

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

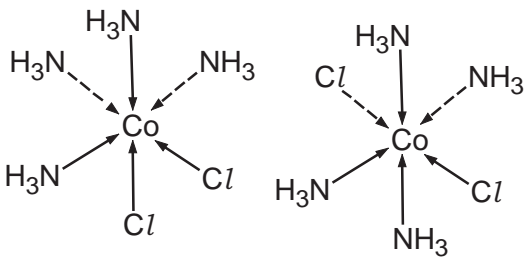
This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began,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

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- 1 (a) Mn [Ar] 3d⁵4s² (1)
Fe²⁺ [Ar] 3d⁶ (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⁺ → Cr²⁺ + e⁻ (1) [1]
- (iv) both have 4s¹ (outer electron structure of 4s² 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) FeO₄²⁻ (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(NH₃)₆]³⁺ (1); X = [Co(NH₃)₅Cl]²⁺ (1) [2]
- (iii) structural isomerism (1) [1]
- (iv) geometric/cis-trans/E-Z isomerism (1) [1]
- (v)
- 
(1)

[Total: 22]

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- 2 (a) (i) thermal decomposition (1) [1]
- (ii) more random dispersal of molecules in gaseous CO₂
OR more random dispersal of (quanta of) energy in gaseous CO₂ (1) [1]
- (iii) +160.4 = 39.7 + 213.6 – S°(CaCO₃) (1)
S°(CaCO₃) = 39.7 + 213.6 – 160.4 = (+)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 Δ_fH°_{products} – Δ_fH°_{reactants}
178.3 = Δ_fH° CaO + (–393.5) – (–1206.9) (1)
Δ_fH° CaO = 178.3 + 393.5 – 1206.9 = –635.1 (kJ mol⁻¹) (1) (must be 1dp) [2]
- (iii) ΔS°_{surroundings} = –Δ_rH°/T OR –178 300/298 (1)
= –598.3 (J K⁻¹ mol⁻¹) (1)
ΔS°_{total} = ΔS°_{system} + ΔS°_{surround} = 160.4 – 598.3 = –437.9 (J K⁻¹ mol⁻¹) (1) [3]
- (iv) When ΔS°_{total} = 0; T = Δ_rH°/ΔS°_{system} (1)
= 178 300/160.4 = 1111.6 K (1)
Represents temperature **above which** reaction becomes **feasible** (1) [3]
- (c) (i) K_p = pCO₂ (1) [1]
- (ii) ΔG = Δ_rH° – TΔS°_{system} = 178.3 – (1473 × 0.1604) (1)
= –57.97 kJ mol⁻¹ (1) (57 969.2 J mol⁻¹)
ΔG = –RTlnK so K_p = e^{–ΔG/RT} (1)
= (+)113.96 (ignore units) (1) [4]

[Total: 19]

- 3 (a) (i) A = (High R) voltmeter (1)
B = salt bridge (1)
C = 1M Cu²⁺ (1)
D = Pt (electrode) (1)
E = equimolar/1M Cr₂O₇²⁻/Cr³⁺ (1) acidified/H⁺ (1) [6]
- (ii) Cu²⁺ + 2e⁻ → Cu (1)
Cr₂O₇²⁻ + 14H⁺ + 6e⁻ → 2Cr³⁺ + 7H₂O (1) [2]
- (iii) Cr₂O₇²⁻ + 14H⁺ + 3Cu → 2Cr³⁺ + 7H₂O + 3Cu²⁺ (1) [1]
- (b) (i) Zn:H₂ = 1:1
pV = nRT so moles H₂ = (10⁵ × 126 × 10⁻⁶)/(8.31 × 303)
= 5.00 × 10⁻³ mol = mol Zn (1)
mass Zn = 5.01 × 10⁻³ × 65.4 = 0.327 g (1) (must be 3 sf) [2]

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(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]

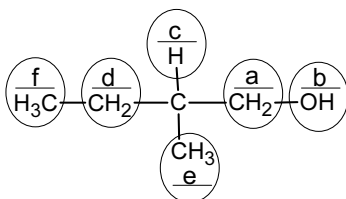
(iii) BaCrO_4 will be precipitated/form solid hence equilibrium moves to right (1)
 K_c unchanged (1)
pH falls (1) [3]

[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]

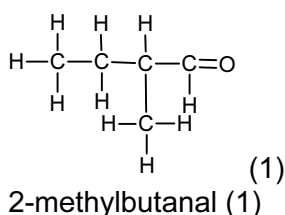
(b) (i) 1:2:1 (1) [1]

(ii)



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

(c) (i)



(ii) oxidation (1) [1]

(iii) $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{COOH}$ /2-methylbutanoic acid (1)
 $2\text{C}_5\text{H}_{10}\text{O}_2 + \text{Na}_2\text{CO}_3 \rightarrow 2\text{C}_5\text{H}_9\text{O}_2\text{Na} + \text{CO}_2 + \text{H}_2\text{O}$ (1) [2]

(iv) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{OH})\text{CN}$ OR (semi-)displayed/skeletal (1)
nucleophilic addition (1)
planar carbonyl (1)
attack either side (gives mix of isomers) (1) [4]

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

[Total: 17]

- 5 (a) (i) Propene/HCl/ or 2-chloropropane (1) [6]
AlCl₃ (1)
CH₃C⁺HCH₃ (1)
(conc) HNO₃ (1)
(conc) H₂SO₄ (1)
NO₂⁺ (1)
- (ii) reduction (1) [2]
Sn/HCl or Fe/HCl (1)
- (b) (i) bromine decolourises (1) [2]
white precipitate (1)
- (ii) C₆H₅OH + 3Br₂ → C₆H₂Br₃OH + 3HBr [2]
1 mark for organic product, 1 mark for rest of equation correct (2)
- (iii) –OH donates electrons to delocalised system/ring (1) [4]
increasing charge density in/activating ring (1)
so increasing attraction for electrophile (1)
–NO₂ electron-withdrawing/deactivating (1)
- (c) phenol more acidic (than ethanol) **OR** equilibrium lies further right **OR** dissociates **into ions** more readily (1) [2]
reduction of charge density stabilises anion (1)
- (d) (i) C₆H₅NH₂ + HCl → C₆H₅NH₃⁽⁺⁾Cl⁽⁻⁾ (1) [1]
- (ii) ethylamine > ammonia > phenylamine (1) [3]
electron-releasing ethyl group increases charge density of N of ammonia (1)
involvement of lone pair (of N) in benzene ring decreases availability to accept proton in phenylamine (1)

[Total: 22]