CAMBRIDGE INTERNATIONAL EXAMINATIONS

Pre-U Certificate

MARK SCHEME for the May/June 2014 series

9791 CHEMISTRY

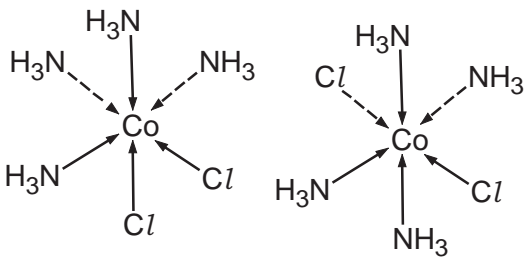**9791/03** Paper 3 (Part B Written), maximum raw mark 100

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.

Cambridge will not enter into discussions about these mark schemes.

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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)
<u>increased shielding</u> with <u>increasing nuclear charge</u> (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 Cl ligands; **X** = one Cl ligand; **Y & Z** = two Cl 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) $\Delta G = \Delta_r H^{\ominus} - T\Delta S^{\ominus}_{system} = 178.3 - (1473 \times 0.1604)$ (1)
$= \underline{-57.97\,kJ\,mol^{-1}}$ (1) ($57\,969.2\,J\,mol^{-1}$)
$\Delta G = -RTlnK$ 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 $H_2 = (10^5 \times 126 \times 10^{-6})/(8.31 \times 303)$
$= 5.00 \times 10^{-3}\,mol = mol\,Zn$ (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 = $0.0122 \times 63.5 = \underline{0.775\,g}$ (1) (0.7747)   **[2]**

    (iii) total mass = 0.327 + 0.775 = 1.102 g
         % = $(0.775/1.102) \times 100 = 70.3\%$ (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
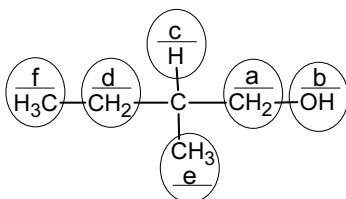   exothermic (1)   **[1]**

    (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)
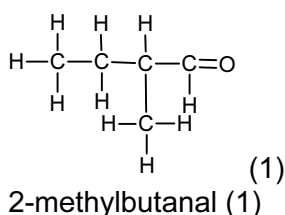   *chiral centre* = carbon with 4 different groups/atoms attached (1)   **[2]**

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

    (ii)

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

  (c) **(i)**

       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 / HCl / or 2-chloropropane (1)
AlCl_3 (1)
$CH_3C^+HCH_3$ (1)
(conc) HNO_3 (1)
(conc) H_2SO_4 (1)
NO_2^+ (1)   [6]

(ii) reduction (1)
Sn / HCl or Fe / HCl (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]