CAMBRIDGE INTERNATIONAL EXAMINATIONS

GCE Advanced Level

MARK SCHEME for the May/June 2014 series

9701 CHEMISTRY

9701/42 Paper 4 (Structured Questions), maximum raw mark 100

This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began, which would have considered the acceptability of alternative answers.

Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

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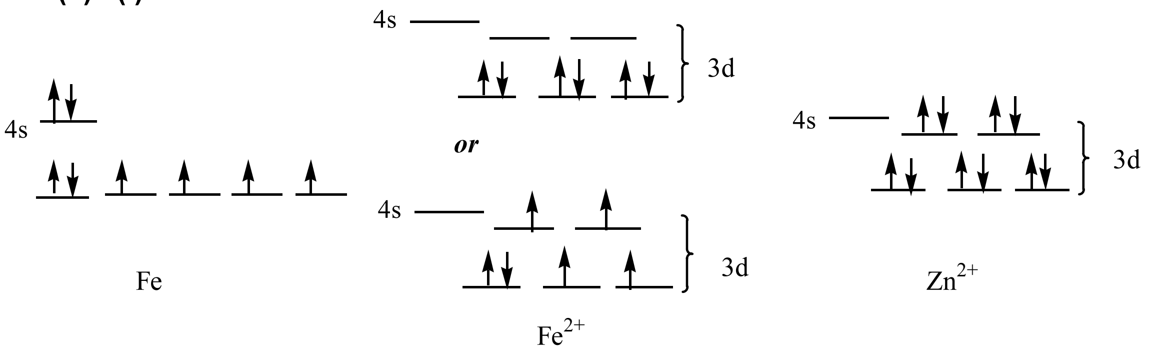
1 (a) (i)



[2]

(ii) (colour due to absorbance of visible light)
due to **electron** promoted (from lower) to upper **orbital / energy level** [1]

in Zn^{2+} there's no space in higher orbital for the electron to go *or* completely filled **<u>d-</u>**orbitals / shell [1]

4

(b) (i) yellow is due to $[CuCl_4]^{2-}$ [1]

reaction is ligand displacement / exchange [1]

(ii) (solution goes blue) due to $[Cu(H_2O)_6]^{2+}$ [1]

blue **ppt.** *or* **(s)** [1]
of $Cu(OH)_2$ *or* $[Cu(H_2O)_4(OH)_2]$ etc. [1]

purple *or* deep / dark blue **solution** *or* **(aq)** [1]
due to $[Cu(NH_3)_4]^{2+}$ *or* $[Cu(NH_3)_4(H_2O)_2]^{2+}$ [1]

7

(c) (i) $2KI + K_2S_2O_8 \longrightarrow 2K_2SO_4 + I_2$ *or*
ionic: $2I^- + S_2O_8^{2-} \longrightarrow 2SO_4^{2-} + I_2$ [1]

(ii) Fe^{2+} is a **homogeneous catalyst** [1]

(iii) equations: $2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$
$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

or verbal equivalent, e.g. reactants are both negative ions, so repel each other *or* Fe^{2+} can be oxidised by $S_2O_8^{2-}$ **and** Fe^{3+} can be reduced by I^- [1]

3

[Total: 14]

2 **(a)** **A:** voltmeter *or* V *or* potentiometer [1]

B: platinum *or* Pt [1]

C: 1 mol dm^{-3} **and** H$^+$ *or* $\mathrm{HC}l$ (*or* 0.5 M H_2SO_4) [1]

D: lead (metal) *or* Pb [1]

4

(b) **(i)** a ✓ in the box next to **–0.17 V** [1]
a comment that the [Pb^{2+}] has decreased **plus** a description of the outcome, e.g. as [Pb^{2+}] decreases (from 1 mol dm^{-3}), $Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$ goes over to the left hand side, *or* as [Pb^{2+}] decreases, Pb^{2+} is less likely to be reduced [1]

(ii) (K_{sp} =) $[Pb^{2+}][\mathrm{C}l^-]^2$ [1]

(iii) if $[\mathrm{PbC}l_2] = 3.5 \times 10^{-2}$, $[Pb^{2+}] = 3.5 \times 10^{-2}$ and $[\mathrm{C}l^-] = 7.0 \times 10^{-2}$
so $K_{sp} = (3.5 \times 10^{-2}) \times (7.0 \times 10^{-2})^2 =$ **1.715 (1.7) × 10^{-4}** mol^3 dm^{-9} (⩾2sf) [1] +[1]

5

(c) **(i)** the (M^{2+}/M) $E^\ominus$ for the two elements are very similar *or* are –0.13 and –0.14 V [1]

$E^\ominus$ (Sn^{4+}/Sn^{2+}) = 0.15 V **and** $E^\ominus$ (Pb^{4+}/Pb^{2+}) = 1.69 V [1]

so Sn^{2+} is quite easily oxidised (to Sn^{4+}) ***or*** is a stronger reductant ***or*** Pb^{2+} is not easily oxidised (to Pb^{4+}) ***or*** Pb^{4+} is a stronger oxidant ***or*** Pb^{4+} is easily reduced [1]

(ii) e.g. $\mathrm{PbC}l_2 + Zn \longrightarrow Pb + \mathrm{ZnC}l_2$ (*or* ionic) [1]
(other acceptable reductants: Fe, Mg, Ca but **not** Na or K)

$Sn^{2+} + Br_2 \longrightarrow Sn^{4+} + 2Br^-$ [1]
(other acceptable oxidants: VO^{2+}, $Cr_2O_7^{2-}$, Ag^+, $\mathrm{C}l_2$, Br_2, F_2, Fe^{3+}, MnO_4^-)

5

(d) **(i)** $Pb^{2+}(g) + 2\mathrm{C}l^-(g) \longrightarrow \mathrm{PbC}l_2(s)$ [1]

(ii) $\Delta H_f = \Delta H_{at} + E(\mathrm{C}l - \mathrm{C}l) + 1^{st}\ IE + 2^{nd}\ IE + 2 \times E_A(\mathrm{C}l) + LE$
–359 = 195 + 242 + 716 + 1450 – 2 × 349 + LE
LE = 2 × 349 – 359 – 195 – 242 – 716 – 1450
LE = **–2264** (kJ mol^{-1}) [3]

(iii) LE($\mathrm{PbC}l_2$) > LE($PbBr_2$) *or* more exothermic *or* stronger lattice [1]

because $\mathrm{C}l^-$/chloride anion has smaller radius/size than Br$^-$/bromide [1]

6

[Total: 20]

3 **(a)** **(i)** **B** and **D** [1] + [1]

(ii) **D** [1]

3

(b) heat with dilute $H^+(aq)$ *or* $H_2SO_4(aq)$ [1]

1

(c) **(i)** K_a larger than that for ethanol because
the ethanoate ion / $CH_3CO_2^-$ is stabilised by charge delocalisation
or
the O–H bond is weakened due to its proximity to C=O / carbonyl group *or* the second electronegative / oxygen atom [1]

K_a smaller than that for chloroethanoic acid because
electron-withdrawing / electronegative chlorine (atom) makes the anion more stable *or* O–H bond weaker *or* H more easily lost [1]

(ii) $[H^+] = \sqrt{([CH_3CO_2H] \times K_a)} = \sqrt{(0.1 \times 1.75 \times 10^{-5})} = \mathbf{1.32(3) \times 10^{-3}}$ (mol dm^{-3}) [1]

$pH = -\log_{10}[H^+] = \mathbf{2.88}$ (**2.9**) [1]

4

(d) **(i)** n(NaOH) at start = $0.1 \times 20/1000 = 2.0 \times 10^{-3}$ mol
n(NaOH) at finish = $\mathbf{1.0 \times 10^{-3}}$ mol [1]

(ii) this is in 30 cm^3 of solution,
so [NaOH] at finish = $1.0 \times 10^{-3} / 0.030 = \mathbf{3.3(3) \times 10^{-2}}$ mol dm^{-3} ($\geqslant$2 s.f.) ecf from **(i)** [1]

(iii) $[H^+] = K_w / [OH^-] = 1 \times 10^{-14} / 3.33 \times 10^{-2} = 3.0 \times 10^{-13}$ mol dm^{-3}
$pH = -\log_{10}[H^+] =$ **12.5(2)** [1]

or $pOH = -\log_{10}(3.33 \times 10^{-2}) = 1.48$
$pH = pK_w - pOH = 14 - 1.48 =$ **12.5(2)** [1]

(iv) pH / vol curve: start at pH 2.88 (2.9) ecf [1]

vertical (over at least 2 pH units) portion at V = 10 cm^3 [1]

levels off at pH 12.5 ± 0.3 ecf [1]

(v) indicator is thymolphthalein [1]

7

[Total: 15]

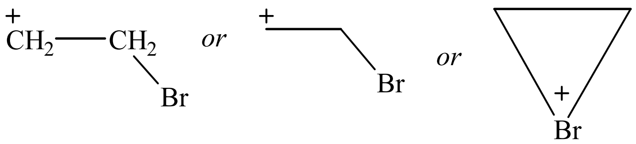
4. **(a)** **(i)** addition
AND
(ii) substitution [1]

1

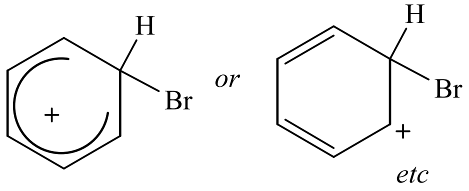
(b) $Br_2 + AlBr_3 \longrightarrow Br^+ + AlBr_4^-$ (*or* can use $AlCl_3$ *or* $FeCl_3$ *or* $FeBr_3$ etc.) [1]

1

(c) **(i)** The two intermediate cations:



[1]



[1]

(ii) The ring (of π electrons) in benzene is a stable configuration *or* is unchanged after the reaction. [1]

3

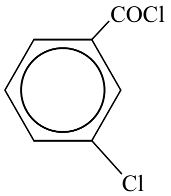
(d) **E** is benzoic acid [1]

reaction 1: heat with $KMnO_4$ (+ OH^- or H^+) [1]

reaction 2: heat with $Cl_2 + AlCl_3$ *or* $FeCl_3$ [1]

3

(e) **G** is [1]



reaction 3: $SOCl_2$ *or* PCl_5 [1]

reaction 4: $LiAlH_4$ [1]

3

[Total: 11]

5. **(a)** **(i)** Na reacts with –OH *or* hydroxyl / alcohol groups [1]

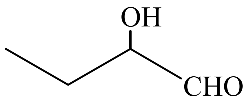
(ii) Fehling's solution reacts with –CHO *or* aldehyde groups [1]

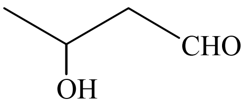
2

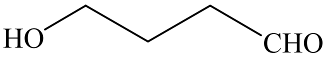
(b) alkene *or* C=C *or* carbon double bond *or* phenol *or* phenylamine [1]

1

(c) $CH_3CH_2CH(OH)CHO$ $CH_3CH(OH)CH_2CHO$ $HOCH_2CH_2CH_2CHO$







[1] + [1] + [1]

3

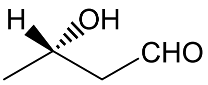
(d) **(i)** the $CH_3CH(OH)$ group *or* the CH_3CO group *or* methyl secondary alcohol *or* methyl ketone [1]

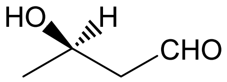
(ii) $CH_3CH(OH)CH_2CHO$ [1]

2

(e) **(i)** optical isomerism [1]

(ii)





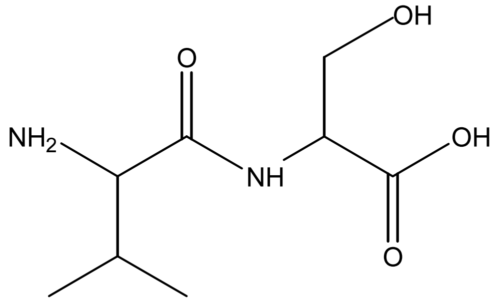
[1]

2

[Total: 10]

Section B

6. (a) (i)



Peptide bond correct [1]
Rest of structure correct (skeletal, displayed or structural formula, or a mix)

(ii) Condensation *or* nucleophilic substitution *or* addition-elimination [1]

(iii) Water / H_2O [1]

4

(b)

DNA	RNA
Contains deoxyribose	Contains ribose
Contains thymine / T	Contains uracil / U
Double strand / chain / helix *or* two strands	Single strand / chain

[3]

3

(c) (i) (met) - leu - thr - pro - glu [1]

(ii) Mutations *or* addition / insertion / deletion / substitution / replacement (of a base) [1]

(iii) Changing A (*or* the 14th base) into U [1]

3

[Total: 10]

7 **(a)** **(i)** (Electrophoresis): the size / shape / M_r of the amino acid *or* its charge [1]

(ii) (Paper chromatography): the partition of the amino acid between, *or* the relative solubility of the compound in, the 2 phases *or* solvent / water and stationary phase / filter paper. [1]

2

(b) Use ninhydrin as a locating agent [1]

1

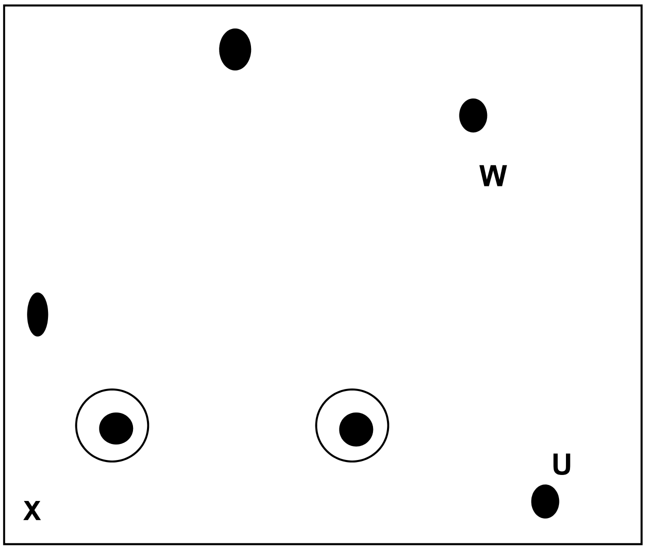
(c) The R_f value or retardation / retention factor *or* the distance travelled by the acid compared to that travelled by a standard sample of the amino acid [1]

1

(d) **R** – glutamic acid; **S** – glycine; **T** – lysine 3 × [1]

3

(e)



3 × [1]

3

[Total: 10]

8. **(a)** **(i)** Any addition polymer (e.g. polyethene, polypropene, polystyrene, PVC, PTFE, PVA, *Teflon*) [1]

(ii) Any condensation polymer (e.g. polyamide, polyester, nylon, *Terylene*, PET, PLA, *Kevlar*, *Nomex*) [1]

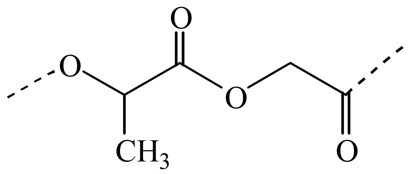
2

(b) Hydrolysis *or* nucleophilic substitution [1]

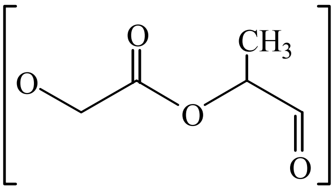
Ester **and** amide / peptide *or* $-CO_2-$ **and** –CONH– [1]

2

(c)



or



Correct ester linkage [1]

CH_3 side chain on only one monomer unit [1]

2

(d) Plant materials do not generally contain unsaturated hydrocarbons / alkenes / C=C [1]

1

(e) **(i)** **Y** van der Waals' forces [1]

Z hydrogen bonding [1]

(ii) **Z,** because it can form hydrogen bonds with water *or* it contains polar CO and NH groups [1]

3

[Total: 10]