



GCE MARKING SCHEME

CHEMISTRY
AS/Advanced

SUMMER 2010

CH5

SECTION A

1. (a) (i) $\Delta H^{\ominus} = -393.5 - 601.7 + 1095.8 = +100.6 \text{ kJ mol}^{-1}$ 1 mark [1]
- (ii) The entropy increases because a gas is formed by the reaction and gases have higher entropies than solids. 1 mark [1]
- (iii) $\Delta S^{\ominus} = 0.1748 \text{ kJ mol}^{-1}\text{K}^{-1}$ 1 mark [1]
- (iv) $\Delta G = \Delta H^{\ominus} - T\Delta S^{\ominus}$ 1 mark
 $\Delta G = 0$ 1 mark
 $T = 100.6 / 0.1748 = 576 \text{ K}$ 1 mark [3]
 (mark consequentially if $\Delta H^{\ominus}$ or $\Delta S^{\ominus}$ incorrect)
 (3 marks for correct answer with no / incomplete working shown)
- (b) Sodium carbonate soluble as ΔG negative (spontaneous reaction), 1 mark
 magnesium carbonate sparingly soluble / insoluble as ΔG positive. 1 mark [2]
or
 Sodium carbonate more soluble than magnesium carbonate,
 ΔG for sodium carbonate more negative than ΔG for magnesium carbonate.
- (c) (i) $[\text{Mg}^{2+}(\text{aq})] = [\text{CO}_3^{2-}(\text{aq})] = 3.16 \times 10^{-3} \text{ mol dm}^{-3}$ 1 mark [1]
- (ii) $K_c = [3.16 \times 10^{-3}]^2 = 1.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$ 1 mark [1]
- (iii) Yes, they are consistent, because as ΔG was positive (and the reaction would not occur spontaneously), K_c must have a very small value. 1 mark [1]
- (iv) Adding extra carbonate ions would push the equilibrium to the left, decreasing the solubility. 1 mark [1]

Total [12]

2. (a) (i) $K_w = [\text{H}^+][\text{OH}^-]$ 1 mark [1]
- (ii) Equilibrium constant increases with temperature, so must be an endothermic process. 1 mark [1]
- (iii) $K_w = 4.3 \times 10^{-14} \text{ (mol}^2 \text{ dm}^{-6}\text{)}$ 1 mark [1]
- (iv) $[\text{H}^+] = \sqrt{4.3 \times 10^{-14}} = 2.07 \times 10^{-7} \text{ mol dm}^{-3}$ 1 mark
(allow 2.1 but not 2)
- $\text{pH} = -\log(2.07 \times 10^{-7}) = 6.7$ 1 mark [2]
(Mark consequentially if K_w or $[\text{H}^+]$ are incorrect)
- (b) (i) End point = 20.0 cm^3 (allow 20 cm^3) 1 mark
 $[\text{NH}_3] \times 25.0 = 0.100 \times 20.0$ 1 mark for setting up equation
 $[\text{NH}_3] = 0.080 \text{ mol dm}^{-3}$ 1 mark (must be two significant figures) [3]
- (ii) $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ / conjugate acid and base mixture 1 mark
 NH_3 reacts with added acid to form NH_4^+ 1 mark
 NH_4^+ dissociates as H^+ reacts with added alkali 1 mark [3]
- (iii) Methyl red 1 mark
 (any additional indicators treated as right / wrong)
 pH range lies on the steep part of the curve 1 mark [2]

Total [13]

3. (a) Any 2 × 1 mark for
A salt bridge:
completes the circuit between the electrode solutions
allows movement of ions
without any mixing of the solutions [2]
- (b) (i) Used as a standard / defined as zero (in standard hydrogen electrode).
1 mark [1]
- (ii) $EMF = 1.23 - 0 = 1.23V$ 1 mark [1]
- (iii) Not operated under standard conditions /
Process not 100% efficient /
Energy lost as heat 1 mark [1]
- (iv) $2H_2 + O_2 \rightarrow 2H_2O$ or $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ 1 mark [1]
- (v) Dependent on the equation used
 $\Delta H^\ominus = -571.6$ or $-285.8 \text{ kJ mol}^{-1}$ 1 mark [1]
- (c) (i) It is difficult to store enough hydrogen onboard 1 mark [1]
- (ii) Risk of hydrogen exploding in air 1 mark [1]
- (iii) Products are not polluting /
No CO₂ greenhouse gas produced/H₂ available from
renewable sources 1 mark [1]
- (d) (i) Mass = $(30/100) \times 1000 = 300 \text{ g}$ 1 mark
No moles NaBH₄ = $300 / 37.84 = 7.93 \text{ moles}$ 1 mark [2]
- (ii) Energy = $7.93 \times 300 = 2379 \text{ kJ}$ 1 mark [1]
(Mark sequentially on the no moles in (i))
- (iii) $7.93 \times 4 = 31.72 \text{ mol H}_2 \text{ gas}$ 1 mark
Volume = $31.72 \times 24 = 761.2 \text{ dm}^3$ 1 mark [2]
(Mark sequentially on the no moles in (i))

Total [15]

SECTION B

4. (a) (i) Rate = $0.0020 / 17.5 = 1.14 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$
(or $1.90 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$) Value 1 mark, units 1 mark [2]
- (ii) Follow the decrease in brown colour due to the Br_2 1 mark
/ use a colorimeter 1 mark [2]
Reference to the measurement of time
- (iii) $\text{Br}_2(\text{aq})$ zero order 1 mark
 $\text{CH}_3\text{COCH}_3(\text{aq})$ first order 1 mark [2]
- (iv) I As the pH increases the rate of reaction decreases 1 mark [1]
- II When pH increases by one unit, $[\text{H}^+]$ decreases by a factor of ten, as does the rate, so must be first order (or equivalent statement) 1 mark [1]
- III A catalyst (as more H^+ speeds the reaction up without being in the equation) 1 mark [1]
- IV Rate = $k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$ 1 mark
Units of k are $\text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ 1 mark
(Mark units for k consequentially if rate equation incorrect) [2]
- (QWC)(iv) A coherent and clearly expressed response using a style appropriate to complex subject matter. [1]
- (b) BN and C can both adopt the same hexagonal structure: [2]
BN and C are isoelectronic (or equivalent statement) 1 mark
(All three) can form three (trigonal) bonds with one unbonded p-orbital 1 mark
(Allow appropriate diagram(s))
- Both BN and C exhibit lubricating properties: [2]
Both BN and C have a layer structure 1 mark
Weak van der Waals forces between layers allow slippage of the layers 1 mark
- C is an electrical conductor but BN is an insulator at room temperature: [2]
Any two from:
In C, delocalisation of electrons (between the unbonded p-orbitals) allows conduction of electricity. 1 mark
Unlike C, in BN each N has a full unbonded p-orbital whereas each B has an empty unbonded p-orbital. 1 mark
In BN, N is more electronegative than B, so electron density not evenly spread. 1 mark
- (QWC)(b) Legible text and accurate spelling, punctuation and grammar so that meaning is clear 1 mark
Information organised clearly and coherently, using specialist vocabulary when appropriate. 1 mark [2]

Total [20]

5. (a) (i) Blue 1 mark precipitate 1 mark [2]
- (ii) $\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu}(\text{OH})_2$
 or $\text{CuSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Cu}(\text{OH})_2 + \text{CaSO}_4$ 1 mark [1]
- (b) (i) Starch 1 mark
 Blue to colourless 1 mark [2]
- (ii) No moles $\text{Na}_2\text{S}_2\text{O}_3 = 12.25 \times 0.100 / 1000 = 1.225 \times 10^{-3}$ 1 mark
 Mass Cu = $1.225 \times 10^{-3} \times 63.5 = 0.0778 \text{ g}$ 1 mark
 % Cu = $0.0778 \times 100 / 31.2 = 0.249 \%$ 1 mark [3]
*(deduct 1 mark if **both** second and third answers not to 3 significant figures)*
- (c) (i) $\text{Cu}^{2+} 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ 1 mark
 $\text{Cu}^+ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ 1 mark [2]
- (ii) 3d orbitals split (by water ligands) 1 mark
 (In an approximately octahedral field) three d-orbitals have lower energy,
 two have higher energy 1 mark
 Electrons absorb (visible light) energy to jump from lower level to higher
 level 1 mark
 The blue colour is that due to the remaining / non-absorbed frequencies
 1 mark
 (Appropriate diagrams are acceptable alternatives). [4]
- (iii) Colour arises from d-d electron transitions, not possible in Cu^+ because the
 3d subshell is full. [1]
- (d) (i) CCl_4 forms two layers / does not mix with water / no reaction 1 mark
 SiCl_4 reacts explosively / exothermically
or
 misty fumes / sharp smelling fumes / acid solution / white ppt. 1 mark
 $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$ 1 mark [3]
 (Allow $\text{Si}(\text{OH})_4$)
- (ii) In PbCl_2 the Pb^{2+} ion is stabilised due to the inert pair (ns^2) effect 1 mark
 1 mark for any **one** of the following
 CCl_2 and SiCl_2 are too unstable to exist because:
 oxidation state IV is more stable than oxidation state II at the top of the
 group
 or oxidation state II increases in stability down the group
 or covalent bonding is more stable than ionic at the top of the group and
 four bonds are needed for an outer octet .
 or inert pair effect becomes more significant down the group [2]

Total [20]



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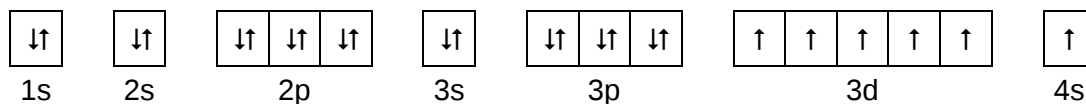
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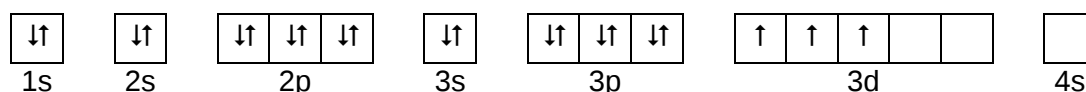
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Q.1 (a) Reacts with both acids **and** bases / behaves as an acid **and** a base. [1]

(b) Chromium atom, Cr [1]



Chromium(III) ion, Cr³⁺ [1]



(c) (i) Orange → yellow [1]

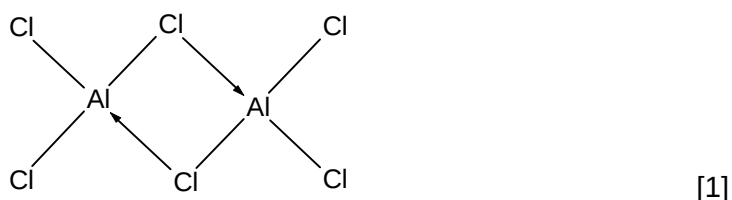
(ii) Cr +6 (1) in both reactant and product - do not accept 6+
no change in oxidation states so not a redox reaction. (1) [2]

(d) Add sodium hydroxide solution dropwise until there is an **excess** / small volume at a time until **excess**. [1]

White precipitate forms with Mg but doesn't dissolve again (therefore not amphoteric). [1]

White precipitate forms with Al then dissolves in excess NaOH (therefore amphoteric). [1]

(e) (i)



(co-ordinate bonds can be shown as lines but are incorrect if shown as arrows from Al to Cl)

Al is electron deficient - do not accept 'AlCl₃ is electron deficient' [1]

Cl has lone pairs [1]

(ii) Tetrahedral (1); four electron pairs and no lone pairs/ four bonding pairs (1) [2]

Total [14]

- Q.2** (a) (i) $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ [1]
- (ii) Higher efficiency / no carbon dioxide emissions / water only / no greenhouse gases / can use renewable energy resources. [1]
Too vague - do not accept clean / no polluting gases / no global warming.
- (iii) A = Salt bridge (1)
B = High resistance voltmeter /potentiometer (1)
C = Platinum electrodes (1) [3]
- (b) (i) $\Delta H = 2 \times \Delta H (\text{H}_2\text{O}) + \Delta H (\text{CO}_2) - \Delta H (\text{CH}_3\text{OH})$
 $= 2 \times -286 + (-394) - (-239)$ (1)
 $= -727 \text{ kJ mol}^{-1}$ (1) [2]
- (ii) Entropy of (methanol) gas is higher than liquid (1)
So entropy change will be more negative (1) [2]
- (iii) $\Delta G = -727000 - (298 \times -81) = -703 \text{ kJ mol}^{-1}$ (1) *Allow ECF*
Negative ΔG means reaction is feasible. (1) [2]
- Total [11]**

Q.3 (a) Any 2 for (1) each from:

- Measure pressure (at constant volume) over time
- Measure volume (at constant pressure) over time
- Colorimetry/ measuring colour over time

1 mark allowed if time not mentioned

[2]

(b) (i) When concentration doubles, rate doubles (1)

Therefore first order or rate is proportional to concentration (*must give reason to obtain this mark*) (1) [2]

Credit possible by alternative methods:

Calculate k for each and show that all values are the same;
Calculate k for one concentration and use to calculate other values.

(ii) $k = \text{Rate} \div [\text{N}_2\text{O}_5]$ e.g. $k = 3.00 \times 10^{-5} \div 4.00 \times 10^{-3}$ (1)
 $= 7.50 \times 10^{-3}$ (1) *must be 3 significant figures*

Units = s^{-1} (1)

[3]

(iii) Rate determining step must have one N_2O_5 molecule as reactant. (1)
Mechanism A matches this rate equation (1) *need reason to get this mark*

Accept reverse argument.

[2]

(c) (i) $K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2}$

[1]

(ii) Increasing temp shifts equilibrium to left / favours endothermic reaction (1) so value of K_p is decreased. (1)

[2]

(iii) $P_{\text{N}_2\text{O}_4} = 9.5 \times 10^3 \text{ Pa}$ (1)
 $K_p = 9.5 \times 10^3 \div (2.81 \times 10^5)^2 = 1.20 \times 10^{-7}$ (1) *Allow ECF*
Units = Pa^{-1} (1) Mark consequentially on answer to (c)(i)

[3]

Total [15]

- Q.4** (a) (i) Transition metals have partially filled *d*-orbitals (in atom or ion) [1]
- (ii) Iron and copper have partially filled d-orbitals in their **ions**, zinc does not [1]
- (b) *QWC: organisation of information clearly and coherently; use of specialist vocabulary where appropriate. (1)*
QWC: selection of a form and style of writing appropriate to purpose and to complexity of subject matter. (1) [2]
- Ligands cause d-orbitals to split
 - into 2 higher energy/ 3 lower energy
 - Electrons absorb light (frequencies) to move to higher energy level
 - Colour seen is colour transmitted/reflected/not absorbed
 - Copper(II) complexes absorb red /orange/yellow/all colours except blue.
[MAX 4 marks from points above]
 - Different ligands cause different splittings / different ΔE .
 - Copper(I) ion has full d-orbitals.
 - So electrons cannot move to upper energy levels.
- [OVERALL MAX 6]
- (c) (i) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ [1]
- (ii) Fe oxidation state goes from +3 to 0 (1) / so it is reduced (1)
 OR C (not CO) oxidation state goes from +2 to +4 (1)/ so it is being oxidised. (1) *Allow ECF* [2]
- (iii) Stable oxidation state of (C is +4 whilst) Pb is +2 (1)
 Due to inert pair effect becoming more significant down the group. (1) [2]
- (d) (i) $6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ [1]
- (ii) Moles $\text{Cr}_2\text{O}_7^{2-} = 23.80 \times 0.0200 \div 1000 = 4.76 \times 10^{-4}$ moles (1)
 Moles $\text{Fe}^{2+} = 4.76 \times 10^{-4} \times 6 = 2.86 \times 10^{-3}$ moles (1) [2]
- (iii) Mass Fe in sample = $2.86 \times 10^{-3} \times 10 \times 55.8 = 1.59$ g (1)
 Percentage Iron = $1.59 \div 1.870 \times 100 = 85.2\%$ (1) [2]

Total [20]

- Q.5** (a) Named compound examples, need both name and use for (1)
- Sodium chlorate(I) = bleach
 - Sodium chlorate(V) = weedkiller
 - PVC = windows frames/guttering/pipes/insulation for electrical wires
 - Dichloromethane – solvent / paintstripper
 - CFCs = refrigerants / aerosol propellants
 - Aldrin / Dieldrin / DDT = Insecticides [1]
- (b) (i) $\text{Cl}_2 + 2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{Cl}^-$ [1]
- (ii) • Emf for reaction of bromide with chlorine is +0.27 V / $E^\ominus$ for chlorine is more positive than for bromine. (1)
- Emf for reaction of bromide with iodine is -0.55 V / $E^\ominus$ for iodine is less positive than for bromine. (1)
 - Reactions are only feasible if Emf is positive / if $E^\ominus$ for oxidising agent is more positive than for species being oxidised. (1)
- [3]
- (c) (i) White precipitate with (sodium) chloride, yellow precipitate with (sodium) iodide [1]
- (ii) *QWC: legibility of text; accuracy of spelling, punctuation and grammar; clarity of meaning. (1)* [1]
- NaCl: Steamy gas / bubbles (1)
 - NaI: Steamy gas / smell of rotten eggs / purple vapour or brown solution or black solid / yellow solid (1 mark for 2 observations)
 - NaCl: NaHSO_4 , HCl / NaI: NaHSO_4 / HI / I_2 / H_2S / SO_2 / S / H_2O (1 mark for 2 products; 2 marks for 4 products)
 - Iodide is easier to oxidise / iodide is a stronger reducing agent than chloride (1)
- [5]
- (d) (i) (Almost) completely dissociates to release H^+ . [1]
- (ii) $K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]}$ [1]
- (iii) $[\text{H}^+] = 10^{-\text{pH}}$ OR $\text{pH} = -\log [\text{H}^+]$ (1)
- $[\text{H}^+] = 5.88 \times 10^{-5} \text{ mol dm}^{-3}$ (1) [2]
- (iv) $K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{(5.88 \times 10^{-5})^2}{0.100}$ (1) = $3.47 \times 10^{-8} (\text{mol dm}^{-3})$ (1)
- (allow consequential answers) [2]
- (v) pH above 7 (up to 10) (1)
- OCl^- in equilibrium with HOCl / OCl^- will remove H^+ from solution (1) [2]

Total [20]



GCE MARKING SCHEME

**CHEMISTRY
AS/Advanced**

SUMMER 2012

CH5

SECTION A

1. (a) 1 dm^3 at 20°C contains 52.9 g and at 0°C it contains 17.5 g (1)
 $\therefore$ amount crystallised = $52.9 - 17.5 = 35.4 \text{ g}$ (1) [2]
- (b) (i) 2 mol of $\text{K}_2\text{S}_2\text{O}_8$ give 1 mol of O_2
 2 mol of $\text{K}_2\text{S}_2\text{O}_8$ give 29.0 dm^3 of O_2 (1)
 $\therefore$ 0.1 mol of $\text{K}_2\text{S}_2\text{O}_8$ gives $29.0/20 = 1.45 \text{ dm}^3$ of oxygen (1) [2]
- (ii) Measure the volume of oxygen produced at specified time intervals /
 Measure the pH of the solution at specified time intervals [1]
- (c) (i) An (inert) electrode that is used to carry the charge / current / electron flow [1]
- (ii) A comment on the relative values (e.g. the persulfate system is the more positive of the two systems) (1)
 The more positive 'reagent' / persulfate ions acts as the oxidising agent, accepting electrons via the external circuit (1)
 - must have the first mark to get second [2]
- (d) (i) The experiments show that both the concentrations of iodide and persulfate have doubled (1) therefore the initial rate should increase four times
 $4 \times 8.64 \times 10^{-6} = 3.46 \times 10^{-5}$ (1) [2]
- (ii) Rate = $k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$ (1)
 $\therefore k = \frac{8.64 \times 10^{-6}}{0.0400 \times 0.0100}$
 $= 0.0216$ (1) $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (1) [3]
- (iii) In the rate equation one $\text{S}_2\text{O}_8^{2-}$ ion reacts with one I^- ion.
 The rate-determining step therefore has to have 1 mole of each reacting, as (only) seen in step 1 [1]

Total [14]

2. (a) - 705 (kJ mol⁻¹) (1) for correct sign (1) for correct number [2]
- (b) (i) hydration
 lattice **breaking** [1]
- (ii) e.g. add a small 'amount' of an alkali / sodium hydroxide / NaOH / OH⁻ ions (1)
 this would remove / react with hydrogen ions giving water, shifting the position
 of equilibrium to the left (removing iodine) (1)
 add Pb²⁺ / Ag⁺ ect. [2]
- (c) (i) Any TWO from
 white / misty fumes (of HI)
 yellow solid / solution (of sulfur)
 brown / black solid / purple vapour (of iodine)
 bubbles / effervescence / fizzing
 One mark for each correct response [2]
- (ii) The values show that chlorine is the best oxidising agent, as it has the most
 positive E⁰ value and therefore iodide is the better reducing agent (1)
 and is 'strong' enough to reduce the sulfuric acid. / OWTTE (1) [2]
- (d) (i) 2 NaOH + Cl₂ → NaOCl + NaCl + H₂O [1]
- (ii) e.g. bleach, kills bacteria [1]
- Total [11]

3. (a) (i)

$$\text{Number of moles of EDTA} = \frac{19.20 \times 0.010}{1000} = 1.92 \times 10^{-4} / 0.000192 \quad [1]$$

- error carried forward throughout (a)

$$(ii) \quad 1.92 \times 10^{-4} / 0.000192 \quad [1]$$

$$(iii) \quad \text{Concentration} = \frac{1.92 \times 10^{-4} \times 1000}{50} = 3.84 \times 10^{-3} / 0.00384 \text{ mol dm}^{-3} \quad (1)$$

$$\text{Concentration} = 3.84 \times 10^{-3} \times 63.5 = 0.244 \text{ g dm}^{-3} \quad (1) \quad [2]$$

$$(iv) \quad \% \text{ Cu} = \frac{0.244 \times 100}{11.56} = 2.11 \quad [1]$$

(b) Transition elements have either a partly filled 3d sub-shell or form ions that have a partly filled 3d sub-shell (1)

However copper forms Cu^{2+} ions that are '3d⁹' / partly filled 3d sub-shell (1)

whereas Zn^{2+} ions are '3d¹⁰' / full 3d sub-shell (1) - any 2 from 3 [2]

QWC Organisation of information clearly and coherently; use of specialist vocabulary where appropriate. [1]

(c)

Complex ion	Shape	Colour
$[\text{CuCl}_4]^{2-}$	tetrahedral	yellow / lime green
$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	octahedral	deep blue

Any two correct (1) all correct (2) [2]

(d) The more negative the ΔH_f value the more stable the oxide (1)

PbO is relatively the more stable / CuO is relatively the less stable (1) [2]

- must have the first mark to get second

(e) (i) Any TWO from

variable oxidation states

partially filled 3d energy levels

ability to adsorb 'molecules'

ability to form complexes with reacting molecules / temporary / co-ordinate bonds

One mark for each correct response [2]

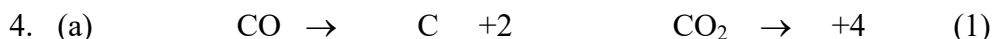
(ii) e.g. to allow lower pressures / temperatures

use recyclable catalysts - needs qualifying

longer lasting / less toxic catalysts [1]

Total [15]

SECTION B



Increase of (positive) oxidation number = oxidation / reducing agents themselves
are always oxidised are always oxidised (1)

OR



Oxidation number of iodine reduced, reduction occurring, CO reducing agent (1) [2]

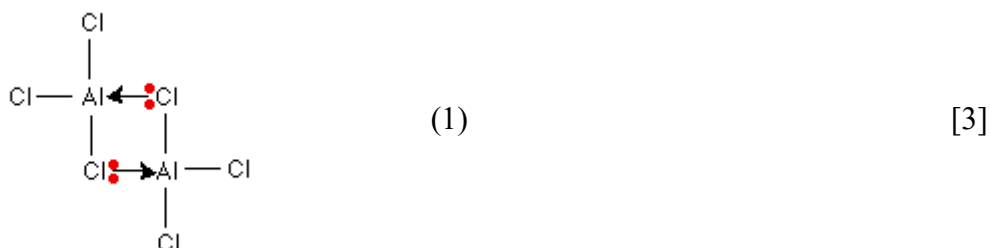
(b) +2 state becomes more stable down the group and +4 becomes less stable. [1]

(c) (i) Add (a little) sodium hydroxide solution (1) to each solution.
A white precipitate (1) of aluminium / lead(II) hydroxide (1) is seen.
When more sodium hydroxide solution is added these precipitates (dissolve giving
a colourless solution). (1) [4]

*QWC Legibility of text: accuracy of spelling, punctuation and grammar;
clarity of meaning.* [1]

(ii) Yellow precipitate (1) $\text{Pb}^{2+} + 2 \text{I}^- \rightarrow \text{PbI}_2$ [2]

(d) (i) The bonding of **aluminium** in the monomer has not completed the octet / suitable
diagram / 6 electrons in its outer shell (1)
When the dimer is formed this octet of bonded electrons is formed (1)



(ii) (As a catalyst) in the chlorination of benzene / making ionic liquids [1]

(iii) I The number of (gaseous) species is increasing, leading to less order [1]

II For the reaction to be just spontaneous $\Delta G = 0$ (1)

substituting $0 = 60\,000 - 88 T$

$T = 60\,000 / 88 = 682 \text{ K} / 409^\circ\text{C}$ (1) [2]

$$(e) \quad K_c = \frac{[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq})[[\text{H}^+](\text{aq})]}{[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})}$$

$$\therefore 1.26 \times 10^{-5} = [\text{H}^+]^2 / 0.10$$

$$\therefore [\text{H}^+]^2 = 1.26 \times 10^{-6} \quad [1]$$

$$\therefore [\text{H}^+] = \sqrt{1.26 \times 10^{-6}} = 1.12 \times 10^{-3} / 0.00112 \quad (1)$$

- error carried forward

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} 1.12 \times 10^{-3} = 2.95 \quad (1) \quad [3]$$

Total [20]

5. (a) (i)
$$K_p = \frac{p\text{SO}_3(\text{g}) \times p\text{NO}(\text{g})}{p\text{SO}_2(\text{g}) \times p\text{NO}_2(\text{g})} \quad (1) \quad \text{there are no units} \quad (1) \quad [2]$$

- (ii) The line for SO_3 / NO at equilibrium should be above the $\text{SO}_2 / \text{NO}_2$ line (1)
as K_p has a value of 2.5, the partial pressures of SO_3 and NO at equilibrium will be greater than the partial pressures of SO_2 and NO_2 . (1)

- accept answer in terms of alternative calculated K_p value

The line for equilibrium should start at 9 hours. (1)
as at equilibrium the concentrations is unchanged as time progresses. (1)

[4]

There may be other acceptable forms of explanation to be discussed at the conference

- (iii) If the temperature rises then the position of equilibrium will move to the left, (reducing the quantities of SO_3 and NO). (1)
This will make the value of K_p smaller. (1) [2]

- (b) (i) Nitric acid is a strong acid and its pH is low / <2 / 1.0 (1)
As aqueous ammonia is added the pH slowly rises (1) until a pH of ~ 3 is reached, when it rises rapidly (1)
At a pH of 8-9, it tails off slowly as ammonia is a weak base. (1)
Accept any 3 from 4 . [3]

Selection of a form and style of writing which is appropriate to purpose and to complexity of subject matter [1]

- (ii) The equivalence point is reached when 20.0 cm^3 of ammonia solution has been added as this is at the mid point of the more vertical section. (1)

Since both reagents have the same concentration and the volumes used are both 20 cm^3 / the same, the number of moles of each are the same (1)

OR the number of moles of both nitric acid and aqueous ammonia are calculated (0.0020) and shown to be the same (1)

$\therefore$ Mole ratio must be 1 : 1 (1) [2]

- (iii) I Ammonium nitrate is the salt of a strong acid and weak base / there is a buffering effect in operation. [1]

II ~ 5.5 [1]

- (iv) Blue, as bromophenol blue is blue at a pH of 4.7 and above [1]

(c) Number of moles of ammonium nitrate = $\frac{40}{80} = 0.50$ (1)

- error carried forward

Concentration of ammonium nitrate solution = $\frac{0.5 \times 1000}{200} = 2.5 \text{ mol dm}^{-3}$ (1)

$\therefore$ Temperature drop = $2.5 \times 6.2 = 15.5^\circ\text{C}$ (1) [3]

Total [20]



GCE MARKING SCHEME

**CHEMISTRY
AS/Advanced**

SUMMER 2013

GCE CHEMISTRY – CH5

SUMMER 2013 MARK SCHEME

- Q.1** (a) Name of any commercially/ industrially important chlorine containing compound e.g. (sodium) chlorate(I) as bleach/ (sodium) chlorate(V) as weedkiller/ aluminium chloride as catalyst in halogenation
- do not accept CFCs [1]
- (b) (i) $K_c = \frac{[HI]^2}{[H_2][I_2]}$ must be square brackets [1]
- (ii) $K_c = \frac{0.11^2}{3.11^2} = 1.25 \times 10^{-3}$ follow through error (ft) [1]
- (iii) K_c has no units ft [1]
- (iv) when temperature increases K_c increases (1)
this means equilibrium has moved to RHS
/ increasing temperature favours endothermic reaction (1)
therefore ΔH for forward reaction is +ve (1)
(mark only awarded if marking point 2 given) [3]
- (c) (i) +2 [1]
- (ii) co-ordinate/ dative (covalent) [1]
- (iii) pink is $[Co(H_2O)_6]^{2+}$ **and** blue is $[CoCl_4]^{2-}$ (1)
(ligand is) Cl^- (1)
(addition of HCl sends) equilibrium to RHS (1) [3]
- (iv) $[Co(H_2O)_6]^{2+}$ shown as octahedral [with attempt at 3D] (1)
 $[CoCl_4]^{2-}$ shown as tetrahedral/ square planar (1) [2]

Total [14]

- Q.2** (a) (i) tangent drawn at $t = 40$ (1)
 rate calculated 0.017 to 0.027 (ignore units) (1) [2]
- (ii) as reaction proceeds less collisions (per unit time) occur [1]
- (b) (i) 1st order shown by:
 calculation of rates at at least 2 concentrations (1)
 statement rate $\propto$ concentration (1)
 OR
 constant half-life (1)
 half-life is 24 minutes (1) [2]
- (ii) rate = $k[\text{N}_2\text{O}_5]$ (1) [1]
- (iii) $k = \text{rate (from (i))} / [\text{N}_2\text{O}_5] \text{ (from graph)}$ (1)
 (mark correct numbers – no need to check evaluation)
 units = minutes^{-1} (1) ft from (ii) [2]
- (iv) (student A more likely to be correct) reaction is 1st order and 1 $[\text{N}_2\text{O}_5]$ involved in rate determining step [1]
- (c) correct curve starting at 100 kPa and becoming horizontal (1)
 horizontal at 250 kPa (1) [2]

Total [11]

- Q.3** (a) an acid is a proton / H^+ donor [1]
- (b) $pH = -\log[H^+]$ / negative log of hydrogen ion concentration [1]
- (c) a low pH corresponds to a high concentration of H^+ (1)
- a strong acid is totally dissociated whilst a weak acid is partially dissociated (1)
- need to consider concentration (of acid solution) as well as strength of the acid (1)
- a concentrated solution of a weak acid could have a lower pH than a dilute solution of a strong acid (1) [4]
- QWC Accuracy of spelling, punctuation and grammar* QWC [1]
- (d) (i) $K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$ [1]
- (ii) $1.75 \times 10^{-4} = \frac{x^2}{0.1}$ (1)
- $x = 4.183 \times 10^{-3}$ (1)
- $pH = 2.38$ (1) [3]
- (e) (i) buffer [1]
- (ii) $RCOOH \rightleftharpoons RCOO^- + H^+$ and $RCOONa \rightarrow RCOO^- + Na^+$ (1)
- added H^+ removed by salt anion/ $A^- + H^+ \rightarrow HA$ (1)
- added OH^- removed by acid/ $OH^- + HA \rightarrow A^- + H_2O$ (1) [3]
- Total [15]**

Q.4 (a) diagram with labels to show

H_2/H^+ shown in electrode (1)

platinum (in both electrodes) (1)

$\text{Fe}^{2+}(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})$ (1)

high resistance voltmeter (1)

salt bridge (1)

gas at 1atm pressure, solutions of concentration 1 mol dm^{-3} , temperature 298K (1)

[any 5]

[5]

(b) (i) successive ionisation energies increase gradually/ the energies of the d orbitals are similar **[1]**

(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} / 3d^{10} 4s^2$ **[1]**

(iii) after 4s electrons lost 3d is full/ stable/ d electrons ionisation energy very high **[1]**

(c) (i) violet solution contains V^{2+} (1)

SEP Zn^{2+}/Zn is more negative than $\text{VO}_3^-/\text{VO}^{2+}$ and $\text{VO}^{2+}/\text{V}^{3+}$ and therefore

releases electrons/ $\text{VO}_3^-/\text{VO}^{2+}$ and $\text{VO}^{2+}/\text{V}^{3+}$ are more positive than

Zn^{2+}/Zn and are stronger oxidising agents (1)

V^{2+} cannot be reduced (to V) since SEP is more negative than Zn^{2+}/Zn (1) **[3]**

(ii) 1.1V (ignore sign) **[1]**

(iii) $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- / \text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ with some indication of direction **[1]**

(iv) if $\text{Zn}^{2+}(\text{aq})$ concentration increased equilibrium moves to LHS (1)

so electrode potential becomes less negative (1) **[2]**

- (d) (i) 2.74×10^{-3} (mol) [1]
- (ii) 1.37×10^{-3} (mol) [1]
- (iii) $M_r \text{KIO}_3 = 214.1$
moles $\text{KIO}_3 = 0.978 / 214.1 = 4.57 \times 10^{-3}$ in 250 cm^3
 4.57×10^{-4} in 25 cm^3 [1]
- (iv) $1.37 \times 10^{-3} / 4.57 \times 10^{-4} = 3$ (1)
equation 1 is correct since 3 moles of iodine formed (mark awarded for reason) (1) [2]

Total [20]

- Q.5**
- (a) (i) atomisation of magnesium / vaporisation of magnesium [1]
- (ii) increased ratio positive charge on nucleus: number of electrons [1]
- (iii) is positive because the (negative) electron is repelled by negative species [1]
- (iv) lattice enthalpy is $-3835(\text{kJ mol}^{-1})$ numerical value (1) negative sign (1) [2]
- (b) (i) gases are more random/ have more disorder / move more freely and therefore have a higher entropy [1]
- (ii) $\Delta S = 21.8 (\text{JK}^{-1}\text{mol}^{-1})$ [1]
- (iii) $\Delta G = \Delta H - T\Delta S$ (1) ft from (ii)
- ΔG must be $-ve$ if reaction to be spontaneous/ to calculate T make $\Delta G = 0$ (1)
- $0 = 318000 - T 21.8$ $T = 14587/21.8$ (K) (1) [3]
- (c) use of aqueous sodium hydroxide (1)
- white precipitate for all possible ions (1)
- excess aqueous sodium hydroxide – precipitate dissolves for Pb^{2+} and Al^{3+} (1)
- use of aqueous (potassium) iodide/ hydrochloric acid/ sulfuric acid / soluble chloride/ soluble sulfate (1)
- result – yellow ppt for $\text{Pb}^{2+} + \text{I}^-$ and no ppt for Al^{3+} / white ppt for $\text{Pb}^{2+} + \text{Cl}^-$ or SO_4^{2-} and no ppt for Al^{3+} [result for both needed] (1) [5]
- QWC Organisation of information clear and coherent* (1)
- Use of specialist vocabulary* (1) QWC [2]
- (d) (i) diagram to show central Al, 4 Cl^- and 4 shared pairs of electrons, all Cl outer electrons, dative pair identifiable [1]
- (ii) chlorination of benzene (1) produces Cl^+ as electrophile (1)
- OR gives ionic liquids (1) with low vapour pressure/ non-volatile/ do not evaporate in use (1)
- OR catalyst (1) in polymerisation of alkenes (1) [2]
- Total [20]**



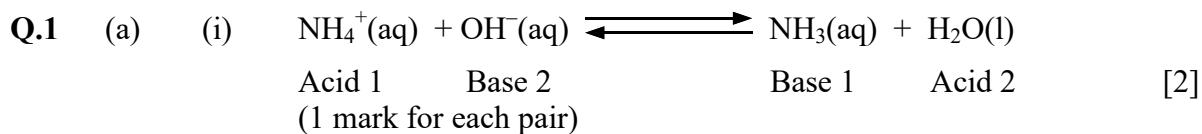
GCE MARKING SCHEME

**CHEMISTRY
AS/Advanced**

SUMMER 2014

GCE CHEMISTRY – CH5
SUMMER 2014 MARK SCHEME

SECTION A



(b) (i)

	$[\text{NH}_4^+(\text{aq})]/\text{mol dm}^{-3}$	$[\text{NO}_2^-(\text{aq})]/\text{mol dm}^{-3}$	Initial rate/ $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.200	0.010	4.00×10^{-7}
2	0.100	0.010	2.00×10^{-7}
3	0.200	0.030	1.20×10^{-6}
4	0.100	0.020	4.00×10^{-7}

(1 mark for each correct answer) [3]

(ii) $k = \frac{4.00 \times 10^{-7}}{0.200 \times 0.010} = 2.0 \times 10^{-4}$ (1)

Units = $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ (1) [2]

(iii) No change [1]

(iv) Increases

If temperature is increased rate increases (1)

and since concentrations do not change the rate constant must increase
 (or similar) (1) [2]

Total [10]

- Q.2**
- (a) $K_w = [H^+][OH^-]$ (1)
 Units = $\text{mol}^2 \text{dm}^{-6}$ (1) [2]
- (b) (i) In pure water $[H^+] = [OH^-]$ or $[H^+] = \sqrt{1.0 \times 10^{-14}}$ (1)
 $\text{pH} = -\log 10^{-7} = 7$ (1) [2]
- (ii) Final volume of solution is 1000 cm^3 so acid has been diluted by a factor of 100 so final concentration of acid is 0.001
 or moles acid = $\frac{0.1 \times 10}{1000} = 0.001$ (1)
 $\text{pH} = -\log 0.001 = 3$ (1) [2]
- (c) $1.78 \times 10^{-5} = \frac{[H^+] \times 0.02}{0.01}$ (1)
 $[H^+] = 8.90 \times 10^{-6}$ (1)
 $\text{pH} = 5.05$ allow 5 or 5.1 (1) [3]
- (d) The solution is a buffer (1)
 Solution contains a large amount of CH_3COOH and CH_3COO^- ions
 (Accept correct equations) (1)
 When an acid is added, the CH_3COO^- ions react with the H^+ ions, removing them from solution and keeping the pH constant (1) [3]

Total [12]

Q.3 (a)



- (b) $20 \text{ dm}^3 \text{ oxygen} = 0.83 \text{ mol}$ (1)
 Moles $\text{H}_2\text{O}_2 = 1.67$ and $[\text{H}_2\text{O}_2] = 1.67 \text{ mol dm}^{-3}$ (1) [2]

- (c) (i) Variable oxidation states / partially filled 3d energy levels / ability to adsorb 'molecules' / form complexes (or temporary bonds) with reacting molecules
 (Accept any two answers)
 Do not accept 'empty / unfilled d-orbitals' [2]

- (ii) 3d orbitals split by ligands (1)
 Three d-orbitals have lower energy, two have higher energy (1)
 Electrons absorb (visible light) energy to jump from lower level to higher level (1)
 The colour is that due to the remaining / non-absorbed frequencies (1)
 (Appropriate diagrams are acceptable alternatives) [4]

QWC Legibility of text; accuracy of spelling, punctuation and grammar, clarity of meaning [1]

- (d) (i) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ [1]
 (ii) $5\text{H}_2\text{O}_2 + 6\text{H}^+ + 2\text{MnO}_4^- \longrightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$ [2]

(Mark consequentially from (i) – 1 mark if formulae correct but equation not balanced properly)

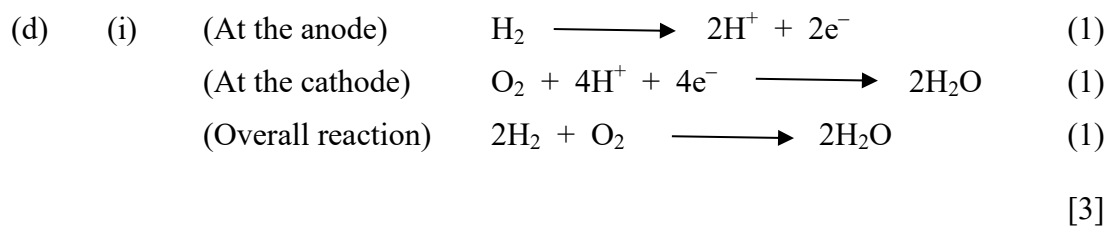
- (iii) Moles $\text{MnO}_4^- = \frac{0.02 \times 14.8}{1000} = 2.96 \times 10^{-4}$ (1)
 Moles $\text{H}_2\text{O}_2 = 7.40 \times 10^{-4}$ (1)
 Concentration $\text{H}_2\text{O}_2 = \frac{7.40 \times 10^{-4}}{0.020} = 0.037 \text{ mol dm}^{-3}$ (1) [3]

- (e) Oxidation state of oxygen starts at -1 (in peroxide) (1)
 Oxidation state in water is -2 (reduced)
 oxidation state in oxygen is 0 (oxidised) (1) [2]

Total [18]

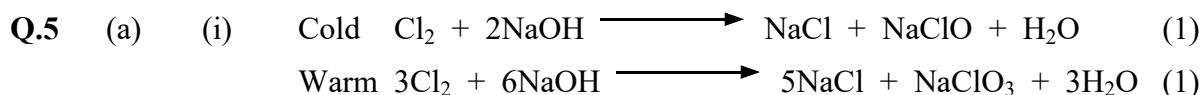
SECTION B

- Q.4** (a) (i) Oxidising agent [1]
- (ii) A = lead(II) chloride / PbCl_2 (1)
- B = chlorine / Cl_2 (1) [2]
- (iii) $[\text{Pb}(\text{OH})_6]^{4-}$ / $[\text{Pb}(\text{OH})_4]^{2-}$ / $\text{Na}_4[\text{Pb}(\text{OH})_6]$ etc. [1]
- (iv) Yellow [1]
- (v) $\text{PbO} + 2\text{HNO}_3 \longrightarrow \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}$ [1]
- (b) (i) Each C atom covalently bonded to three other C atoms forming layers (1)
- Layers held together by weak intermolecular forces (1)
- BN is isoelectronic with C so it forms similar structures (1)
- Graphite conducts electricity since electrons are delocalised but in BN, each N has a full unbonded p-orbital and each B has an empty unbonded p-orbital so it does not conduct electricity (1) [4]
- (Accept electrons are not delocalised in BN so it does not conduct electricity)
- QWC The information is organised clearly and coherently, using specialist vocabulary where appropriate* [1]
- (ii) Wear-resistant coatings/catalyst support/for mounting high power electronic components / drills in industry / cutting instruments [1]
- (c) (i) $\Delta G = \Delta H - T \Delta S$ ($\Delta G = 0$ for reaction to be spontaneous) (1)
- $T = \frac{1.92}{0.0067}$ (1)
- $T = 286.6 \text{ K}$ (1) [3]
- (ii) Changes in temperature (above or below 286.6 K) caused the tin to change form making it unstable (and causing it to disintegrate) [1]



- (ii) Hydrogen is difficult to store / takes up large volume / too flammable / explosive / produced from fossil fuels which leads to a net energy loss / Pt electrodes very expensive [1]

Total [20]



[2]

(ii) Disproportionation [1]

- (b) P can (extend the normal octet of electrons) by using 3d orbitals /
 P can promote 3s electron to 3d orbital (1)
 N cannot do this since it is in the second period / 3d orbitals not available (1)
 [2]

- (c) The terms involved are: lattice breaking enthalpy which is endothermic (1)
 and hydration enthalpy which is exothermic (1)
 $\Delta H_{\text{solution}} = \Delta H_{\text{lattice breaking}} + \Delta H_{\text{hydration}}$ (or similar) (1)
 If $\Delta H_{\text{solution}}$ is negative then the ionic solid will be soluble (1)

[4]

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter [1]

- (d) (i) Iodide (1)
 Only one with less positive standard potential than
 Fe^{3+} , Fe^{2+} half-cell (1)
 (2nd mark can be obtained from calculation value and statement) [2]

- (ii) $\text{Pt(s)} | \text{Fe}^{2+}(\text{aq}), \text{Fe}^{3+}(\text{aq}) || \text{Ce}^{4+}(\text{aq}), \text{Ce}^{3+}(\text{aq}) | \text{Pt(s)}$ (1)
 $\text{EMF} = 1.45 - 0.77 = 0.68 \text{ V}$ (1) [2]

- (e) (i) $K_c = \frac{[\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{OH}]}$ (1)
 No units (1) [2]

- (ii) $\text{moles} = \frac{1.25 \times 32.0}{1000} = 0.04(0)$ [1]

- (iii) $[\text{CH}_3\text{COOH}] = 0.04$, therefore 0.06 used in reaction and
 $[\text{CH}_3\text{COOCH}_3] = 0.06$, $[\text{H}_2\text{O}] = 0.06$ and
 $[\text{CH}_3\text{OH}] = 0.083 - 0.06 = 0.023$ (1)
 $K_c = \frac{0.06 \times 0.06}{0.04 \times 0.023} = 3.91$ (1) [2]

- (iv) Value of K_c decreases since the equilibrium shifts to the left /
 the forward reaction is exothermic [1]

Total [20]



GCE A level

1095/01-A



S15-1095-01A

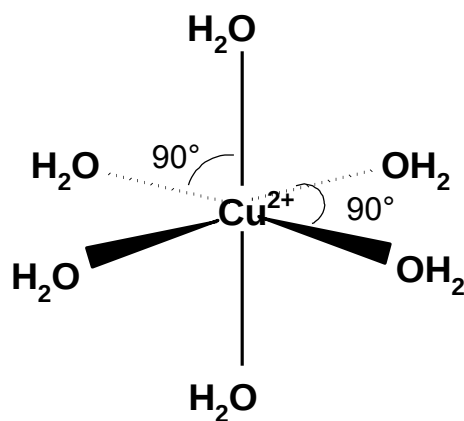
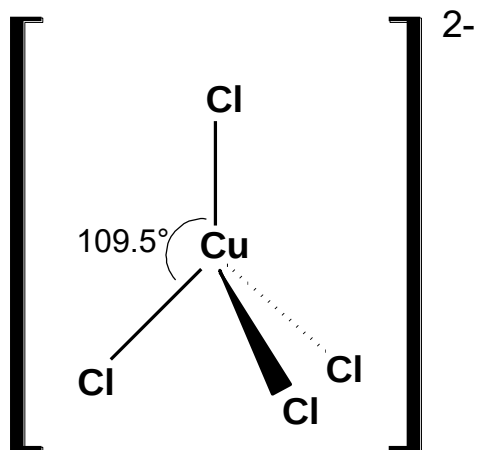
**CHEMISTRY – PERIODIC TABLE
FOR USE WITH CH5**

P.M. MONDAY, 15 June 2015

CH5

SECTION A

1. (a) (i) Species with lone pair that can bond to a metal atom/ion (1) [1]
- (ii) Must clearly show which atoms are bonded and the 3D structure
1 mark each (2) [2]



- (iii) Ligands cause d-orbitals to split into three lower and two higher (1)
Electrons move from lower level to higher level by absorbing some frequencies (1)
Light not absorbed gives colour seen (1) [3]
- (iv) $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ (1) Royal blue (1) [2]

(b) (i) $K_p = \frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}}$ do not accept if [] included [1]

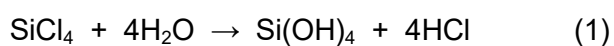
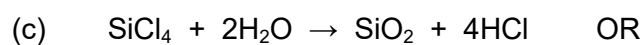
(ii) I. 1.3×10^5 (Pa) [1]

II. $P_{PCl_5} = 3.0 \times 10^5 - 1.3 \times 10^5 = 1.7 \times 10^5$ (1) (ecf from part I)

$K_p = (1.3 \times 10^5 \times 1.3 \times 10^5) / 1.7 \times 10^5 = 9.9 \times 10^4$ (1)

Pa (1) [3]

III. Endothermic as equilibrium shifts to products when temperature increases [1]



Silicon has available empty d-orbitals whilst carbon does not /
Silicon can expand its octet whilst carbon cannot (1) [2]

Total [16]

2. (a) $2 \times (0) + 3 \times (-394) - (-826) - 3 \times \Delta H_f^\theta(\text{CO}) = -23$ (1)
- $$2 \times (\Delta H_f^\theta(\text{Fe})) + 3 \times (\Delta H_f^\theta(\text{CO}_2)) - (\Delta H_f^\theta(\text{Fe}_2\text{O}_3)) - 3 \times \Delta H_f^\theta(\text{CO}) = -23$$
- (1)
- $$-1182 + 826 + 23 = 3 \times \Delta H_f^\theta(\text{CO})$$
- $$-333 = 3 \times \Delta H_f^\theta(\text{CO})$$
- $$-111 \text{ kJ mol}^{-1} = \Delta H_f^\theta(\text{CO})$$
- (1) [3]
- (b) Gases have higher entropies than solids as the molecules have a greater degree of freedom / disorder [1]
- (c) (i) $\Delta G = \Delta H - T \Delta S = -23 - (298 \times 9/1000)$ (1)
- $$= -25.7 \text{ kJ mol}^{-1}$$
- (1) [2]
- (ii) A reaction is feasible when ΔG is negative (1)
- No temperature exists where ΔG is positive / ΔG is negative at all temperatures (1) [2]
- (iii) Higher temperature used to increase rate of reaction [1]
- Total [9]**

3. (a) +1 occurs due to inert pair of s-electrons (1)
Inert pair effect becomes more significant down the group (1) [2]

- (b) (i)

B	H	
78.14	21.86	
10.8	1.01	
7.235	21.644	(1)
1	3	

Empirical formula = BH_3 (1) [2]

- (ii) Number of moles = $1/22.4 = 4.46 \times 10^{-2}$ moles (1)

$$M_r = 1.232 / 4.46 \times 10^{-2} = 27.6 \text{ (1)}$$

Molecular formula = B_2H_6 (1) [3]

- (c) Outer/valence shell of electrons is not full / does not have an octet [1]

- (d) $\text{B}_5\text{H}_9 + 15\text{H}_2\text{O} \rightarrow 5\text{H}_3\text{BO}_3 + 12\text{H}_2$ [1]

- (e) The compound is less stable than the elements [1]

- (f) Any 3 from 4 points for (1) each

All atoms the same in graphite / BN alternate in boron nitride (1)

Atoms in layer of BN lie above each other but are not in graphite (1)

B—N bonds are polarised (or indicated dipole) but graphite is non-polar (1)

p-electrons in BN are localised but in graphite are delocalised (1) [3]

QWC Organisation of information clearly and coherently; use of specialist vocabulary where appropriate [1]

- (g) Mass number = 7 Atomic number = 3 [1]

Total [15]

SECTION B

4. (a) Filtration [1]
- (b) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ [1]
- (c) (i) Carbon O.S. at start = +3; Carbon O. S. at end = +4 [1]
- (ii) $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$ [1]
- (d) Colour change of manganate(VII) is used to indicate the change [1]
- (e) Volume of manganate(VII) = 27.92 cm^3 (1)
- Moles manganate = $27.92 \times 0.020 / 1000 = 5.584 \times 10^{-4} \text{ mol}$ (1)
- Moles oxalate = $5.584 \times 10^{-4} \times 5/2 = 1.396 \times 10^{-3} \text{ mol}$ (1)
- Concentration = $1.396 \times 10^{-3} / 25 \times 10^{-3} = 0.0558 \text{ mol dm}^{-3}$ (1) [4]
- (f) (i) $K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$ [1]
- (ii) $[\text{H}^+]^2 = K_a \times [\text{HCOOH}] = 1.8 \times 10^{-4} \times 0.2 = 0.36 \times 10^{-4}$ (1)
- $[\text{H}^+] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ (1)
- $\text{pH} = -\log [\text{H}^+] = 2.22$ (1) [3]
- (iii) A buffer keeps the pH almost constant when **small amounts** of acid or base are added (1)
- $\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+$ (1)
- Adding acid shifts the equilibrium to the left which removes H^+ /
 Adding base removes H^+ shifts equilibrium to right which replaces H^+ (1)
 OR answer in terms of H^+ reacting with methanoate from
 sodium methanoate when acid added (1) and methanoic acid replacing H^+
 when base removes H^+ (1)
- MAX 3 [3]
- QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter* [1]
- (g) (i) Orange to green [1]
- (ii) CrO_4^{2-} (1) Yellow (1) [2]

Total [20]

5. (a) Lead(II) iodide or PbI_2 (1) Bright yellow (1) [2]
- (b) $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2$ (1)
- The precipitate is copper(I) iodide (stated or clearly indicated by state symbols) (1) [2]
- (c) Bromine has a more positive $E^\ominus$ than iodine so it is a stronger oxidising agent (1)
- Bromine is able to oxidise iodide (1)
- Bromine has a less positive $E^\ominus$ than chlorine so it is a weaker oxidising agent (1)
- Bromine is not able to oxidise chloride (1)
- MAX 3
- OR Calculate EMF for each reaction (1 each) and state that positive EMF means reaction is feasible (1) [3]
- QWC Legibility of text, accuracy of spelling, punctuation and grammar, clarity of meaning* [1]
- (d) 1 mark for each two products or observations
 KHSO_4 HI H_2S SO_2 S I_2 [MAX 2 for products]
- Yellow solid rotten egg smell steamy fumes
- Black solid or brown solution or purple fumes
- MAX 3 [3]
- (e) (i) Measure time taken for a sudden colour change (1)
 Rate = $1 \div \text{time}$ (1) [2]
- (ii) I. pH 1 has a concentration of H^+ ten times higher than pH 2. [1]
- II. Order with respect to H_2O_2 = 1 (1)
 Order with respect to I^- = 1 (1)
 Order with respect to H^+ = 0 (1) [MAX 2 for the stated orders]
 Rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$ (1) [3]
- III. $k = 0.028$ (1) $\text{mol}^{-1}\text{dm}^3 \text{s}^{-1}$ (1) [ecf from rate equation] [2]
- IV. Rate equation is unchanged and increasing temperature increases the value of the rate constant [1]

Total [20]



GCE A level

1095/01-A



S16-1095-01A

**CHEMISTRY – PERIODIC TABLE
FOR USE WITH CH5**

A.M. WEDNESDAY, 22 June 2016

GCE CHEMISTRY - CH5
SUMMER 2016 MARK SCHEME

SECTION A

1. (a) (i) Calculation of rates, at least two concentrations (1)
As concentration doubles, rate doubles (1)
Accept answers in terms of time instead of rate calculation
e.g. [0.064] 20 s, [0.032] 40 s (1)
As concentration doubles, time halves therefore rate doubles (1)
In both cases, values from graph must be used in order to award first mark
[2]
- (ii) I Zero order (1)
First order (1) [2]
- II Rate = $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$ [1]
- III 7.0×10^{-5} (1)
 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (1)
Error carried forward (ecf) from parts I and II [2]
- (b) (i) The slowest step in the reaction [1]
- (ii) First step has 2 molecules of NO_2 as the only reactant (1)
(e.g. $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$)
Second step has CO as reactant with products from step 1 (1)
(e.g. $2\text{NO} + \text{O}_2 + 2\text{CO} \rightarrow 2\text{NO} + 2\text{CO}_2$)
Both equations must be balanced
[2]
- Total [10]

2. (a) A weak acid is one that partially dissociates (in aqueous solution) (1)
 A dilute acid is one where a small amount of acid has been dissolved in a large volume of water (1) [2]
- (b) (i) $0.1 \text{ mol dm}^{-3} \text{ HCl}$ / **W** (1)
 Only acid with pH of 1 / curve starts at 1 / strong acid since centre of vertical region is around pH 7 (1) [2]
- (ii) $0.1 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$ / **Y** (1)
 Weak acid since vertical region of curve is between 6 and 10 /
 centre of vertical region is around pH 8 /
 part of curve shows buffering effect (1)
 pH is about 3 at start so concentration cannot be 0.001 (1) [3]
- (iii) Thymol blue (1)
 pH range coincides with pH change during sharp rise in curve **B** (1) [2]
- (iv) Volume NaOH at equivalence point = 30.0 cm^3 (1)
 Concentration NaOH = $0.083(3) \text{ mol dm}^{-3}$ (1)
 Ecf from part (i) [2]
- (c) Salt hydrolysis occurs $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$
 (Accept NH_4^+ partially dissociates to release H^+) [1]

Total [12]

3. (a) $K_w = [\text{H}^+][\text{OH}^-] \text{ mol}^2 \text{ dm}^{-6}$ [1]
- (b) $\text{pH} = 7$, therefore $[\text{H}^+] = 1.0 \times 10^{-7}$ (1)
- $$[\text{OH}^-] = \frac{5.13 \times 10^{-13}}{1.0 \times 10^{-7}} = 5.13 \times 10^{-6} \quad (1)$$
- $[\text{OH}^-] > [\text{H}^+]$ therefore solution is alkaline (1)
- Alternative method
- $$[\text{H}^+] = 7.16 \times 10^{-7} \text{ at } 100^\circ\text{C} \quad (1)$$
- $\text{pH} = 6.15$ (1)
- $\text{pH} 7$ above neutral so $[\text{OH}^-] > [\text{H}^+]$ and solution is alkaline (1) [3]
- (c) Half-cell where hydrogen at 1 atm (1)
- Bubbles over a Pt electrode in contact with $1 \text{ mol dm}^{-3} \text{H}^+(\text{aq})$ at 298K (1) [2]
- (d) (i) $\Delta H = (-394) + 2(-286) - (-75)$ (1)
- $$\Delta H = -891 \text{ kJ mol}^{-1} \quad (1) \quad [2]$$
- (ii) Heat per unit mass $\text{H}_2 = \frac{286}{2.02} = 141.6 \text{ kJ g}^{-1}$ (1)
- $$\text{Heat per unit mass } \text{CH}_4 = \frac{891}{16.04} = 55.5 \text{ kJ g}^{-1} \quad (1) \quad [2]$$
- (e) The fuel cell uses electrochemical methods to get energy from hydrogen / generates EMF / creates a flow of electricity (1)
- Hydrogen is oxidised producing H^+ ions and electrons at anode (1)
- (Accept equation)
- Oxygen is reduced at the cathode to water (1)
- (Accept equation) [3]
- QWC Legibility of text; accuracy of spelling, punctuation and grammar, clarity of meaning* [1]
- (f) (i) $K_p = \frac{(\text{pNH}_3)^2}{(\text{pH}_2)^3(\text{pN}_2)}$ do not accept [] [1]
- (ii) $\text{pH}_2 = 58 \text{ atm}$ and $\text{pNH}_3 = 16 \text{ atm}$ (1)
- $$K_p = 7.3 \times 10^{-5} \quad (1)$$
- Units = atm^{-2} (1)
- Ecf from part (i) but not from incorrect partial pressures [3]

Total [18]

SECTION B

4. (a) (i) Good catalysts [1]
- (ii) Cu^+ has full 3d orbitals (1)
(Accept electronic configuration)
Electrons cannot move from lower energy 3d orbitals to higher ones (1)
[2]
- (b) Suitable example of ligand substitution (1)
e.g. reaction of excess ammonia solution with $\text{CuSO}_4/[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
Suitable observation (1)
e.g. formation of royal blue solution
Correct formula (1)
e.g. $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$
Suitable example of precipitation (1)
e.g. reaction between CuSO_4 and NaOH
Suitable observation (1)
e.g. pale blue precipitate
Correct formula (1)
e.g. $\text{Cu}(\text{OH})_2$ [6]
- QWC The information is organised clearly and coherently, using specialist vocabulary where appropriate* [1]
- (c) (i) Starch [1]
- (ii) Moles $\text{S}_2\text{O}_3^{2-} = 4.80 \times 10^{-3}$ (1)
Moles Cu^{2+} in original solution = 1.92×10^{-2} (1)
Mass Cu = 1.22 g (1)
Percentage Cu = 59.5 % (1) [4]
- (d) (i) Salt bridge (1)
It completes the circuit by allowing the ions to move (1) [2]
- (ii) Cu electrode since electrons flow to it through the external circuit /
Cu has more positive E^θ - do not accept 'higher E^θ ' [1]
- (iii) 0.78 V [1]
- (iv) No – Fe better reducing agent / has more negative E^θ / emf is negative [1]

Total [20]

5. (a) (i) Oxidation state II becomes more stable / oxidation state IV becomes more unstable (1)
Inert pair effect / the two outer s electrons become more stable (as group is descended) (1) [2]
- (ii) Carbon dioxide is acidic while lead(II) oxide is amphoteric (1)
e.g. $\text{CO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ (1)
 $\text{Pb}^{2+} + 2\text{OH}^- \rightarrow \text{Pb}(\text{OH})_2$
 $\text{Pb}(\text{OH})_2 + 2\text{OH}^- \rightarrow [\text{Pb}(\text{OH})_4]^{2-}$ (1)
or
 $\text{PbO} + 2\text{HNO}_3 \rightarrow \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O}$
 $\text{PbO} + 2\text{OH}^- + \text{H}_2\text{O} \rightarrow [\text{Pb}(\text{OH})_4]^{2-}$ (1)
Carbon monoxide is a reducing agent while lead(IV) is an oxidizing agent (1)
e.g. $\text{CO} + \text{CuO} \rightarrow \text{CO}_2 + \text{Cu}$ (1)
 $\text{PbO}_2 + 4\text{HCl} \rightarrow \text{PbCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ (1) [6]
- QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter* [1]
- (b) (i) A gas (and a liquid) forms / more moles form in the reaction and the molecules have more freedom [1]
(ii) $\Delta S = 530 \text{ (J K}^{-1} \text{ mol}^{-1})$ [1]
(iii) $\Delta G = 135 - 298(0.53)$ (1)
 $\Delta G = -22.9 \text{ (kJ mol}^{-1})$ (1)
 ΔG is negative so the reaction is feasible (1) [3]
- (c) $\Delta H_f = \Delta H_{\text{at}}\text{Ba} + \text{I.E. Ba} + \Delta H_{\text{at}}\text{Cl}_2 + \text{E.A. Cl} + \Delta H_{\text{lat}}\text{BaCl}_2$ (1)
Doubling value for forming 2Cl and 2Cl^- (1)
(These marks can be obtained from Born-Haber cycle)
 $\Delta H_f \text{BaCl}_2 = 176 + 1468 + 242 - 728 - 2018$ (1)
 $\Delta H_f \text{BaCl}_2 = -860 \text{ (kJ mol}^{-1})$ (1) [4]
- (d) $\text{NaCl} / \text{Cl}^-$ (1)
 $\text{NaClO}_3 / \text{ClO}_3^-$ (1) [2]

Total [20]