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) $[Mg^{2+}(aq)] = [CO_3^{2-}(aq)] = 3.16 \times 10^{-3} \text{ mol dm}^{-3}$ 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 = $-\log(2.07 \times 10^{-7}) = 6.7$ 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* $H_2 + ½O_2 \rightarrow H_2O$ 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]