rate calculation; check for this on the graph*

Tangent shown on graph (1)
Reaction gets faster *(not slope increases)* or starts slower (1)
Due to autocatalysis or catalysed by a product or by H^+ (1)
Rate slows down again or curve flattens out (1)
As **W** decreases (towards zero) or used up or reactants used up (1)
Maximum rate tangent can be drawn accurately (1)
Initial rate tangent; position after origin uncertain or greater error with smaller range or gradient/rate is changing (1)

10

(b)(i) Order with respect to **W** = 2 (1)

At pH = 3, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3} and
at pH = 2.82, $[H^+] = 1.5 \times 10^{-3}$ mol dm^{-3} (1)

Hence order with respect to $[H^+] = 1$ (1)

Rate = $k[\mathbf{W}]^2 [H^+]$ (*this scores 4 marks*) (1)

$k = \dfrac{8.8\times10^{-5}}{0.04^2\times10^{-3}} = 55$ mol^{-2} dm^6 s^{-1} (1)

5

NB *Value of k not marked consequentially to incorrect orders*
Working does not have to be shown

(ii) Initial rate = $k \times 0.1^2 \times 10^{-2.9} = 6.9 \times 10^{-4}$ (mol dm^{-3} s^{-1}) (1)

NB *Marked consequentially to incorrect k but not to an incorrect rate equation*

Graph: starts steeper (1)
crosses (1)
approaches final [**X**] = 0.10 (1)

Differences: as $[H^+]$ present at the start, initial rate higher (1)
rate does not increase as $[H^+]$ constant or solution buffered (1)
Similarity: graph finishes at same asymptote to [**X**] *(must be stated)* (1)

7

NB *If own incorrect lower initial rate used score max 3 for*
*graph less steep (1); approaches final [**X**] = 0.10 (1) asymptote to [**X**] stated (1)*

(c)(i) $K_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$ (1)

(But $[H^+] \approx [HCO_3^-]$ hence) $[H^+] = \sqrt{K_1[H_2CO_3]}$ *(this scores 2)* (1)

Moles $CO_2 = \dfrac{pV}{RT} = \dfrac{100\times10^3\times0.134\times10^{-3}}{8.31\times298}$ or $\dfrac{0.134}{24.8}$ (1)

$= 0.0054$ mol in 200 cm^3

Hence $[H_2CO_3] = 0.027$ mol dm^{-3} *(mark consequential on moles of CO_2)* (1)

$[H^+] = \sqrt{4.0\times10^{-7}\times0.027} = 1.04 \times 10^{-4}$ (mol dm^{-3}) *(mark consequential)* (1)

pH = 3.9 to 4.1 *(allow consequential to $[H^+]$)* (1)

6

(ii) $\left(K_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]} \text{ hence}\right) \dfrac{[HCO_3^-]}{[H_2CO_3]} = \dfrac{K_1}{[H^+]}$ (1)

$\dfrac{[HCO_3^-]}{[H_2CO_3]} = \dfrac{4.0\times10^{-7}}{10^{-7.4}} = 9.7$ to 10.3 (*this scores 2*) (1)

Hence most CO_2 in blood, existing as H_2CO_3, is converted into HCO_3^- (1)

3

NB *Allow equilibrium displaced to the right or CO_2 (aq) / H_2CO_3 dissociates*

(iii) HCO_3^- must be partially neutralised by NaOH

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad \text{or} \quad \frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{K_2}{[H^+]}$$ (1)

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{4.8\times10^{-11}}{10^{-10}} = 0.48 \quad (\textit{this scores 2})$$ (1)

$HCO_3^- + OH^- \longrightarrow H_2O + CO_3^{2-}$ assume x mol NaOH added (1)

After reaction: $(0.2 - x)$ mol x mol (1)

Hence, $\frac{x}{0.2-x} = 0.48$ and $x = 0.065$ mol (1)

Hence mass NaOH = $0.065 \times 40 = 2.6$ (g) (1)

6

Question 3

(a) (i) **A** = $CuCl_2$ or $[Cu(H_2O)_6]^{2+}\ 2Cl^-$ (1)
B = $[CuCl_4]^{2-}$ (1)
C = $CuCl$ or Cu_2SO_4 (1)
D = $[Cu(NH_3)_2]^+$ (1)
E = $Cu(OH)_2$ or $Cu(OH)_2xH_2O$ where x = 0 to 4 (1)
F = $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (1)
B is tetrahedral stated or sketched *(allow only if **B** correct)* (1)
*(allow names for **A** to **F**)* **7**

(ii) $SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$ (1)
$2Cu^{2+} + 2Cl^- + 2H_2O + SO_2 \longrightarrow SO_4^{2-} + 4H^+ + 2CuCl$ (1)
or $2[CuCl_4]^{2-} + 2H_2O + SO_2 \longrightarrow SO_4^{2-} + 4H^+ + 2CuCl + 6Cl^-$ **2**

(iii) Air oxidises [Cu(I) back to Cu(II)] (1)
Cu^+ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ or full *d* sub-shell/block (1)
Energy required to excite an electron is outside range of (visible) light
or d–d transitions not possible (1)
3

(b)(i) Uses data to deduce that **J** = $HClO_3$ process (1)
formula (1)
(allow process mark for dividing by A_r)

$KClO_3 + H_2SO_4 \longrightarrow KHSO_4 + HClO_3$ (1)
$3HClO_3 \longrightarrow 2ClO_2 + HClO_4 + H_2O$ species (1)
(allow ionic equations) balance (1)
5

(ii) $5Fe^{2+} + ClO_2 + 4H^+ \longrightarrow 5Fe^{3+} + Cl^- + 2H_2O$ species (1)
balance (1)

$5H_2S + 2ClO_2 \longrightarrow 5S + 2H^+ + 2Cl^- + 4H_2O$ species (1)
(allow equations with S_8 etc) balance (1)
4

NB *The 'species' marks may be obtained from the equations below*

$ClO_2 + 4H^+ + 5e^- \longrightarrow Cl^- + 2H_2O$
$Fe^{2+} \longrightarrow Fe^{3+} + e^-$
$H_2S \longrightarrow S + 2H^+ + 2e^-$

(iii) **K** does not contain Cl^- ions (1)
K = $NaClO_2$ (fits 90.5) *(scores 2)* (1)
$Na_2O_2 + 2ClO_2 \longrightarrow 2NaClO_2 + O_2$ (1)
Disproportionation: 1:2 ratio of Cl^-: other Cl species deduced from data (1)
$3NaClO_2 \longrightarrow NaCl + 2NaClO_3$ species (1)
balance (1)
6

(c)(i) Oxide deduced to be BaO_2 (1)

$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$ (1)

$BaSO_4$ insoluble *(allow if state symbol given in an equation)* (1)

Layer of $BaSO_4$ coats solid BaO_2 and protects it (1)

4

(ii) H_2O_2 reduces $KMnO_4$ or MnO_4^- (1)

$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$ (1)

Oxidation state/number oxygen $-1 \rightarrow 0$ or manganese $7 \rightarrow 2$ (1)

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ (1)

$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$ (1)

H_2O_2 oxidises KI or I^- (1)

$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ (1)

Oxidation state/number oxygen $-1 \rightarrow -2$ or iodine $-1 \rightarrow 0$ (1)

$2I^- \longrightarrow I_2 + 2e^-$ (1)

$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$ (1)

Max **9**

Question 4

(a)(i) In CH_3Cl the C δ+ (is subject to nucleophilic attack/substitution) or has an electron deficient C (1)

In C_6H_5Cl, π cloud or electron rich ring (repels nucleophile) or C – Cl bond stronger or extended delocalisation includes Cl (1)

2

(ii)

C	H	Cl
52.2	3.72	44.1
12	1	35.5
4.35	3.72	1.24

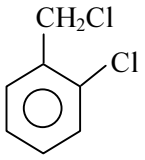
(1)

Hence, 3.50 2.99 1

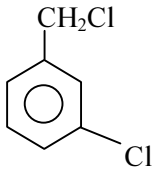
Therefore $C_7H_6Cl_2$ (1)

1.00 g gives 0.892 g AgCl = $\frac{0.892}{143.5} = 6.216 \times 10^{-3}$ mol (1)

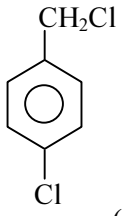
161 g gives 1 mol AgCl or 1 g contains 6.216×10^{-3} mol of chlorine (1)


(1)

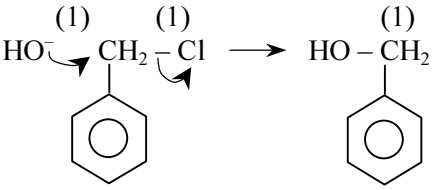
and


(1)

and


(1)

Mechanism:



NB Allow full marks for an S_N1 mechanism

NB Allow max 2 for two correct arrows if an aliphatic compound used

Name: nucleophilic substitution (1)

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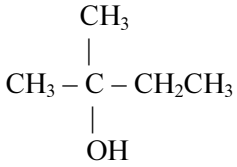
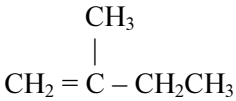
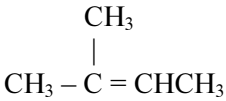
(b)(i) **P** is


(1)

Reaction with hot conc. H_2SO_4 gives


(1)

and

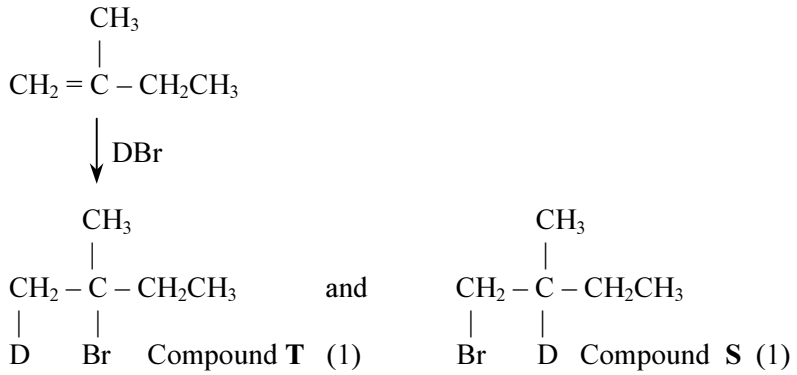

(1)

nmr peak areas 2, 3, 2, 3 ∴ **Q** (1) (or fits data) and 3, 3, 1, 3 or 6, 1, 3 ∴ **R** (1)

*NB If **P** is wrong up to 4 marks can be scored consequentially if TWO correct alkene products given.*

*NB If alcohol **P** incorrect, **Q** can be identified using given nmr data hence the following 9 marks can be scored.*

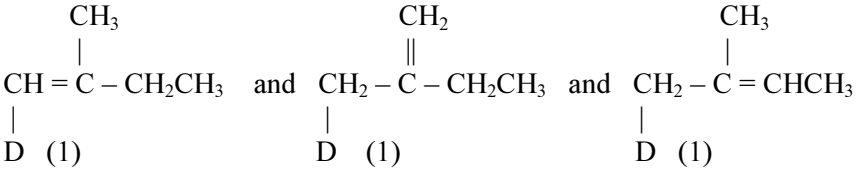
Compound **Q** with DBr



S formed via a primary carbocation hence a minor product
or **T** formed via a tertiary carbocation hence a major product (1)

NB *Penalise 1 if labels of **T** and **S** reversed*
NB *CE if DBr removed from **S**, lose last 6 marks*

Other products formed when **T** reacts with KOH(alc)



nmr peak areas

1, 3, 2, 3 (1) **V** or **W**

2, 2, 2, 3 ∴ **U** (1) or fits data given

2, 3, 1, 3 (1) **V** or **W**

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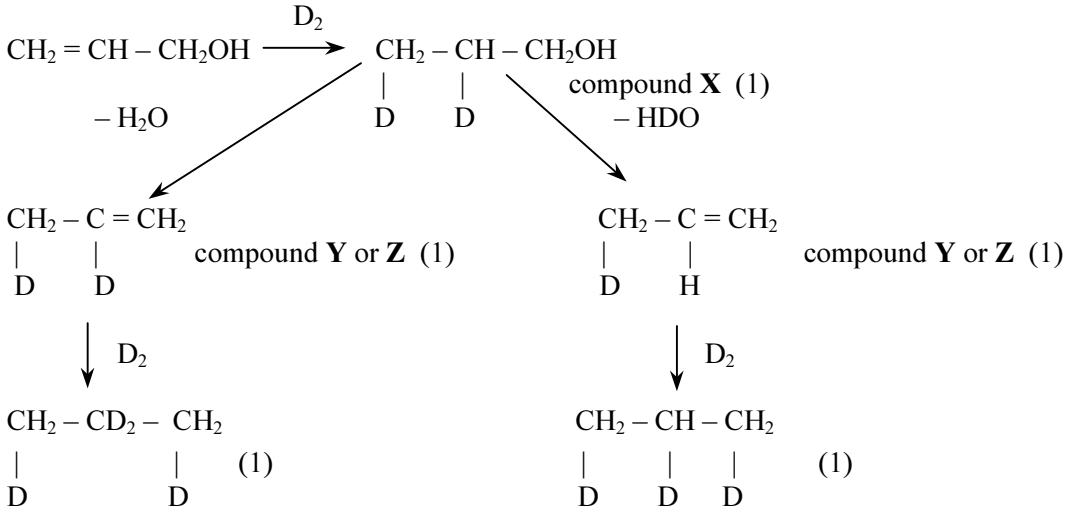
(ii)



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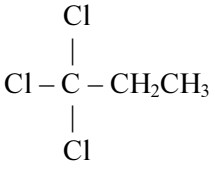
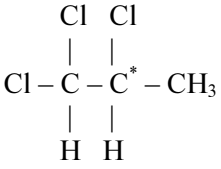
(c) Isomers of $C_3H_5Cl_3$

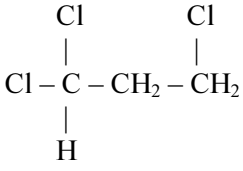


1,1,1-

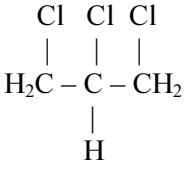


1,1,2-

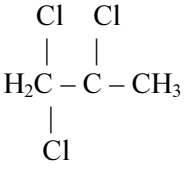
* optical isomer (1)



1,1,3-



1,2,3-



1,2,2-

Marks: three correct (1); four correct (2); five correct (3)

NB *Apply list principle if more than five isomers given* **4**

$C_3H_5Cl_3$: *m/z* values for molecular ion peaks

41 +	35	or 35	or 35	or 37
	35	35	37	37
	35	37	37	37
m/z	146	148	150	152

Marks: four correct *m/z* values (1); four peaks (1) **2**

m/z		Relative abundances	Ratio %	Allow %
146	35 35 35	$\frac{3}{4}\times\frac{3}{4}\times\frac{3}{4}=\frac{27}{4^3}$	27 ~42	27 ~67
148	35 35 37	$\frac{3}{4}\times\frac{3}{4}\times\frac{1}{4}\times 3=\frac{27}{4^3}$	27 ~42	9 ~ 23
150	35 37 37	$\frac{3}{4}\times\frac{1}{4}\times\frac{1}{4}\times 3=\frac{9}{4^3}$	9 ~14	3 ~7.5
152	37 37 37	$\frac{1}{4}\times\frac{1}{4}\times\frac{1}{4}=\frac{1}{4^3}$	1 ~1.6 (2)	1 ~2.5 (1)

2

Question 5 (a)

Period	Bonding	Physical property	Chemical property
Trend	Ionic to covalent **B1**	Melting point high to low **P1**	Reaction with water: solution pH 7 ➔ 0 or more acidic or reaction more violent **C1**
Explanation	Change in ionisation energy or electronegativity **B2**	Electrostatic attraction strong **P2**	Hydrolysis reactions for ionic compounds or dissolve **C2**
Explanation	Atomic radius decreases or nuclear charge increases **B3**	Intermolecular forces weak or van der Waals **P3**	Hydrolysis for covalent compounds **C3**
Example 1: Group 1 or 2	Ionic **B4**	High melting point **P4**	pH ~ 7 **C4**
Example 2: Group 3	Polar covalent **B5**	Sublimes **P5**	pH ~ 3 **C5**
Example 3: Group 4, 5 or 6	Covalent **B6**	Low melting point **P6**	pH ~ 1 **C6**

Group	Bonding	Physical property	Chemical property
Trend	Covalent to ionic **B7**	Low for head element **P7**	Acidic to neutral **C7**
Explanation	Atomic/ionic radius or electronegativity **B8**	Head element has partial covalent bonding **P8**	Hydrolysis for head element **C8**
Explanation	Charge density or polarisability **B9**		
Example	Li/Na or Be/Mg or B or Al/Tl **B10**		

Question 5 (b)

Oxidation states

TE electrons lost from outer *s* sub-shell (1)
electrons then lost from *d* sub-shell (1)
ionisation energies can be achieved or low (1)
ions stabilised by complex formation (1)

Non-TE electrons lost/gained to achieve a noble gas configuration (1)
$\sum$I.E provided by lattice or hydration energy or bond energies (1)
further electron lost from an inner shell (1)
much larger increase in energy required (1)

Allow any six correct statements

Non-transition element illustration:
e.g. nitrogen in N_2O; NO; HNO_2; NO_2; HNO_3
or $Cl_2 + H_2O \longrightarrow HClO + HCl$ (1)

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NB *A minimum of two oxidation states given or two compounds in different oxidation states*

Coloured ions

TE incomplete d sub-shell (1)
d sub-shell energy split (1)
(visible) light energy absorbed (1)
electrons promoted to higher energies (1)
colour seen due to energy not absorbed or reflected (1)

Non-TE electrons in s or p sub-shells (1)
energy to promote electrons outside visible region (1)
large amount of energy needed for electron promotion (1)

Allow any six correct statements

Non-transition element illustration:
e.g. PbO; PbS; PbI_2; NO_2; KI_3 (1)

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Complex ions

TE vacant (d) orbitals (1)
can accept electron pairs from ligands (1)

Non-TE no <u>low energy</u> vacant orbitals or cannot use d orbitals (1)
bonds not formed (1)

Non-transition element illustration:
e.g. SO_4^{2-}; $AlCl_4^-$; BH_4^-; CO_3^{2-}; $[Al(H_2O)_6]^{3+}$ (1)

5

Catalysts

TE	good adsorption properties	(1)
	reactions involved transfer electrons between reactants	(1)
	variable oxidation states of facilitate electron transfer	(1)
Non-TE	poor adsorption properties	(1)
	fixed oxidation states	(1)
	electrons would need to enter higher shell	(1)
	not energetically advantageous	(1)

Allow any five correct statements

Non-transition element illustration:

e.g. $AlCl_3$; BCl_3 in Friedel–Craft reactions (1)

6

NB *A reaction with the catalyst must be given*
Do not allow just an enzyme