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) $K_w = [H^+][OH^-]$ 1 mark [1]

(ii) Equilibrium constant increases with temperature, so must be an endothermic process. 1 mark [1]

(iii) $K_w = 4.3 \times 10^{-14}$ ($mol^2 dm^{-6}$) 1 mark [1]

(iv) $[H^+] = \sqrt{4.3} \times 10^{-14} = 2.07 \times 10^{-7}$ mol dm^{-3} 1 mark
(allow 2.1 but not 2)

pH = –log (2.07×10^{-7}) = 6.7 1 mark [2]
(Mark consequentially if K_w or $[H^+]$ are incorrect)

(b) (i) End point = 20.0 cm^3 (*allow* 20 cm^3) 1 mark
$[NH_3] \times 25.0 = 0.100 \times 20.0$ 1 mark for setting up equation
$[NH_3]$ = 0.080 mol dm^{-3} 1 mark (must be two significant figures) [3]

(ii) $NH_4^+ \rightleftharpoons NH_3 + H^+$ / 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 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 CO_2 greenhouse gas produced/H_2 available from renewable sources 1 mark [1]

(d) (i) Mass = (30/100) × 1000 = 300 g 1 mark
No moles $NaBH_4$ = 300 / 37.84 = 7.93 moles 1 mark [2]

(ii) Energy = 7.93 × 300 = 2379 kJ 1 mark [1]
(*Mark consequentially on the no moles in* (i))

(iii) 7.93 × 4 = 31.72 mol H_2 gas 1 mark
Volume = 31.72 × 24 = 761.2 dm^3 1 mark [2]
(*Mark consequentially on the no moles in* (i))

Total [15]

SECTION B

4. (a) (i) Rate = 0.0020 / 17.5 = 1.14×10^{-4} mol dm^{-3} min^{-1}
(*or* 1.90×10^{-6} mol dm^{-3} s^{-1}) Value 1 mark, units 1 mark [2]

(ii) Follow the decrease in brown colour due to the Br_2
/ use a colorimeter 1 mark
Reference to the measurement of time 1 mark [2]

(iii) $Br_2(aq)$ zero order 1 mark
$CH_3COCH_3(aq)$ 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, [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 [CH_3COCH_3] [H^+] 1 mark
Units of k are mol^{-1} dm^{+3} 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) $Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$
or $CuSO_4 + Ca(OH)_2 \rightarrow Cu(OH)_2 + Ca\,SO_4$ 1 mark [1]

(b) (i) Starch 1 mark
Blue to colourless 1 mark [2]

(ii) No moles $Na_2S_2O_3 = 12.25 \times 0.100 / 1000 = 1.225 \times 10^{-3}$ 1 mark
Mass Cu $= 1.225 \times 10^{-3} \times 63.5 = 0.0778$ 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) Cu^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ 1 mark
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
$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ 1 mark [3]
(Allow $Si(OH)_4$)

(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 insert pair effect becomes more significant down the group [2]

Total [20]

GCE MARKING SCHEME

CHEMISTRY
AS/Advanced

SUMMER 2011

CHEMISTRY - CH5

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

(b) Chromium atom, Cr [1]

↓↑	↓↑	↓↑ ↓↑ ↓↑	↓↑	↓↑ ↓↑ ↓↑	↑ ↑ ↑ ↑ ↑	↑
1s	2s	2p	3s	3p	3d	4s

Chromium(III) ion, Cr^{3+} [1]

↓↑	↓↑	↓↑ ↓↑ ↓↑	↓↑	↓↑ ↓↑ ↓↑	↑ ↑ ↑	
1s	2s	2p	3s	3p	3d	4s

(c) (i) Orange → yellow [1]

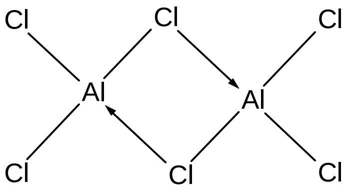
(ii) Cr +6 (1) in both reactant and product - do not accept 6+
no change in oxidation states so not a redox reaction. (1) [2]

(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)



[1]

(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 '$AlCl_3$ 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) $H_2 + ½ O_2 \rightarrow H_2O$ [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) $\Delta H = 2 \times \Delta H\ (H_2O) + \Delta H\ (CO_2) - \Delta H(CH_3OH)$
= 2 x -286 + (-394) –(-239) (1)
= -727 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) ΔG = -727000 – (298x -81) = -703 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 = Rate ÷ [N_2O_5] e.g. k = $3.00 \times 10^{-5} \div 4.00 \times 10^{-3}$ (1)
= 7.50×10^{-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) $K_p = \frac{p_{N_2O_4}}{p_{NO_2}^{\,2}}$ [1]

(ii) Increasing temp shifts equilibrium to left / favours endothermic reaction (1) so value of K_p is decreased. (1) [2]

(iii) P_{N2O4} = 9.5×10^3 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) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ [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) $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$ [1]

(ii) Moles $Cr_2O_7^{2-}$ = 23.80 x 0.0200 ÷ 1000 = 4.76 x 10^{-4} moles (1)
Moles Fe^{2+} = 4.76 x 10^{-4} x 6 = 2.86 x 10^{-3} moles (1) [2]

(iii) Mass Fe in sample = 2.86 x 10^{-3} x 10 x 55.8 = 1.59 g (1)
Percentage Iron = 1.59 ÷ 1.870 x 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) $Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$ [1]

(ii)
- Emf for reaction of bromide with chlorine is +0.27 V / E^θ for chlorine is more positive than for bromine. (1)
- Emf for reaction of bromide with iodine is -0.55 V / E^θ for iodine is less positive than for bromine. (1)
- Reactions are only feasible if Emf is positive / if E^θ 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) $K_a = \dfrac{[H^+][OCl^-]}{[HOCl]}$ [1]

(iii) $[H^+] = 10^{-pH}$ OR $pH = -\log [H^+]$ (1)
$[H^+] = 5.88 \times 10^{-5}$ mol dm^{-3} (1) [2]

(iv) $K_a = \dfrac{[H^+][OCl^-]}{[HOCl]} = \dfrac{(5.88 \times 10^{-5})^2}{0.100}$ (1)= 3.47×10^{-8} (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 g (1) [2]

(b) (i) 2 mol of $K_2S_2O_8$ give 1 mol of O_2
2 mol of $K_2S_2O_8$ give 29.0 dm^3 of O_2 (1)
$\therefore$ 0.1 mol of $K_2S_2O_8$ gives 29.0/20 = 1.45 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 = $k\,[S_2O_8^{2-}]\,[I^-]$ (1)

$$\therefore\ k = \frac{8.64 \times 10^{-6}}{0.0400 \times 0.0100}$$

= 0.0216 (1) $dm^3\ mol^{-1}\ s^{-1}$ (1) [3]

(iii) In the rate equation one $S_2O_8^{2-}$ 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 $P6^{2+}$ / 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 E^θ value and therefore iodide is the better reducing agent (1) and is 'strong' enough to reduce the sulfuric acid. / OWTTE (1) [2]

(d) (i) $2\,NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$ [1]

(ii) e.g. bleach, kills bacteria [1]

Total [11]

3. (a) (i)

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

- error carried forward throughout (a)

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

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

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

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

(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 '$3d^9$' / partly filled 3d sub-shell (1)
whereas Zn^{2+} ions are '$3d^{10}$' / 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
$[CuCl_4]^{2-}$	tetrahedral	yellow / lime green
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	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 [1]
longer lasting / less toxic catalysts

Total [15]

SECTION B

4. (a) CO → C +2 CO_2 → +4 (1)

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

OR

I_2O_5 → I +5 I_2 → I_2 0 (1)

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

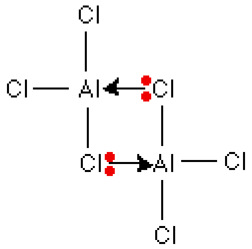
(b) +2 state becomes mores stable down the group and +4 becomes less stable. [1]

(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) $Pb^{2+} + 2\,I^- \rightarrow PbI_2$ [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)



(1) [3]

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

$T = 60\,000 / 88 = 682$ K / 409°C (1) [2]

(e) $$K_c = \frac{[[\mathrm{Al(H_2O)_5(OH)}\ ]^{2+}(aq)][[H^+](aq)]\}}{[[\mathrm{Al(H_2O)_6}]^{3+}(aq)]}$$

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

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

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

- error carried forward

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

Total [20]

5. (a) (i) $K_p = \dfrac{pSO_3(g) \times pNO(g)}{pSO_2(g) \times pNO_2(g)}$ (1) there are no units (1) [2]

(ii) The line for SO_3 / NO at equilibrium should be above the SO_2 / 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 $= \dfrac{40}{80} = 0.50$ (1)

- error carried forward

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

$\therefore$ Temperature drop = 2.5 × 6.2 = 15.5°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) $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$ must be square brackets **[1]**

(ii) $K_c = \dfrac{0.11^2}{3.11^2} = 1.25 \times 10^{-3}$ 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 α concentration (1)

OR

constant half-life (1)

half-life is 24 minutes (1) **[2]**

(ii) rate = k[N_2O_5] (1) **[1]**

(iii) k = rate (from (i))/ [N_2O_5] (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 [N_2O_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) $K_a = \dfrac{[HCOO^-][H^+]}{[HCOOH]}$ **[1]**

(ii) $1.75 \times 10^{-4} = \dfrac{x^2}{0.1}$ (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)

$Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ (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 VO_3^-/VO^{2+} and VO^{2+}/V^{3+} and therefore

releases electrons/ VO_3^-/VO^{2+} and VO^{2+}/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) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e$ / $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e$ with some indication of direction **[1]**

(iv) if $Zn^{2+}(aq)$ 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 KIO_3 = 214.1

moles KIO_3 = 0.978/ 214.1 = 4.57×10^{-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(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) $\Delta S = 21.8$ ($JK^{-1}mol^{-1}$) **[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 = 14587/14600 (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 Pb^{2+} + I^- and no ppt for Al^{3+} / white ppt for Pb^{2+} + 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

Q.1 (a) (i) $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$

Acid 1 Base 2 Base 1 Acid 2 [2]
(1 mark for each pair)

(b) (i)

	$[NH_4^+(aq)]$/mol dm^{-3}	$[NO_2^-(aq)]$/mol dm^{-3}	Initial rate/mol dm^{-3} 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	$\mathbf{4.00 \times 10^{-7}}$

(1 mark for each correct answer) [3]

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

Units = $mol^{-1}\ dm^3\ s^{-1}$ (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 = $mol^2\ dm^{-6}$ (1) [2]

(b) (i) In pure water $[H^+] = [OH^-]$ or $[H^+] = \sqrt{1.0 \times 10^{-14}}$ (1)

$pH = -\log 10^{-7} = 7$ (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 = $\dfrac{0.1 \times 10}{1000} = 0.001$ (1)

$pH = -\log 0.001 = 3$ (1) [2]

(c) $1.78 \times 10^{-5} = \dfrac{[H^+] \times 0.02}{0.01}$ (1)

$[H^+] = 8.90 \times 10^{-6}$ (1)

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)

$$\mathrm{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}} : \mathrm{H}$$ [1]

(b) 20 dm^3 oxygen = 0.83 mol (1)

Moles H_2O_2 = 1.67 and $[H_2O_2]$ = 1.67 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) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ [1]

(ii) $5H_2O_2 + 6H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$ [2]

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

(iii) Moles MnO_4^- = $\dfrac{0.02 \times 14.8}{1000} = 2.96 \times 10^{-4}$ (1)

Moles H_2O_2 = 7.40×10^{-4} (1)

Concentration H_2O_2 = $\dfrac{7.40 \times 10^{-4}}{0.020}$ = 0.037 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) $[Pb(OH)_6]^{4-}$ / $[Pb(OH)_4]^{2-}$ / $Na_4[Pb(OH)_6]$ etc. [1]

(iv) Yellow [1]

(v) $PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$ [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)

$T = \dfrac{1.92}{0.0067}$ (1)

T = 286.6 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]

(d) (i) (At the anode) $H_2 \longrightarrow 2H^+ + 2e^-$ (1)

(At the cathode) $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (1)

(Overall reaction) $2H_2 + O_2 \longrightarrow 2H_2O$ (1)

[3]

(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]

Q.5 (a) (i) Cold $Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O$ (1)

Warm $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$ (1)

[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)

ΔH solution = ΔH lattice breaking + ΔH hydration (or similar) (1)

If ΔH 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) [2]
(2nd mark can be obtained from calculation value and statement)

(ii) $Pt(s)\,|\,Fe^{2+}(aq), Fe^{3+}(aq)\,||\,Ce^{4+}(aq), Ce^{3+}(aq)\,|\,Pt(s)$ (1)

EMF = 1.45 – 0.77 = 0 .68 V (1) [2]

(e) (i) $K_c = \dfrac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$ (1)

No units (1) [2]

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

(iii) $[CH_3COOH] = 0.04$, therefore 0.06 used in reaction and

$[CH_3COOCH_3] = 0.06$, $[H_2O] = 0.06$ and

$[CH_3OH] = 0.083 - 0.06 = 0.023$ (1)

$K_c = \dfrac{0.06 \times 0.06}{0.04 \times 0.023} = 3.91$ (1) [2]

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

Total [20]