AQA

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QUALIFICATIONS
ALLIANCE

General Certificate of Education

Chemistry 6821

AEA   Advanced Extension Award

Mark Scheme

2008 examination - June series

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Question 1

(a) Hydrogen bonds/attraction between the <u>lone pair</u> on the nitrogen and the $H^{(\delta+)}$ of water   (1) **1**

(b) $C_5H_5N + H_2O \rightleftharpoons C_5H_5N^+H + OH^-$ *penalise $C_5H_6N^+$ here only*
                                                           allow $C_5H_5NH^+$ (1)

$C_5H_5N^+H + H_2O \rightleftharpoons C_5H_5N + H_3O^+$ (1)

$$K_a = \frac{[C_5H_5N][H_3O^+]}{[C_5H_5N^+H]}$$

(1) **3**

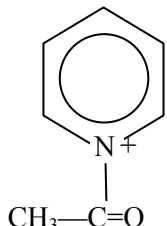*Allow $[H^+]$*   *[NOT conseq on error in M2]*

(c) N (atom) forms a bond with each of two carbon (atoms)   **M1**

Delocalised bond/e^- cloud/π cloud/π bond/ delocalised electrons (using unpaired electron)   **M2**

1 electron from N and 1 from each of 5 C   **M3**

Lone pair is available to accept a proton/H^+ / to be donated $\therefore$ Lewis base   **M4**

*[if lone pair incorporated into ring, lose **M2 and M3**]*

(d)(i)

must have charge

(1)

(d)(ii) $C_5H_5N^+COCH_3 + C_2H_5OH \rightarrow CH_3COOC_2H_5 + C_5H_5N^+H$ (1)
treat missing '+' as repeat error   *allow $C_5H_5N + H^+ / C_5H_5NH^+ / C_5H_6N^+$*   **2**

Total 10

Question 2

General Sig Fig rule: minimum 3 s.f. – no max – penalise once per QUESTION

(a)(i)   Rate = $\underline{k \times [C_3H_6]}$ *accept [cyclopropane] / [(CH₂)₃] / [CH₂CH₂CH₂]*   (1)

   $= 6.71 \times 10^{-4} \times 0.5 = \underline{3.36 \times 10^{-4}}$ mol dm^{-3} s^{-1} (1)   **2**

(a)(ii) $6.71 \times 10^{-4}/3.14 \times 10^{-33} = \underline{2.14 \times 10^{29}}$ (1)

   At higher temperatures <u>many more</u> molecules have energy > activation energy   (1)   **2**

(a)(iii) $\log\dfrac{(3.14 \times 10^{-33})}{(6.71 \times 10^{-4})} = - \dfrac{E_a}{2.30 \times 8.31} \times \left(\dfrac{1}{298} - \dfrac{1}{773} \right)$ (1)

   $(3 \times 8.31 \times 773)/2 = \underline{9.64}$ (kJ mol^{-1}) (allow ans in J mol^{-1})   *ignore incorrect units*   (1)

   $E_a = \underline{272}$ (kJ mol^{-1}) (allow ans in J mol^{-1})   *Not conseq*   *ignore incorrect units*   (1)

   Activation energy is <u>much</u> greater than mean energy   (1)
                    qualified 'greater' / high numerical ratio – e.g. 30 times
    NOT conseq on error in mean or E_a value

   Some molecules do have $E \geq E_a$ *conseq on error in mean / E_a values*   (1)

   Then collisions will allow more molecules to gain the <u>required</u>/<u>sufficient</u> energy   (1)   **6**

(a)(iv)   Using enthalpy formation values:

   $\Delta H = \Delta H$(propene) - ΔH(cyclopropane)
   $= 20.4 – 53.3 = \underline{-32.9}$ (kJ mol^{-1})   (1)

   Using bond enthalpy values:

   ΔH = bonds broken – bonds formed

   $= 2 \times 345 – 612 = \underline{+ 78}$ (kJ mol^{-1})   (1)

   -32.9 / ΔH_f likely to be more reliable/closer to true value   (1)

   (ΔH_f is specific to individual compounds) bond enthalpies are average value, therefore less accurate/not specific   (1)

   Strain in the ring / high bond pair – bond pair repulsion / small bond angle in ring   (1)   **5**

(b)(i)   Mass dissolved = $1.69 \times 0.03/100 = 5 \times 10^{-4}$ g   **0r** n(CO₂) = 1.69/44 = 0.0384 (mol)   (1)
   Moles = $5 \times 10^{-4}/44 = 1.15 \times 10^{-5}$ Moles = $0.0384 \times 0.03/100 = 1.15 \times 10^{-5}$ (1)   **2**

(b)(ii) $K_a = [H^+]^2/[H_2CO_3]$ / $[H^+] = \sqrt{K_a[H_2CO_3]}$ / correct substitution (1)

$[H^+] = \sqrt{(4.17 \times 10^{-7} \times 1.15 \times 10^{-5})} = 2.19 \times 10^{-6}$ *Conseq on moles in (i)* (1)

pH = 5.66   *Conseq on [H⁺]   minimum 2 decimal places* (1)

Assumes that $[H_2CO_3]$ remains unchanged (because is a weak acid) / $[H^+] = [HCO_3^-]$ (1) **4**
    requires explanation in words

(b)(iii)

$K_a = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$ / correctly substituted expression (1) **M1**

$K_a = \dfrac{(1.00 \times 10^{-6}) \times (1.00 \times 10^{-5} + 2x)}{(2.5 \times 10^{-4} - 2x)}$ $\Big|$ $K_a = \dfrac{(1.00 \times 10^{-6}) \times (1.00 \times 10^{-5} + x)}{(2.5 \times 10^{-4} - x)}$ (1) **M2**

But in 1.0 dm³ initial moles of HCO_3^- = original $[H^+] = 1.00 \times 10^{-5}$ / 1.0425×10^{-5} (1) **M3**

$0.417 = \dfrac{(1.00 \times 10^{-5} + 2x)}{(2.5 \times 10^{-4} - 2x)}$ $\Big|$ $0.417 = \dfrac{(1.00 \times 10^{-5} + x)}{(2.5 \times 10^{-4} - x)}$

$2.834x = 9.42 (2.5 \times 10^{-4} - 2x) 10^{-5}$ $\Big|$ $2.834x = 9.42 (2.5 \times 10^{-4} - x) 10^{-5}$ (1) **M4**

x = 3.33×10^{-5} / 3.31×10^{-5} $\Big|$ x = 6.62/2 = 3.33×10^{-5} / 6.66/2 = 3.31×10^{-5} (1) **M5**

Mass = moles × 56(.1) so mass = 1.86×10^{-3} / 1.83×10^{-3}g   *conseq on moles in (5)* (1) **M6 6**

Error in (iii) – candidates uses original [H₂CO₃] rather than [H₂CO₃ – (2)x]

$K_a = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$ / $[HCO_3^-] = \dfrac{K_a [H_2CO_3]}{[H^+]}$ (= (2)x) / correctly substituted expression (1) **M1**

$[HCO_3^-] = \dfrac{4.17 \times 10^{-7} (2.5 \times 10^{-4})}{1.00 \times 10^{-6}}$ = 1.0425×10^{-4} mol dm⁻³ **(0) M2**
    missing –(2)x loses M2 & M4

But in 1.0 dm³ initial moles of HCO_3^- = original $[H^+] = 1.00 \times 10^{-5}$ / 1.0425×10^{-5} (1) **M3**

Extra moles HCO_3^- (due to added CaO) = $1.0425 \times 10^{-4} - 1.00 \times 10^{-5} = 9.43 \times 10^{-5}$ mol **(0) M4**

2 mol HCO_3^- are produced by 1 mol of CaO so moles of CaO = 3.18×10^{-5} (1) **M5**
i.e. moles HCO₃⁻ ÷ 2   *conseq on moles in (4)*

Mass = moles × 56(.1)   so mass = 2.64 × 10-3 g   *conseq on moles in (5)* (1) **M6 6**

(b)(iii) **Additional allowed answer**

$K_a = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$ / $[HCO_3^-] = \dfrac{K_a\,[H_2CO_3]}{[H^+]}$ $(= x)$ / correctly substituted expression   (1) **M1**

$x = \dfrac{4.17 \times 10^{-7}\,(2.5 \times 10^{-4} - x)}{1.00 \times 10^{-6}}$ $x = 7.35 \times 10^{-5}\ mol\ dm^{-3}$ (1) **M2**

But in 1.0 dm^3 initial moles of HCO$_3^-$ = original [H$^+$] = 1.00×10^{-5} / 1.0425×10^{-5} (1) **M3**

Extra moles HCO$_3^-$ (due to added CaO) = 6.35×10^{-5} mol   (1) **M4**

2 mol HCO$_3^-$ are produced by 1 mol of CaO so moles of CaO = 3.18×10^{-5} (1) **M5**

i.e. moles HCO$_3^-$ ÷ 2   conseq on 'extra' moles in (4)
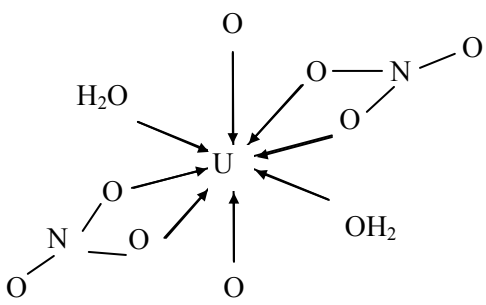
Mass = moles × 56(.1)   so mass = 1.78×10^{-3} g   *conseq on moles in (5)*   (1) **M6**   **6**

(b)(iv) Raising T will cause less CO$_2$ to dissolve because process is exothermic/gases less soluble at higher temperatures   (1)

Increasing <u>partial pressure/percentage</u> CO$_2$ will cause more CO$_2$ to dissolve   (1)

Raising T causes pH rise **and** increasing partial pressure/% causes pH fall   (1)   **3**
        only award if correct directions in amount of CO$_2$ dissolved in M1 and M2

Question 3

(a)(i) Only minute/small amounts of ^{234}U and ^{235}U isotopes present **or** mostly/significantly more ^{238}U (1) **1**

(a)(ii) No difference in chemistry (1)

as chemistry determined by electron arrangement which is <u>same</u> for all isotopes (1) **2**

(b)(i) $[Al(H_2O)_6]^{3+} + H_2O \; \rightleftharpoons \; [Al(H_2O)_5(OH)]^{2+} + H_3O^+$ (1) **1**

(b)(ii) $U^{3+}(aq) < Al^{3+}(aq)$ / $U^{3+}(aq)$ less acidic as U^{3+} (much) larger/has lower charge density (1)

So less polarisation of water molecule/O-H bond / less weakening of O-H bond (1)

U^{4+} has higher charge/smaller radius/higher charge density than U^{3+}, (so polarises water molecules more strongly)   *NOT $[U(H_2O)_6]^{4+}$* (1) **3**

(c)(i)

8 coordinate bonds = arrow heads (1)

Correct NO_3 attachment (1)

Rest correct (1)

(c)(ii) Bond angles 180 °, 90° **and** 60° shown on diagram *(values not required)*
All three correct (2)   any two correct (1)   *Not 2×equatorial angles* (2) **5**

(d)(i) $UCl_5 + 2H_2O \; \rightarrow \; UO_2^+ + 5Cl^- + 4H^+$ **or** $+ Cl^- + 4HCl$ (1) **1**

(d)(ii) $UO_2^+ + 4H^+ + e^- \rightarrow U^{4+} + 2H_2O$ (1)

$UO_2^+ \rightarrow UO_2^{2+} + e^-$ (1)

$2UO_2^+ + 4H^+ \rightarrow UO_2^{2+} + U^{4+} + 2H_2O$ *Not conseq* (1)

UO_2^+, OS +5, forms U^{4+}, OS +4, which is reduction   **and**
UO_2^+, OS +5, forms UO_2^{2+}, OS +6, which is oxidation (1) **4**

(e)(i) $3U^{4+} + 2AuCl_4^- + 6H_2O \rightarrow 2Au + 3UO_2^{2+} + 12H^+ + 8Cl^-$ species (1)
                                        $+ 8HCl + 4H^+$ balance (1) **2**
allow HCl with H^+ missing on right hand side for species

(e)(ii) So different amount of U^{4+} formed (1)

Hence different amount of Au deposited (1)   **2**

(f)(i) Moles $UO(C_2O_4).6H_2O = 1.30 \times 10\text{-}3$ mol (1)

Moles water lost $= 2.61 \times 10\text{-}3$ mol / via M_r calculation (1)

Mole ratio $\approx 2:1$ so 2 moles water lost   so formula $= UO(C_2O_4).4H_2O$ (1)   **3**

(f)(ii) N.B There was an error in the concentration of the potassium manganate(VII) solution given on the paper (0.500 instead of 0.0500 mol dm^{-3}). The following methods for (f)(ii) are based on this error. For the first method answers have been included for 0.0500 mol dm^{-3} in bold.

Moles $UO(C_2O_4).6H_2O$ = moles $C_2O_4^{2-} = \underline{6.67 \times 10^{-4}}$ mol (1) **M1**

Moles $MnO_4^- = \underline{5.35 \times 10^{-3}}$ mol   **[5.35 x 10^{-4} mol]** (1) **M2**

Moles MnO_4^- reacting with $C_2O_4^{2-} = 2.67 \times 10^{-4}$ mol   *conseq on M1* (1) **M3**

Moles MnO_4^- reacting with U $= 5.08 \times 10^{-3}$ mol   *conseq on M2 & M3*   **[2.68 x 10^{-4} mol]** (1) **M4**

Mole ratio U : $MnO_4^- = 6.67 \times 10^{-4}$: 5.08×10^{-3} = 1:8 / 1:7.66   **[2.48: 1]** (1) **M5**

Number of e$^-$ lost by one U $= 5 \times 8 = 40$e$^-$ / $5 \times 7.66 = 38$e$^-$

(1) **M6** **6**

[5÷2.48 = 2e$^-$ ∴ U(IV) oxidised to U(VI)]

Or, using moles of electrons method

Moles $UO(C_2O_4).6H_2O$ = moles $C_2O_4^{2-} = \underline{6.67 \times 10^{-4}}$ mol (1) **M1**

Moles $MnO_4^- = \underline{5.35 \times 10^{-3}}$ mol (1) **M2**

Moles electrons removed by $MnO_4^- = 5.35 \times 10^{-3} \times 5 = 0.02675$ *conseq on M2* (1) **M3**

Moles e$^-$ removed from one $UO(C_2O_4).6H_2O$ $= \dfrac{0.02675}{6.67 \times 10^{-4}} = 40.1$ *conseq on M1 & M3*	Moles e$^-$ removed from one $C_2O_4^{2-}$ $= 6.67 \times 10^{-4} \times 2 = 1.34 \times 10^{-3}$ *conseq on M1*	(1) **M4**
Electrons removed from one $C_2O_4^{2-}$ = 2	Moles e$^-$ removed from one U $= 0.02675 - 1.34 \times 10^{-3} = 0.0254$	(1) **M5**
Number of e$^-$ lost by one U $= 40.1 - 2 = 38(.1)$ *conseq on M4*	Number e$^-$ lost by one U $= \dfrac{0.0254}{6.67 \times 10^{-4}} = 38(.1)$ *conseq on M1 & M5*	(1) **M6** **6**

Question 4

Penalise a bond which is <u>clearly</u> drawn to the wrong atom once only

(a) $C_6H_5COOCH_3 + 4[H] \rightarrow C_6H_5CH_2OH + CH_3OH$ (1)

$CH_3CONHCH_3 + 4[H] \rightarrow CH_3CH_2NHCH_3 + H_2O$ *allow $C_2H_5NHCH_3$*   (1)   **2**

(b)(i)   alkenes <u>and</u> aromatic rings are electron rich (centres)/high electron density   (1)

Carbonyl groups have δ+ carbon   (1)

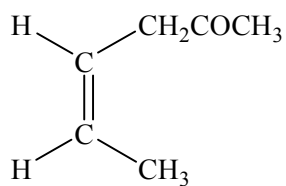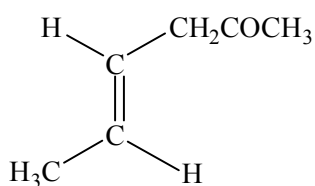hydride ions are nucleophiles/have lone pair/are repelled by electron   (1)   **3**

(b)(ii)
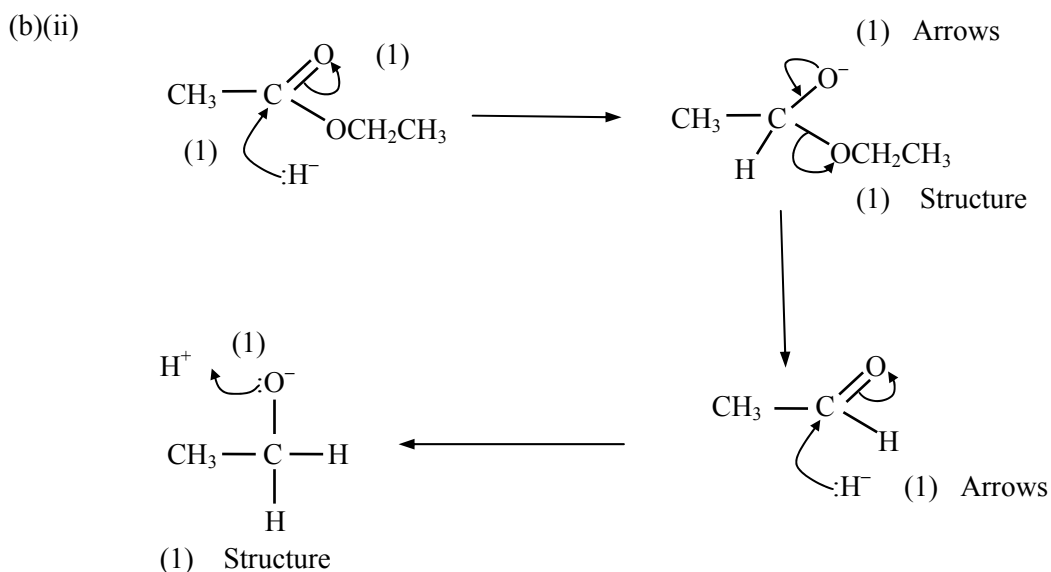
Lone pairs not required in mechanism   *[Not arrows from '-' charges]*   **7**

(c) $LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$ (1)
A <u>large</u> volume of explosive/flammable gas is formed   (1)   **2**
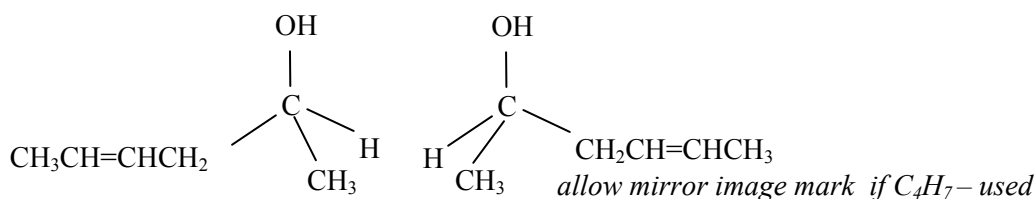
(d)(i)   structure of hex-4-en-2-one   *<u>linear</u> structure earns **M1** only*

incorrect structure = 0 for both marks

2

structure with double bond   (1)   *geometrical isomer*   (1)

(d)(ii)   structure of hex-4-en-2-ol   *if error in C=C position in (d)(i), allow repeated error here*

CH$_3$CH=CHCH$_2$ H   H   CH$_2$CH=CHCH$_3$
                    CH$_3$ CH$_3$ *allow mirror image mark if C$_4$H$_7$– used*

Structure with clear chiral carbon (1)   *Mirror image* (1)   *ignore errors in dots/wedge*

(C of) carbonyl group is (trigonal) <u>planar</u> (may be clarified by a diagram)   (1)

Attack (on C atom) <u>equally likely</u> from either side of the group (may be clarified by a diagram)   (1)   **4**
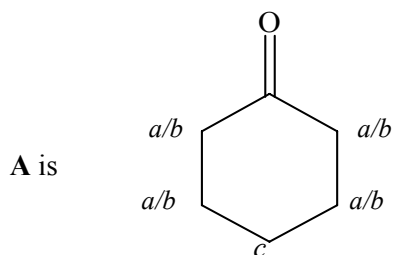
(e)   **C** has a C=C double bond since reacts with bromine /   (1)
or from absorption <u>at</u> 1650 cm^{-1} in the infra-red

A <u>and</u> **B** have a C=O from absorptions <u>at</u> 1720 <u>and</u> 1780 cm^{-1} in the ir   (1)

C has an OH(<u>alcohol</u>) from absorption <u>over range</u> 3250-3550 cm^{-1} in the ir   (1)
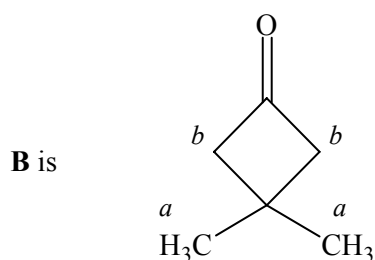
C must be tertiary alcohol since cannot be oxidised by acidified potassium dichromate(VI)   (1)
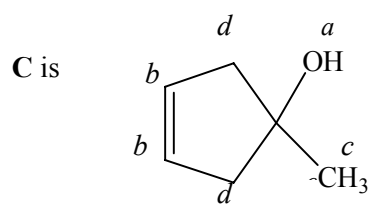
A is

structure   (1)

a:b:c = 4:4:2   (1)
upper <u>pair</u> must be one of the 4's, ditto lower <u>pair</u>

B is

structure   (1)

a:b = 6:4   (1)

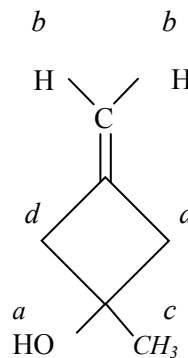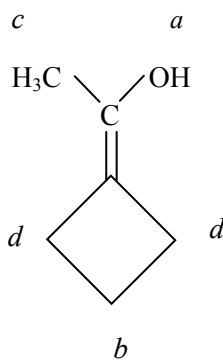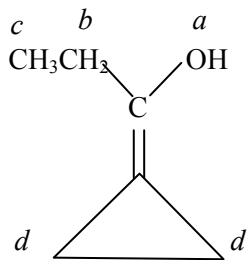**C** is

structure   (1)

a:b:c:d = 1:2:3:4   (1)

10

allow the following alternative structures for C

Question 5

(a)

T1 (both reactions are exothermic $\therefore$) K_p / K_c decreases with increase in temp. (1)

T2 low temperature needed for good yield (1)

T3 10% conversion suggests that a temperature lower than 250 ^{o}C should be used (1)
accept 'the yield mentioned in the question' in place of 10% conversion

T4 but faster rate (of production) at an elevated temperature (1)

T5   250 ^{o}C provides compromise between rate and yield (1) **5**
250 ^{o}C must be mentioned either in T3 or in T5

P1 K_p / K_c does not change with a change in pressure (1)

P2 both reactions have fewer gas moles on rhs of equation   allow 'both' from T1 (1)

P3 ($\therefore$) use of a high pressure needed for a good yield (1)

P4 10% conversion suggests that a higher pressure higher than 70 atm should be used (1)

P5 qualified high costs of high pressure plants – *e.g. high build/energy etc. costs* (1)

P6 70 atm. compromise between yield and costs   *70 atm. must be mentioned either in P4 or in P6* (1)

P7 an increase in pressure has no effect on the rate of production/reasoned statement that pressure increases rate of reaction – *e.g. molecules closer together etc.* (1) **7**

C1 catalysts provide an alternative route of lower activation energy (1)

C2 more collisions/molecules will have E ≥ E$_{cat}$ (than E ≥ E$_{uncat}$)   *E$_{cat}$ may be implied from '$\therefore$ more..'* (1)

C3 more collisions successful in unit time/higher proportion of collisions are successful with catalyst (1)
not just 'more collisions are successful'

C4 ($\therefore$) rate (of production) faster in presence of a catalyst (1)

C5 allows operating temperature to be lower (1)

C6 rate of forward and reverse reactions increased equally   *allow 'speed' in place of 'rate' here* (1)

C7 K_p unchanged – no effect on yield (1) **7**

R1 heterogeneous - to provide surface for adsorption/chemisorption to occur (1)

R2 holding reactant molecules closely together/ weakened bonds / intermediate formed with reactant molecule(s) (1)

R3 copper-based - transition metal and can change oxidation state (during intermediate formation and breakdown to give products) (1) **3**
ignore 'd' orbital arguments

17 max

Q   correct use of technical language in at least two sections   (1)

W   written in sentences and all four sections attempted   (1)

C   answers presented in a logical form in not less than three sections   (1)   **3**

Total 20

(b)

M1 sulphur, chlorine and silicon all have covalent bonds (1)

M2 sulphur and chlorine both small molecules / simple molecular / *allow S_4-S_8 and Cl_2* (1)

M3 (weak) intermolecular forces/van der Waals' etc. <u>broken</u>/<u>overcome</u> on melting (1)

M4 magnitude of van der Waals' / induce dipole- dipole attractions increase with number of electrons /size/ surface area *(accept M_r)* (1)

M5 S_8 /sulphur molecule has more electrons/is bigger/has more surface area than Cl_2/chlorine molecule (1)
accept converse argument

If covalent bonds are broken 0 for M3, M4 and M5

M6 silicon has giant covalent / macromolecular structure (1)

M7 strong/many covalent bonds must be broken ∴ a <u>lot of energy needed</u> (1) **7**

L1 the charge on Mg^{2+} = charge on Be^{2+} > charge on Na^+ *need all 3 with charge numbers* (1)

L2 the radius of Mg^{2+} < radius of Na^+ but > radius of Be^{2+} *need all 3 with charge numbers* (1)
if error in charge numbers in L1, allow refs to metal ions here

L3 ∴ attraction of O^{2-} / oxide ion for Be^{2+} > Mg^{2+} > Na^+ *need all 3 with charge numbers* (1)

L4 the stronger the attraction between anion and cation, the greater the value of LE/description of LE (1)

L5 Be^{2+} is very small / has a large (surface) charge density (1)

L6 ∴O^{2-} ion polarised leading to partial covalent character in BeO (1)

L7 MgO more ionic in character/ much less polarisation of O^{2-} ion (1) **7**
separate statements needed for L6 and L7, NOT just a comparison

A1 Na_2O is ionic/contains O^{2-} ion (1)

A2 O^{2-} reacts with water forming OH^- ions/ionic equation (1)

A3 Al_2O_3 is ionic with large degree of covalent character (1)

A4 Reacts with <u>both</u> acids and bases/can act as <u>both</u> acid <u>and</u> base/equations (1)

A5 SO_2 is covalent molecule (1)

A6 reacts with water forming H_2SO_3 / equation = $SO_2 + H_2O \rightarrow 2HSO_3$ **PLUS**
which (partially) dissociates to form H^+ ions / equations = *ignore 'fully dissociates'* (1)
$H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$ / $H_2SO_3 \rightleftharpoons H^+ + HSO_4^-$ *allow '$\rightarrow$' arrow in place of '$\rightleftharpoons$'*

A7 Trend - Na_2O basic; Al_2O_3 amphoteric; SO_2 acidic (1)

A8 Metals form basic, non-metals form acidic, oxides *accept 'less metallic, more acidic' trend* (1) **8**

17 max

Q   correct use of technical language in at least two sections   (1)

W   written in sentences and all four sections attempted   (1)

C   answers presented in a logical form in not less than three sections   (1)   **3**

Total 20