CAMBRIDGE INTERNATIONAL EXAMINATIONS GCE Advanced Level

MARK SCHEME for the May/June 2014 series

9701 CHEMISTRY

9701/41

Paper 4 (Structured Questions), maximum raw mark 100

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Section A

1 (a) (i) m. pt. is high(er)/large(r)/greater (for iron) [1] density is high(er)/large(r)/greater (for iron) [1] (ii) (higher m. pt. due to) strong attraction between cations and electrons or more delocalised electrons [1] (higher density due to) greater A_r and smaller radius [1] (b) (i) components to be added: voltmeter or V [1] salt bridge [must be labelled] [1] (ii) M1: A and B copper (metal) or Cu and iron (metal) or Fe [1] either C or D as 1 mol dm⁻³/1 M M2: Cu²⁺ or CuSO₄ or CuCl₂ or Cu (NO₃)₂ etc. and C and D М3 Fe²⁺ or FeSO₄ etc. [1] (iii) $E_{cell}^{\theta} = 0.34 + 0.44 = 0.78$ (V) [1] (iv) if C is Fe^{2+} ; (as [C] increases), the E of the Fe^{2+} /Fe increases/becomes more positive/ less negative so the overall cell potential/ E_{cell} would decrease/become less positive/more negative [1] or if C is Cu²⁺; (as [C] increases), the E of the Cu²⁺/Cu increases/becomes more positive/less negative [1] so the overall cell potential/E_{cell} would increase/become more positive/less negative [1] (c) (i) (colour change is) colourless to pink/pale purple or (end point is the first) permanent (pale) pink/pale purple colour [1] (ii) $\{n(MnO_4^-) = 0.02 \times 18.1/1000 = 3.62 \times 10^{-4} \text{ mol}\}$ $n(Fe^{2+}) = 5 \times n(MnO_4^-) = 1.81 \times 10^{-3} \text{ mol}$ [1]

mass of Fe =
$$55.8 \times 1.81 \times 10^{-3} = 0.101 \text{ g} (M2 \times 55.8) \text{ ecf}$$
 [1]

$$M_{\rm r}$$
 = mass/moles = 0.500/1.81 × 10⁻³ = **276.2** ecf [1]

[Total: 16]

2 (a) (i) A *complex* is a compound/molecule/species/ion formed by a central metal atom/ion surrounded by/bonded to one or more ligands/groups/molecules/anions [1]

A *ligand* is a species that contains a **lone pair** of electrons that forms a **dative bond** to a metal atom/ion/or a lone pair donor to metal atom/ion [1]

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(ii) $\begin{bmatrix}
H_2O \\
H_2OM_{M_1,...} \\
H_2O
\end{bmatrix}$ and $\begin{bmatrix}
CI \\
CI \\
CI
\end{bmatrix}$ $CI \\
CI$ CI C

correct 3D structures: [1] + [1] octahedral and tetrahedral [1]

both structures [1] geometric or cis-trans [1]

(b) (i)
$$Cu(II)$$
 is [Ar] $3d^9$ [1] $Cu(I)$ is [Ar] $3d^{10}$ [1]

(ii) Cu(II): d orbitals/subshell are split (in ligand field) and
electron moves from lower to upper orbital or an electron is promoted/excited
in doing so it absorbs a photon/light [2]

Cu(I): no gap in upper orbital/all orbitals are full [1]

(c) (i)
$$\Delta H^{e} = +2 \times 33.2 - 157.3 + 302.9 = (+) 212 \text{ kJ mol}^{-1} \text{ ecf}$$
 [2]

(ii)
$$\Delta H^{\text{e}} = -168.6 + 2 \times 157.3 = (+)146 \text{ kJ mol}^{-1}$$
 allow ecf from (c)(i) [1] high T/temperature since ΔH is positive/endothermic [1]

[Total: 16]

3 (a) heat in dilute
$$HCl(aq)$$
 (or $H_2SO_4(aq)$) [1]

(b) (i) four isomers [1]

[1]

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(ii) must be skeletal

(iii) CO_2H $+ CO_2 \text{ or } HO_2C-CO_2H$ [1]

(c) (i)
$$K_{w} = [H^{+}][OH^{-}]$$
 [1]

- (ii) In $0.15 \,\text{mol dm}^{-3} \,\text{NaOH}$, $[OH^{-}] = 0.15 \,\text{mol dm}^{-3}$ $[H^{+}] = K_{\text{w}}/[OH^{-}]$, so $[H^{+}] = 1 \times 10^{-14}/0.15 = 6.67 \times 10^{-14} \,\text{mol dm}^{-3}$ [1] $pH = -\log_{10}[H^{+}] = 13.18 \,(13.2) \,\text{ecf from } [H^{+}]$ [1]
- (iii) piperidine is a poorer proton acceptor or piperidine is partially ionised [1]
- (iv) piperidine should be a **stronger base/more basic** than ammonia because of the electron-donating (alkyl/CH₂) groups [1]

(d) (i)
$$n(HCl)$$
 at start = $0.1 \times 20/1000 = 2.0 \times 10^{-3} \text{ mol}$
 $n(HCl)$ at finish = $2 \times 10^{-3} - 1.5 \times 10^{-3} = 0.0005/5 \times 10^{-4} \text{ mol}$ [1]

- (ii) this is in 30 cm³ of solution, so [HC] at finish = $0.5 \times 10^{-3}/0.030 = 1.67 \times 10^{-2} \text{ mol dm}^{-3}$ pH = $-\log_{10}(1.67 \times 10^{-2}) = 1.78$ ecf from (d)(i) [1]
- (iii) pH/vol curve: start at pH 11.9 [1] vertical portion at V = 15 cm³ [1] levels off at pH 1.8
- (iv) indicator is B [1]

[Total: 16]

4 (a) three from phenol (secondary) alcohol (primary) amine arene/aryl/benzene

 $3 \times [1]$

[1]

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(b) (i)

step 1: HCN + NaCN or HCN + base [1]

step 2:
$$H_2$$
 + Ni or LiA l H $_4$ or Na + ethanol [1]

(ii) bromine decolourises *or* goes from orange to colourless *or* white ppt. formed [1]

e.g.

HO
CHO
2 or 3 bromines in ring
Br

[1]

(c)

(i)
$$NaO$$
 NH_2 NaO NaO

(ii)
$$\stackrel{\text{HO}}{\underset{\text{HO}}{\bigvee}} \stackrel{\text{OH}}{\underset{\text{NH}_3}{\bigvee}}$$
 (or ionic) [1]

 M1: amide
 [1]

 M2: alcoholic ester
 [1]

 M3: both phenolic esters
 [1]

 [5] max [4]

(d) amide [1] ester

[Total: 14]

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- **5** (a) (i) –OH *or* hydroxyl groups (allow alcohol groups) [1]
 - (ii) alkenes or C=C (double) bonds or carbon double bonds [1]
 - (iii) CH₃CH(OH) or CH₃CO- groups [1]
 - (b) V is $CH_3CH(OH)CH=CH_2$ [1]

(c) compound V shows optical isomerism

(ecf for 'geometric(al)' if candidate's V is capable of cis-trans) [1]

[Total: 8]

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6 (a)

feature	level of bonding
formation of α-helix	secondary
formation of disulfide bonds	tertiary
formation of ionic bonds	tertiary
linking amino acids	primary

[3]

(b)

ir	1
block letter	name
J	Deoxyribose
K	Cytosine
L	Phosphate
М	Thymine

4 × [1]

(c) (i) H/hydrogen (bonds between bases)

[1]

(ii) Bonds are weak **and** so require relatively little energy to break/are easily broken

[1]

(d)

	(sugar, J)	(base, M)
DNA	deoxyribose	thymine/T
RNA	ribose	uracil/U

[1]

[Total: 10]

7 (a) Expression:
$$n = \frac{100 \times 2.5}{1.1 \times 74}$$
 or equivalent [1]

n = 3.1 hence **G** has three carbon atoms [1]

(b) (i) $(\delta 1.1)$ RCH₃ or RCH₂R or methyl or CH₃

(δ 2.2) (R)CH₂CO(R) or CH₃CO(R)

(δ 11.8) (R)COOH or (R)CONH(R)

 $3 \times [1]$

[1]

[1]

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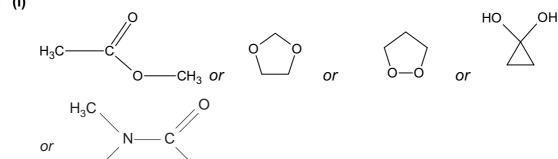
(ii) The (–OH) peak at δ 11.8 (disappears) [1]

because of (O)H-D exchange *or* equation showing this (e.g. R-OH + $D_2O \rightleftharpoons R$ -OD + HOD)

(iii) $CH_3CH_2CO_2H$ [1]

(c) (i)

H₂C



(ii) If methyl ethanoate: δ 2.0–2.1

δ 3.3–4.0

Or if 1, 3-dioxolane: δ 3.3–4.0 [1]

δ 3.3–5.0

Or if 1, 2-dioxolane: δ 0.9–1.4 [1] δ 3.3–4.0

Or if dihydroxycyclopropane: δ 0.9–1.4 [1]

δ 0.5–6.0

[Total: 11]

- 8 (a) (i) Amide or ester or peptide [1]
 - (ii) Hydrolysis [1]
 - (iii) Drug **B** [1]
 - (iv) two ester and one amide groups circled [2]
 - (b) (i) At point Q because the hydrocarbon tails region is hydrophobic/non-polar/ form van der Waals only or can dissolve in the fat-soluble area
 - (ii) They all contain polar *or* hydrogen-bonding (groups) [1]
 - (c) (i) range 1×10^{-9} to 1×10^{-7} m [1]
 - (ii) (higher frequency radiation could) cause tissue/cell damage or mutation or harmful to cells[1]

[Total: 9]