CAMBRIDGE INTERNATIONAL EXAMINATIONS

Pre-U Certificate

MARK SCHEME for the May/June 2014 series

9791 CHEMISTRY

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

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CAMBRIDGE
International Examinations

1 **(a)** Mn [Ar] $3d^5 4s^2$ (1)
Fe^{2+} [Ar] $3d^6$ (1) [2]

(b) **(i)** The **energy required** to **remove an electron** (1)
from **each atom** in a **mole** (1)
of gaseous atoms (1) [3]

(ii) addition of (successive) electrons to an inner subshell (1)
increased shielding with increasing nuclear charge (1)
attraction of nucleus for outer electrons remains approx. constant (1) [3]

(iii) $Cr^+ \rightarrow Cr^{2+} + e^-$ (1) [1]

(iv) both have $4s^1$ (outer electron structure cf $4s^2$ for others) (1)
2nd electron removed from subshell / shell / orbital nearer to / less shielded from the nucleus (1)
so 2nd electron more tightly held / greater attraction (1) [3]

(c) **(i)** (+3 for Sc) increasing to (+7 for) Mn then down (to +2 for Zn) (1)
(initial) increase due to increasing no. of d electrons (1)
decrease due to increasing ionisation energies / nuclear charge (1) [3]

(ii) FeO_4^{2-} (1) [1]

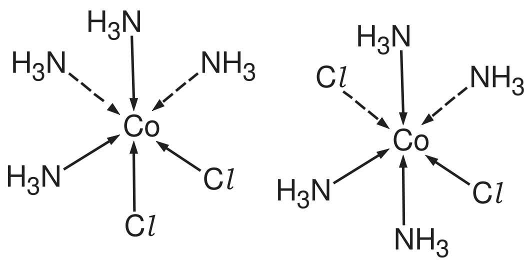
(d) **(i)** ratio indicates amount of **free** Cl^- ions
OR W = $3Cl^-$; **X** = $2Cl^-$; **Y** & **Z** = $1Cl^-$ (1)
OR W = no C*l* ligands; **X** = one C*l* ligand; **Y** & **Z** = two C*l* ligands [1]

(ii) **W** = $[Co(NH_3)_6]^{3+}$ (1); **X** = $[Co(NH_3)_5Cl]^{2+}$ (1) [2]

(iii) structural isomerism (1) [1]

(iv) geometric / cis-trans / *E–Z* isomerism (1) [1]

(v)



(1) [1]

[Total: 22]

2 (a) (i) **thermal decomposition** (1) [1]

(ii) more random dispersal of molecules in gaseous CO_2
OR more random dispersal of (quanta of) energy in gaseous CO_2 (1) [1]

(iii) $+160.4 = 39.7 + 213.6 - S^{\ominus}(CaCO_3)$ (1)
$S^{\ominus}(CaCO_3) = 39.7 + 213.6 - 160.4 = (+)\underline{92.9}$ ($J\ K^{-1}\ mol^{-1}$) (1) (must be 1dp) [2]

(b) (i) The **enthalpy / energy change** of a reaction is **independent of the route** (1)
providing starting and final conditions are the same (1) [2]

(ii) Cycle or $\Delta_f H^{\ominus}_{products} - \Delta_f H^{\ominus}_{reactants}$
$178.3 = \Delta_f H^{\ominus}$ CaO + (–393.5) – (–1206.9) (1)
$\Delta_f H^{\ominus}$ CaO = 178.3 + 393.5 – 1206.9 = $\underline{-635.1}$ ($kJ\,mol^{-1}$) (1) (must be 1dp) [2]

(iii) $\Delta S^{\ominus}_{surroundings} = -\Delta_r H^{\ominus}/T$ **OR** –178 300 / 298 (1)
= $\underline{-598.3}$ ($J\ K^{-1}\ mol^{-1}$) (1)
$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surround}$ = 160.4 – 598.3 = $\underline{-437.9}$ ($J\,K^{-1}\,mol^{-1}$) (1) [3]

(iv) When $\Delta S^{\ominus}_{total} = 0$; $T = \Delta_f H^{\ominus}/\Delta S^{\ominus}_{system}$ (1)
= 178 300 / 160.4 = $\underline{1111.6\,K}$ (1)
Represents temperature **above which** reaction becomes **feasible** (1) [3]

(c) (i) $K_p = pCO_2$ (1) [1]

(ii) $\Delta G = \Delta_r H^{\ominus} - T\Delta S^{\ominus}_{system}$ = 178.3 – (1473 × 0.1604) (1)
= $\underline{-57.97\,kJ\,mol^{-1}}$ (1) (57 969.2 $J\,mol^{-1}$)
$\Delta G = -RT\ln K$ so $K_p = e^{-\Delta G/RT}$ (1)
= (+)$\underline{113.96}$ (ignore units) (1) [4]

[Total: 19]

3 (a) (i) **A** = (High R) voltmeter (1)
B = salt bridge (1)
C = 1M Cu^{2+} (1)
D = Pt (electrode) (1)
E = equimolar / 1M $Cr_2O_7^{2-}$ / Cr^{3+} (1) acidified / H^+ (1) [6]

(ii) $Cu^{2+} + 2e^- \rightarrow Cu$ (1)
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (1) [2]

(iii) $Cr_2O_7^{2-} + 14H^+ + 3Cu \rightarrow 2Cr^{3+} + 7H_2O + 3Cu^{2+}$ (1) [1]

(b) (i) $Zn:H_2 = 1:1$
pV = nRT so moles $H_2 = (10^5 \times 126 \times 10^{-6}) / (8.31 \times 303)$
= 5.00×10^{-3} mol = mol Zn (1)
mass Zn = $5.01 \times 10^{-3} \times 65.4$ = $\underline{0.327\,g}$ (1) (must be 3 sf) [2]

(ii) amount copper = $4.88 \times 10^{-3} \times 5/2 = 0.0122$ mol (1)
mass copper = 0.0122×63.5 = 0.775 g (1) (0.7747) [2]

(iii) total mass = 0.327 + 0.775 = 1.102 g
% = (0.775 / 1.102) × 100 = 70.3% (1) [1]

(c) (i) OH^- reacts with H^+ (1)
so equilibrium moves to right (producing more CrO_4^{2-}) (1) [2]

(ii) (more orange = more dichromate hence) equilibrium has moved left
so (by le Chatelier's principle, forward) reaction is endothermic / reverse is exothermic (1) [1]

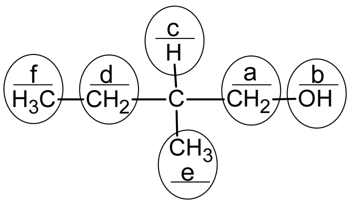
(iii) $BaCrO_4$ will be precipitated / form solid hence equilibrium moves to right (1)
K_c unchanged (1)
pH falls (1) [3]

[Total: 20]

4 (a) (*enantiomers* = stereoisomers that are) non-superimposable mirror images of each other (1)
chiral centre = carbon with 4 different groups / atoms attached (1) [2]

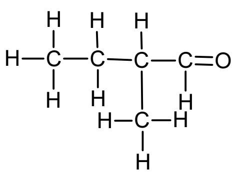
(b) (i) 1:2:1 (1) [1]

(ii)



6 correct = 3; 4 / 5 correct = 2; 2 / 3 correct = 1 (3) [3]

(c) (i)



(1)
2-methylbutanal (1) [2]

(ii) oxidation (1) [1]

(iii) $C_2H_5CH(CH_3)COOH$ / 2-methylbutanoic acid (1)
$2C_5H_{10}O_2 + Na_2CO_3 \rightarrow 2C_5H_9O_2Na + CO_2 + H_2O$ (1) [2]

(iv) $CH_3CH_2CH(CH_3)CH(OH)CN$ OR (semi-)displayed / skeletal (1)
nucleophilic addition (1)
planar carbonyl (1)
attack either side (gives mix of isomers) (1) [4]

(v) 2-hydroxy-3-methylpentanoic acid (or unambiguous formula) (1)
hydrolysis (1) [2]

[Total: 17]

5 (a) (i) Propene / HC*l* / or 2-chloropropane (1)
A*l*C*l*$_3$ (1)
$CH_3C^+HCH_3$ (1)
(conc) HNO_3 (1)
(conc) H_2SO_4 (1)
NO_2^+ (1) [6]

(ii) reduction (1)
Sn / HC*l* or Fe / HC*l* (1) [2]

(b) (i) bromine decolourises (1)
<u>white</u> precipitate (1) [2]

(ii) $C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$
1 mark for organic product, 1 mark for rest of equation correct (2) [2]

(iii) **–**OH donates electrons to delocalised system / ring (1)
increasing charge density in / activating ring (1)
so increasing <u>attraction</u> for electrophile (1)
$–NO_2$ electron-withdrawing / deactivating (1) [4]

(c) phenol more acidic (than ethanol) **OR** equilibrium lies further right **OR** dissociates **into ions** more readily (1)
reduction of charge density stabilises anion (1) [2]

(d) (i) $C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^{(+)}Cl^{(-)}$ (1) [1]

(ii) ethylamine > ammonia > phenylamine (1)
electron-releasing ethyl group increases charge density of N cf ammonia (1)
involvement of lone pair (of N) in benzene ring decreases availability to accept proton in phenylamine (1) [3]

[Total: 22]