MARK SCHEME for the May/June 2015 series

9791 CHEMISTRY

9791/03   Paper 3 (Part B Written), maximum raw mark 100

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1 (a) (i) Cathode / positive electrode (1)
Electrons gained / reduction (1) [2]

(ii) $O_2(g) + 4H^+(aq), 2H_2O(l)|Pt$
Correct species right way around and Pt. (1)
State symbols, (commas and) vertical lines correct. (1) [2]

(iii) +0.02 V (1) [1]

(iv) $CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$ (1) [1]

(b) (i) $\Delta G = -6 \times 96\,500 \times 1.21$ (1)
$= -700\,590 = -701$ (kJ mol^{-1}) (1) [2]

(ii) <u>Negative</u> sign of ΔG indicates that the reaction is <u>feasible.</u> (1) [1]

(iii) $\Delta G = \Delta H - T\Delta S$; $\Delta S = \underline{\dfrac{\Delta H - \Delta G}{T}}$

$\Delta S = \dfrac{-726\,000 - -701\,000}{298}$ (1)

$\Delta S = -83.9 / 83.89$ (1)
J K^{-1} mol^{-1} (1) [3]

(iv) $T = \Delta H^{\ominus} / \Delta S^{\ominus} = -726000 / -83.9$
$= 8653$ K (1)
<u>Above</u> this temperature the reaction ceases to be feasible. (1) [2]

[Total: 14]

2 (a) (i) (Decrease across Period 4) increasing nuclear charge with constant
shielding / electrons in same shell (1)
so increasing nuclear attraction / pull. (1) [2]

(ii) TM pattern relatively constant. (1) [1]

(b) (i) More electrons involved for TMs / for K and Ca only 4s electrons
involved in metallic bonding but for TMs 3d and 4s involved. (1) [1]

(ii) Higher nuclear charge (in Ni) (holds 3d electrons more tightly). (1) [1]

(c) (i) $3d_{z^2}$ and $3d_{x^2-y^2}$ labelled on top two lines and $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ on
bottom three lines (1) [1]

(ii) Two orbitals ($3d_{z^2}$ and $3d_{x^2-y^2}$) point along cartesian axes and three
orbitals ($3d_{xy}$, $3d_{xz}$ and $3d_{yz}$) point between. (1)
Approach of ligands repels 3d electrons. (1)
Raising of energy greater for $3d_{z^2}$ and $3d_{x^2-y^2}$ as <u>greater</u> repulsion (1) [3]

    (iii) Energy absorbed in promoting electron (from lower to higher energy 3d orbitals) (1)
is in visible region of EM spectrum. (1)
Colour seen is complementary colour (of colour corresponding to absorbed frequency). (1)   [3]

(d) **(i)** (Large value of K indicates) forward reaction (much) more favourable / equilibrium lies to the right. (1)
Increase in number of moles / from 4 to 7 accompanying forward reaction makes $\Delta S_{(syst)}$ <u>+ve.</u>
or
Bonds broken = bonds formed in complex so ΔH small hence, from $\Delta G = \Delta H - T\Delta S$, given ΔG is negative, ΔS is (probably) positive. (1)   [2]

    (ii) Optical (1)   [1]

    (iii) No plane or line of symmetry in the ion/not superimposable on its mirror image. (1)   [1]

    (iv)
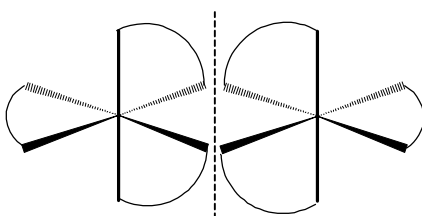
    (1) + (1)   [2]

[Total: 18]

3 **(a)** Cu electrode and $Cu^+(aq)$ as one half-cell (on right) (1)
$Cu^{2+}(aq)/Cu^+(aq)$ with Pt electrode as other half-cell (on left) (1)
All solutions 1 molar (or equimolar in Cu^{2+}/Cu^+ half-cell) (1)
Salt bridge and <u>high resistance</u> voltmeter (1)   [4]

(b) Cu^+ / reactant is being both oxidised and reduced at the same time. (1)   [1]

(c) **(i)** $[Cu^{2+}(aq)]/[Cu^+(aq)]^2$ (1)   [1]

    (ii) $\ln K = \dfrac{1 \times 96\,500 \times 0.36}{8.31 \times 298}$ (= 14.0(2854166)) (1)
$K = 1.24 \times 10^6$ (1)   [2]

    (iii) $K = 1.24 \times 10^6 = 1/[Cu^+(aq)]^2$ (1)
$[Cu^+(aq)] = \sqrt{(1/1.24 \times 10^6)} = 8.99 \times 10^{-4}$ (3 sig figs needed) (1)   [2]

(d) $K_{sp} = [Cu^+(aq)][Br^-(aq)]$ (1)
$[Br^-(aq)] = 3.20 \times 10^{-8}/5.72 \times 10^{-7} = 0.0559$ (mol dm^{-3}) (1)   [2]

[Total: 12]

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4 (a) (i) Carboxylic Acid Level (1) [1]

(ii) **Step 1** $CH_3CH_2MgBr + CO_2 \rightarrow CH_3CH_2COOMgBr$ (1)
Step 2 $CH_3CH_2COOMgBr + H_2O \rightarrow CH_3CH_2COOH + Mg(OH)Br$ (1)
Step 3 $CH_3CH_2COOH + PCl_5 \rightarrow CH_3CH_2COCl + HCl + POCl_3$
or $CH_3CH_2COOH + SOCl_2 \rightarrow CH_3CH_2COCl + SO_2 + HCl$ (1)
Step 1 = down a level / 4 to 3
Step 2 and Step 3 = moving within a level / stays at 3 (1) [4]

(b) (i) Ester (1) [1]

(ii) $HOOCC_6H_4COOH / ClOCC_6H_4COCl$ (1)
$HOCH_2CH_2OH$ (1) [2]

(iii) Hydrolysis (1) [1]

(iv) $^-OOCC_6H_4COO^-$ (1)
$HOCH_2CH_2OH$ (1) [2]

(v) Reduction (1) [1]

(vi) $HOCH_2C_6H_4CH_2OH$ (1)
$HOCH_2CH_2OH$ (1) [2]

(c) (i) Electrophilic Substitution (1) [1]

(ii) Lewis acid / $AlCl_3$ / $FeBr_3$ / $AlBr_3$ (1) [1]

(iii) (Harder to brominate because) side chains electron withdrawing / negative
inductive effect. (1)
Reduces charge / electron density of ring / π cloud / (ring) deactivating (1)
Reduces susceptibility to attack by / reduces attraction for electrophile (1) [3]

[Total: 19]

5 (a) (i) Fructose / anticlockwise-rotating isomer has stronger optical activity. (1) [1]

(ii) Graph is equivalent to $\ln(C_0/C_t)$ vs t / reference to the first order
rate equation. (1)
Straight line <u>through origin</u> / <u>therefore proportional,</u> (1)
indicates (pseudo) first order. (1) [3]

(iii) (labelled) 'triangle' correctly drawn on graph (1)
gradient calculated in range 0.0363 – 0.0368 (1)
Allow alternative method using first order rate equation
min^{-1} (1) [3]

(b) (i) <u>shape</u> of the active site (1) [1]

(ii) $^-OOCCH=CHCOO^- + H_2O \rightarrow {}^-OOCCH_2CH(OH)COO^-$ (1) [1]

(iii)

trans / E   cis / Z   (1) + (1)   [2]
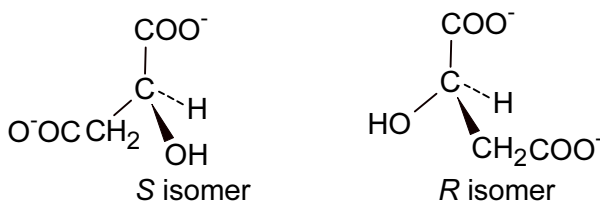
(iv)
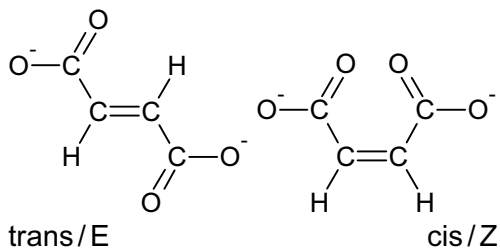
S isomer   R isomer   (1) + (1)

With H / lowest priority pointing away   (1)

Remaining groups in order of decreasing priority
clockwise = R / anticlockwise = S   (1)   [4]

(v) Optically inactive product / H$^+$ non-stereoselective   (1)
Racemate forms   (1)   [2]

(c) (i) <u>Carbonyl</u> group planar   (1)
Equal chance of attack (by CN$^-$) from either side   (1)   [2]

(ii) (2)R,(3)S and (2)S(3)R,   (1)
due to a plane / line of symmetry.   (1)
Meso   (1)   [3]

[Total: 22]

6 (a) (i) P =

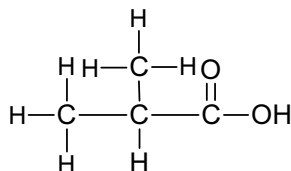   (1)

IR absorption at 1700 for C=O and a (broad) absorption at 3000
for O–H (so carboxylic acid)   (1)
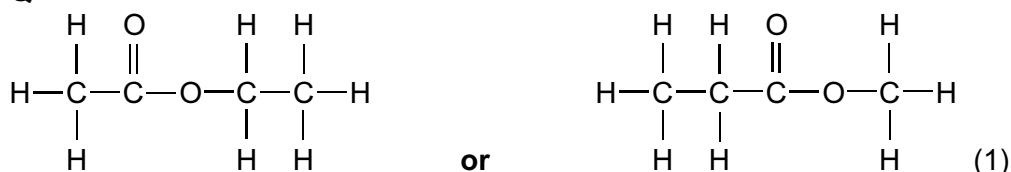3 signals = 3 environments; (ratio 6:1:1)   (1)
Doublet at 1.25 = 2 × CH$_3$; singlet at 12 = OH and multiplet = CH
next to CH$_3$ groups   (1)   [4]

(ii) **Q =**

```
    H  O        H  H                    H  H  O        H
    |  ||       |  |                    |  |  ||       |
H—C—C—O—C—C—H                      H—C—C—C—O—C—H
    |          |  |                    |  |          |
    H          H  H        or          H  H          H            (1)
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IR absorption at 1750 for C=O but no O–H absorption so ester   (1)
3 signals = 3 environments; (ratio 3:2:3)   (1)
Singlet = CH_3 next to C=O **or** –O–; quadruplet = CH_2;
triplet = CH_3 next to CH_2 (1)   [4]

(b) (i) Nucleus has overall magnetic moment / nucleus has spin ½   (1)
in an external magnetic field energy levels (of two different orientations)
split.   (1)
Energy difference corresponds to (absorption of) radio frequency waves. (1)   [3]

(ii) $(CH_3)_4Si$ / tetramethylsilane / TMS   (1)   [1]

(iii) Electrons orbiting around the proton shield it from external field. (1)
The closer a proton is to an electronegative atom the more electron
density is withdrawn from around it / more deshielded,   (1)
so the further downfield/left the signal is / larger chemical shift / higher
the frequency absorbed.   (1)   [3]

[Total: 15]