Candidate Name	Centre Number	Candidate Number
		2

GCE A level

1095/01

CHEMISTRY CH5

A.M. MONDAY, 28 June 2010

1¾ hours

Merged WJEC Paper 5s & Mark Schemes

June 2010 - June 2016

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

1095 01 01

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- a copy of the **Periodic Table** supplied by WJEC.
  Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

SECTION A

Answer **all** *the questions in the spaces provided.*

1. *(a)* Magnesium carbonate decomposes on heating.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

(i) Given the enthalpy change of formation, $\Delta H_f^{\ominus}$, values below, calculate the enthalpy change, $\Delta H^{\ominus}$, for the decomposition of magnesium carbonate. [1]

Species	Enthalpy change of formation $\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CO_2(g)$	–393.5
$MgCO_3(s)$	–1095.8
MgO(s)	–601.7

.....

.....

.....

(ii) The entropy change, $\Delta S^{\ominus}$, for the decomposition is 174.8 J mol^{-1}K^{-1}. Explain why there is an increase in entropy for this reaction. [1]

.....

.....

(iii) Convert the value of $\Delta S^{\ominus}$ into units of kJ mol^{-1}K^{-1}. [1]

.....

.....

(iv) Using your answers to *(a)*(i) and (iii), determine, in degrees K, the temperature above which magnesium carbonate would decompose spontaneously. [3]

.....

.....

.....

(b) The solution of ionic compounds such as magnesium carbonate or sodium carbonate in water at 20 °C (room temperature) can be represented by the equations

$$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$$

$$Na_2CO_3(s) \rightleftharpoons 2Na^+(aq) + CO_3^{2-}(aq)$$

Use the free energy change, ΔG, values in the table to comment on the solubilities of magnesium carbonate and sodium carbonate in water. [2]

Solution	Free Energy Change ΔG / kJ mol^{-1}
$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	+28.2
$Na_2CO_3(s) \rightleftharpoons 2Na^+(aq) + CO_3^{2-}(aq)$	–4.3

.....

.....

.....

Examiner only

(c) As solids do not affect the position of equilibrium, for the solution equilibrium

$$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$$

the simplest expression for the equilibrium constant, K_c, can be written

$$K_c = [Mg^{2+}(aq)][\ CO_3^{2-}(aq)]$$

(i) Given that the solubility of $MgCO_3$ at 20 °C is 3.16×10^{-3} mol dm^{-3}, state the molar concentrations of magnesium ions, $Mg^{2+}(aq)$, and carbonate ions, $CO_3^{2-}(aq)$, in a saturated $MgCO_3$ solution. [1]

.....

.....

(ii) Hence calculate the value of K_c at 20 °C. [1]

.....

.....

(iii) Giving your reasons, state whether the value of K_c is consistent with the value of the free energy change, ΔG, given for this reaction in *(b)*. [1]

.....

.....

(iv) By applying Le Chatelier's Principle to the chemical equation above, and giving your reasons, state the effect on the solubility of magnesium carbonate of adding sodium carbonate to the solution. [1]

.....

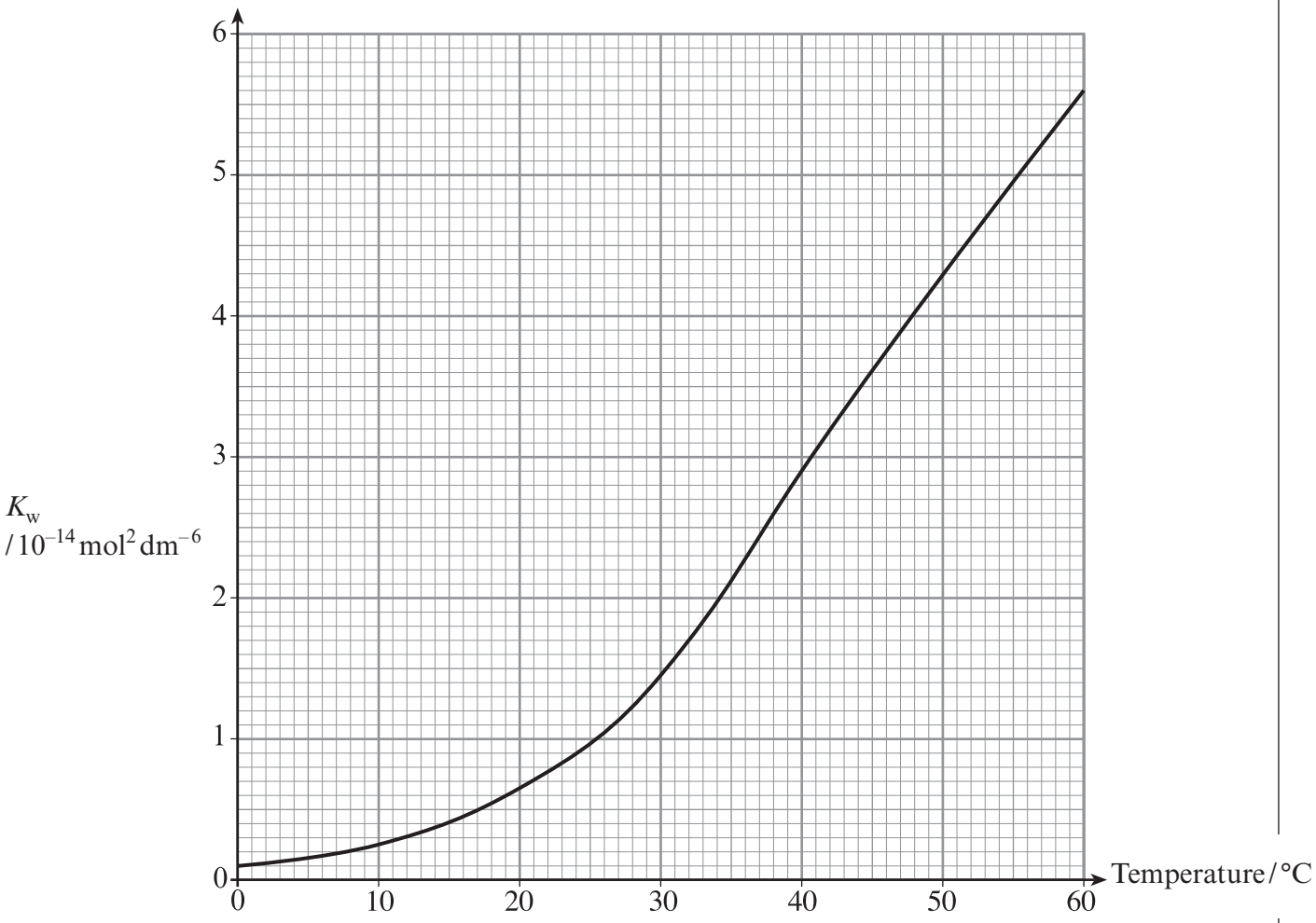
.....

Total [12]

BLANK PAGE

Examiner only

2. *(a)* The diagram shows the variation of the ionic product of water, K_w, with temperature.



(i) Give the expression for the ionic product of water, K_w. [1]

(ii) By reference to the diagram, and giving your reasoning, state whether the ionisation of water is an exothermic or an endothermic process. [1]

.....

.....

(iii) Use the diagram to determine the value (mol^2 dm^{-6}) of K_w at 50 °C. [1]

.....

.....

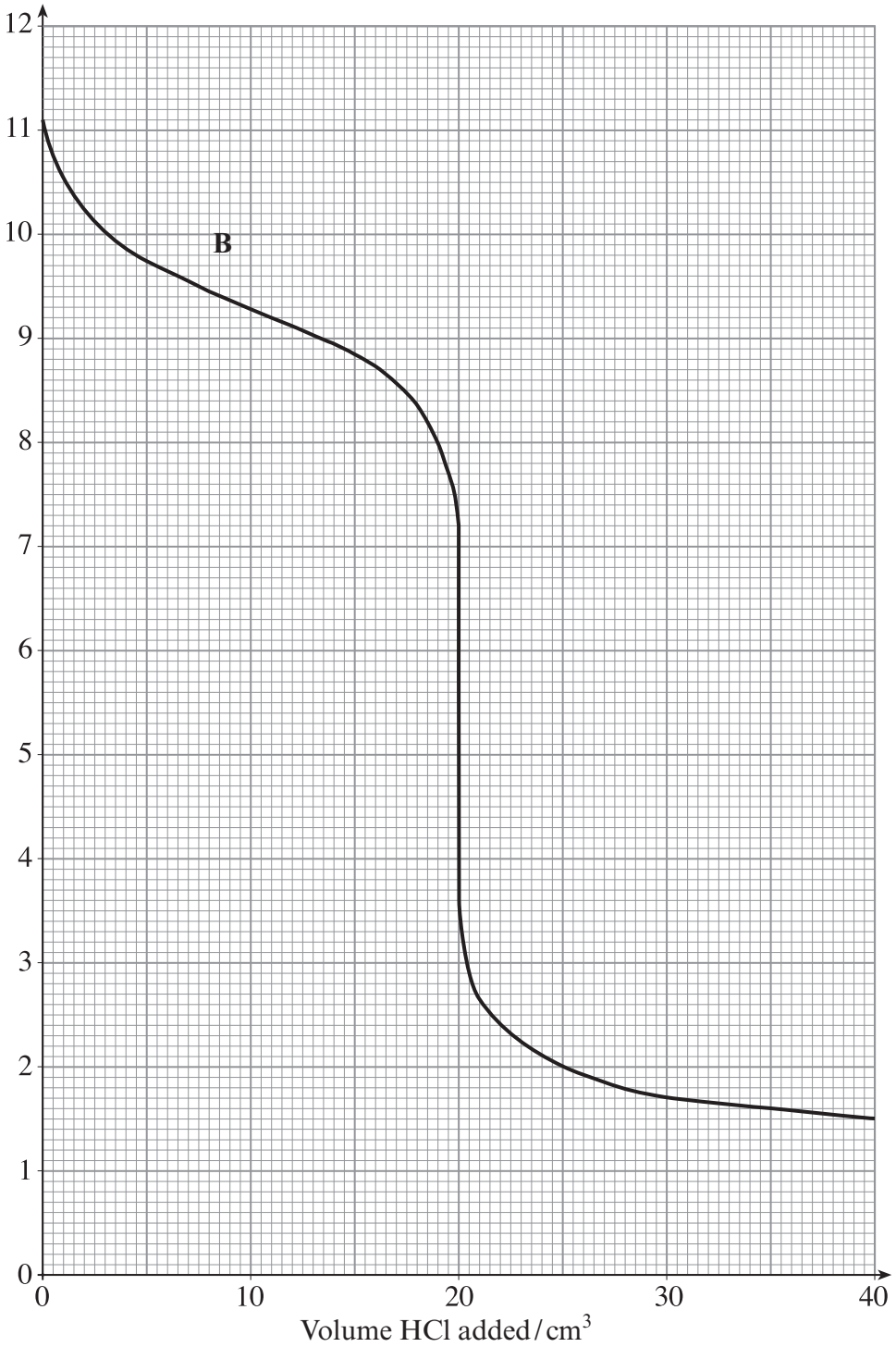
(iv) Hence calculate [H^+] and the pH of pure water at 50 °C. [2]

.....

.....

(b) The diagram below shows how pH changes during the course of a titration when hydrochloric acid of concentration 0.100 mol dm^{-3} is added from a burette to 25.0 cm^3 of aqueous ammonia.

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$



(i) Calculate, to **two** significant figures, the concentration of the aqueous ammonia solution. [3]

.....

.....

.....

Examiner only

(ii) Explain why a buffering effect occurs in the region of the curve marked with the letter **B**, where a mixture of $NH_3(aq)$ and $NH_4Cl(aq)$ is present. [3]

.....

.....

.....

.....

.....

(iii) Giving your reasoning, state which of the following indicators would be suitable for the titration of ammonia against hydrochloric acid. [2]

Indicator	pH range
Bromothymol blue	6.0 - 7.6
Methyl red	4.2 - 6.3
Methyl yellow	2.9 - 4.0
Phenolphthalein	8.2 - 10.0

.....

.....

.....

Total [13]

Examiner only

3. *Read the passage below and then answer questions (a) to (d) in the spaces provided.*

Hydrogen Fuel Cells

Although fuel cells have been around since 1839, it took another 120 years until NASA demonstrated some of their potential applications when providing power during space flights.

A fuel cell works like an electrochemical cell (battery) but does not run down or need recharging. It will produce electricity and heat as long as fuel (hydrogen) is supplied. A fuel cell consists of two electrodes—an anode where oxidation occurs and a cathode for reduction—sandwiched around an electrolyte. Replacing the salt bridge of conventional electrochemical cells, several electrolyte systems have been tried such as phosphoric acid or a solid electrolyte based on polymeric fluorocarbons. The relevant electrode potentials are

$2H^+ + 2e^- \rightleftharpoons H_2$ $\qquad E^{\ominus} = 0\,V$

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\qquad E^{\ominus} = 1.23\,V$

Hydrogen is fed to the anode, and oxygen (air) to the cathode. Activated by a catalyst, usually involving a layer of platinum and carbon a few nanometres thick, hydrogen atoms separate into protons and electrons, which take different paths to the cathode. The electrons go through an external circuit, creating a flow of electricity. The protons migrate through the electrolyte. Fuel cells can be used to power vehicles or to provide electricity and heat to buildings.

A significant barrier to using fuel cells in vehicles is hydrogen storage. Most fuel-cell vehicles powered by hydrogen store the hydrogen as a compressed gas in pressurized tanks. Due to the low energy density of hydrogen, it is difficult to store enough hydrogen onboard to allow vehicles to travel the same distance as petrol-powered vehicles.

A potentially energy-dense water-based fuel is based on sodium tetrahydridoborate(III) (30% by mass $NaBH_4$ in water). A catalyst induces rapid hydrogen production

$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2$ $\qquad \Delta H^{\ominus} = -300\,kJ\,mol^{-1}$

and pure humidified H_2 is delivered to the engine or fuel cell. The exothermic reaction requires no heat input and sodium borate, $NaBO_2$, can be recycled into $NaBH_4$.

– End of passage –

Examiner only

(a) State the function performed by both the salt bridge in an electrochemical cell and the electrolyte in a fuel cell. *(lines 6-7)* [2]

.....

.....

(b) (i) Explain why the $2H^+ + 2e^- \rightleftharpoons H_2$ electrode has an electrode potential of zero. *(line 10)* [1]

.....

.....

(ii) Calculate the EMF of the hydrogen fuel cell. *(lines 10-11)* [1]

.....

.....

(iii) Give **one** reason why the EMF calculated in *(b)*(ii) is not attained in practice, with 0.7 V being a typical value for a fuel cell. [1]

.....

.....

(iv) Write a balanced equation for the overall reaction which occurs in the cell. *(lines 10-11)* [1]

.....

.....

(v) Given that $\Delta H_f^{\ominus} H_2O(l) = -285.8\,kJ\,mol^{-1}$, calculate the enthalpy change, $\Delta H^{\ominus}$, for the equation in *(b)*(iv). [1]

.....

.....

Examiner only

(c) (i) State **one** disadvantage, mentioned in the passage, of using hydrogen fuel cells to power vehicles. *(lines 18-21)* [1]

.....

.....

(ii) Give a second disadvantage, not mentioned in the passage, of using hydrogen as a fuel in vehicles. [1]

.....

.....

(iii) State **one** advantage of using a hydrogen fuel cell compared to the combustion of petrol. [1]

.....

.....

(d) When 1 kg of the water-based fuel (30% $NaBH_4$ by mass) is reacted to produce hydrogen, calculate *(lines 22-26)*

(i) the mass, and hence the number of moles, of $NaBH_4$ in 1 kg of the water-based fuel, [2]

.....

.....

(ii) the energy given out (kJ) by 1 kg of the water-based fuel, [1]

.....

.....

(iii) the volume of hydrogen gas produced. [2]

[Assume 1 mol H_2 gas occupies a volume of 24 dm^3]

.....

.....

.....

.....

Total [15]

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* Bromine, Br_2, reacts with propanone, CH_3COCH_3, in aqueous solution.

$$Br_2(aq) + CH_3COCH_3(aq) \rightarrow HBr(aq) + CH_3COCH_2Br(aq)$$

(i) If the initial bromine concentration, $[Br_2(aq)]$, was $0.0020\,mol\,dm^{-3}$ and the Br_2 was completely used up in 17 min 30 seconds, calculate the rate of the reaction (including units). [2]

(ii) Outline one method which could be used to determine the rate for this reaction. [2]

(iii) The following results were obtained when propanone and bromine were reacted in acid solution.

Rate of reaction / $mol\,dm^{-3}\,min^{-1}$	$[Br_2(aq)]$ / $mol\,dm^{-3}$	$[CH_3COCH_3(aq)]$ / $mol\,dm^{-3}$
6.80×10^{-5}	0.10	0.40
1.36×10^{-4}	0.10	0.80
1.36×10^{-4}	0.20	0.80

Determine the orders of reaction with respect to $Br_2(aq)$ and with respect to $CH_3COCH_3(aq)$. [2]

(iv) A separate experiment was carried out to determine the effect of pH on the rate of reaction.

Rate of reaction / $mol\,dm^{-3}\,min^{-1}$	$[Br_2(aq)]$ / $mol\,dm^{-3}$	$[CH_3COCH_3(aq)]$ / $mol\,dm^{-3}$	pH
1.36×10^{-3}	0.10	0.80	0
1.36×10^{-4}	0.10	0.80	1
1.36×10^{-5}	0.10	0.80	2

I State how the rate of reaction varies with change in pH. [1]

II Using the table, show that the reaction is first order with respect to H^+ ions. [1]

III State the role of H^+ ions in the reaction. [1]

IV Write the full rate equation for the reaction, giving the units for the rate constant. [2]

(QWC) [1]

(b) Both boron nitride, BN, and carbon, C, form hexagonal graphite-type structures. Explain why

- BN and C can both adopt the same hexagonal structure;
- both BN and C exhibit lubricating properties;
- C is an electrical conductor but BN is an insulator at room temperature. [6]

(QWC) [2]

Total [20]

5. *(a)* *Bordeaux Mixture* is one of the earliest fungicides, first used about 1885. It can be prepared by mixing copper sulfate solution with excess limewater (calcium hydroxide solution).

(i) State what you would observe when copper sulfate solution is mixed with limewater. [2]

(ii) Write an equation for the reaction that occurs. [1]

(b) A sample of *Bordeaux Mixture* was analysed to determine its copper content. Firstly, it was reacted with excess potassium iodide

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$

and the iodine produced was then titrated against sodium thiosulfate solution.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

(i) Name the indicator used for the titration and state the colour change at the end-point. [2]

(ii) If a 31.2 g sample of *Bordeaux Mixture* required 12.25 cm^3 of sodium thiosulfate solution with concentration 0.100 mol dm^{-3} $Na_2S_2O_3$ to react with the liberated iodine, calculate the mass of copper in the sample and hence the % Cu by mass in *Bordeaux Mixture*. Your answers should be given to **three** significant figures. [3]

(c) Copper can exist as Cu^{2+} or Cu^+ compounds.

(i) Write the full electron configurations for Cu^{2+} ions **and** Cu^+ ions. [2]

(ii) Explain why most Cu^{2+} compounds are coloured blue in the presence of water. [4]

(iii) Briefly explain why most Cu^+ compounds are colourless or white. [1]

(d) (i) State what would be observed, and give equations for any reactions, when tetrachloromethane, CCl_4, and silicon(IV) chloride, $SiCl_4$, are separately added to water. [3]

(ii) Explain why lead forms a solid chloride $PbCl_2$, but the corresponding CCl_2 and $SiCl_2$ are too unstable to exist. [2]

Total [20]

WJEC
CBAC

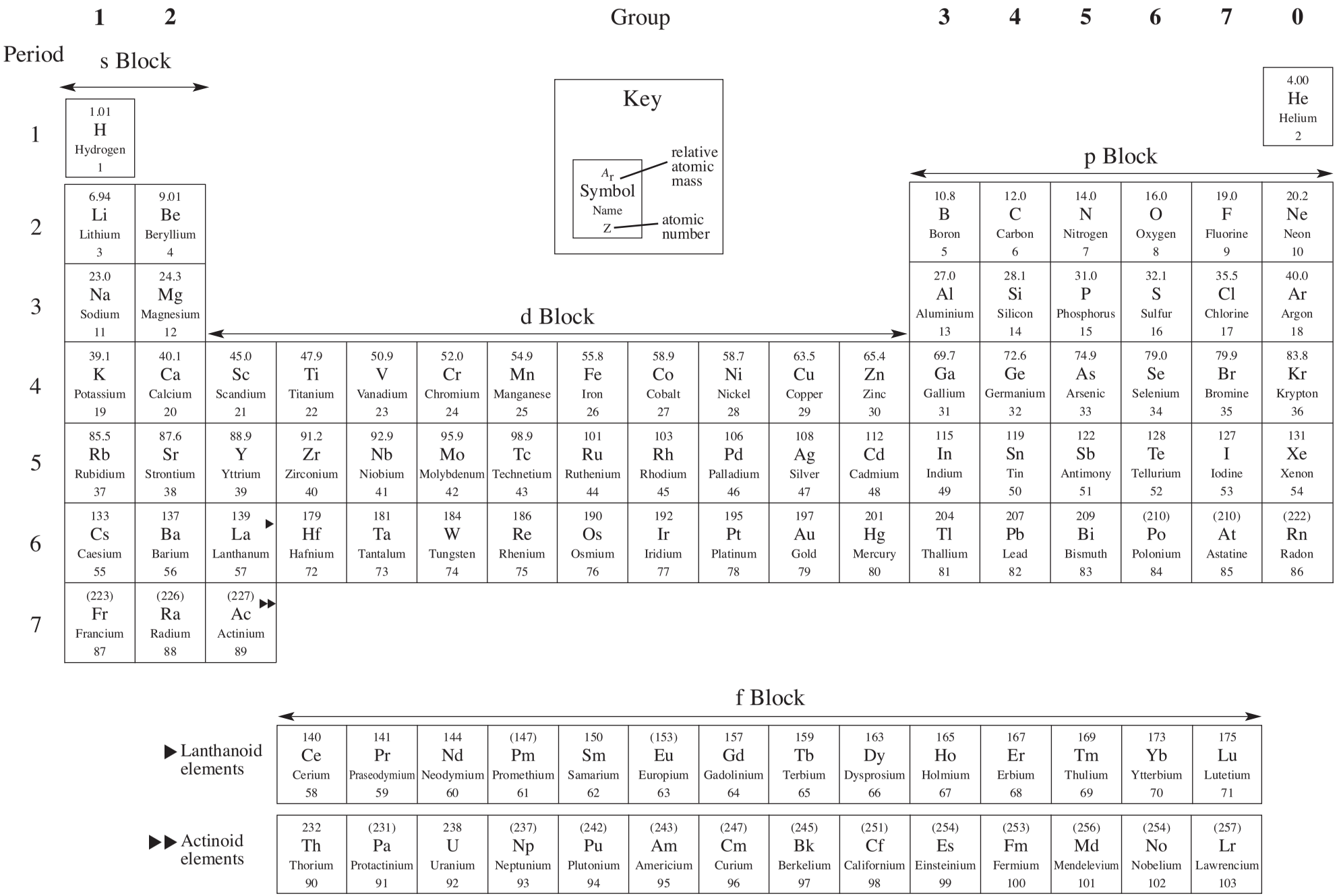
GCE A level

1095/01-A

CHEMISTRY CH5
DATA SHEET

A.M. MONDAY, 28 June 2010

THE PERIODIC TABLE



WJEC
CBAC

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]

Surname	Centre Number	Candidate Number
Other Names		2

WJEC CBAC

GCE A level

1095/01

CHEMISTRY CH5

A.M. FRIDAY, 24 June 2011

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator
- an 8 page answer book;
- a copy of the **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

1095 010001

SECTION A

Answer **all** *questions in the spaces provided.*

1. Chromium and aluminium both form amphoteric compounds.

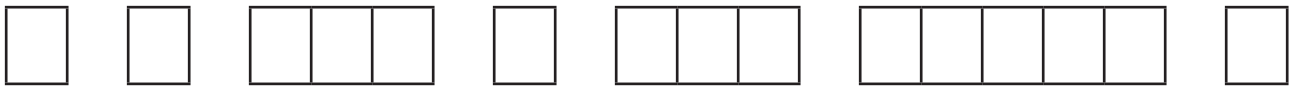
(a) State what is meant by the term *amphoteric*. [1]

.....

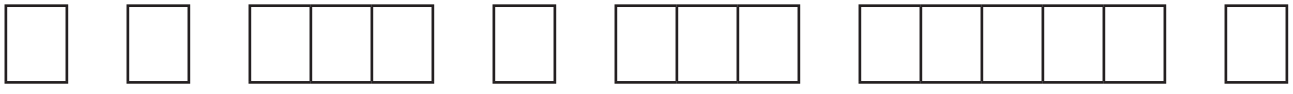
.....

(b) Use arrows in boxes to show the electronic structures of the chromium atom and the Cr^{3+} ion. [2]

Chromium atom, Cr



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



(c) When sodium hydroxide solution is added to a solution of potassium dichromate(VI), $K_2Cr_2O_7$, the following reaction occurs.

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

(i) State the colour change that is seen. [1]

.....

(ii) Use the oxidation states of chromium to show that this is not a redox reaction. [2]

.....

.....

Examiner only

(d) Aluminium chloride is a compound of the amphoteric element aluminium, whilst magnesium chloride contains the non-amphoteric element magnesium. Explain how sodium hydroxide can be used to distinguish between solutions of these two compounds. [3]

.....

.....

.....

.....

(e) Aluminium chloride, $AlCl_3$, commonly exists as the dimer Al_2Cl_6.

(i) Draw the structure of the dimer formed, and explain why the two $AlCl_3$ monomers join together. [3]

.....

.....

.....

.....

(ii) Aluminium chloride monomer may combine with another chloride ion to form tetrachloroaluminate(III) ions, $AlCl_4^-$. Using valence shell electron pair repulsion theory (VSEPR), state and explain the shape of this anion. [2]

.....

.....

.....

.....

Total [14]

Examiner only

2. Fuel cells have been proposed as an alternative method of providing energy for vehicles. These use chemical reactions within electrochemical systems to generate electricity.

(a) A typical fuel cell uses hydrogen as a fuel and reacts this with oxygen. The two half-equations for the processes occurring at the electrodes are given in the table below.

Half-equation	$E^{\ominus}$ / V
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	1.23

(i) Write an equation for the overall reaction occurring. [1]

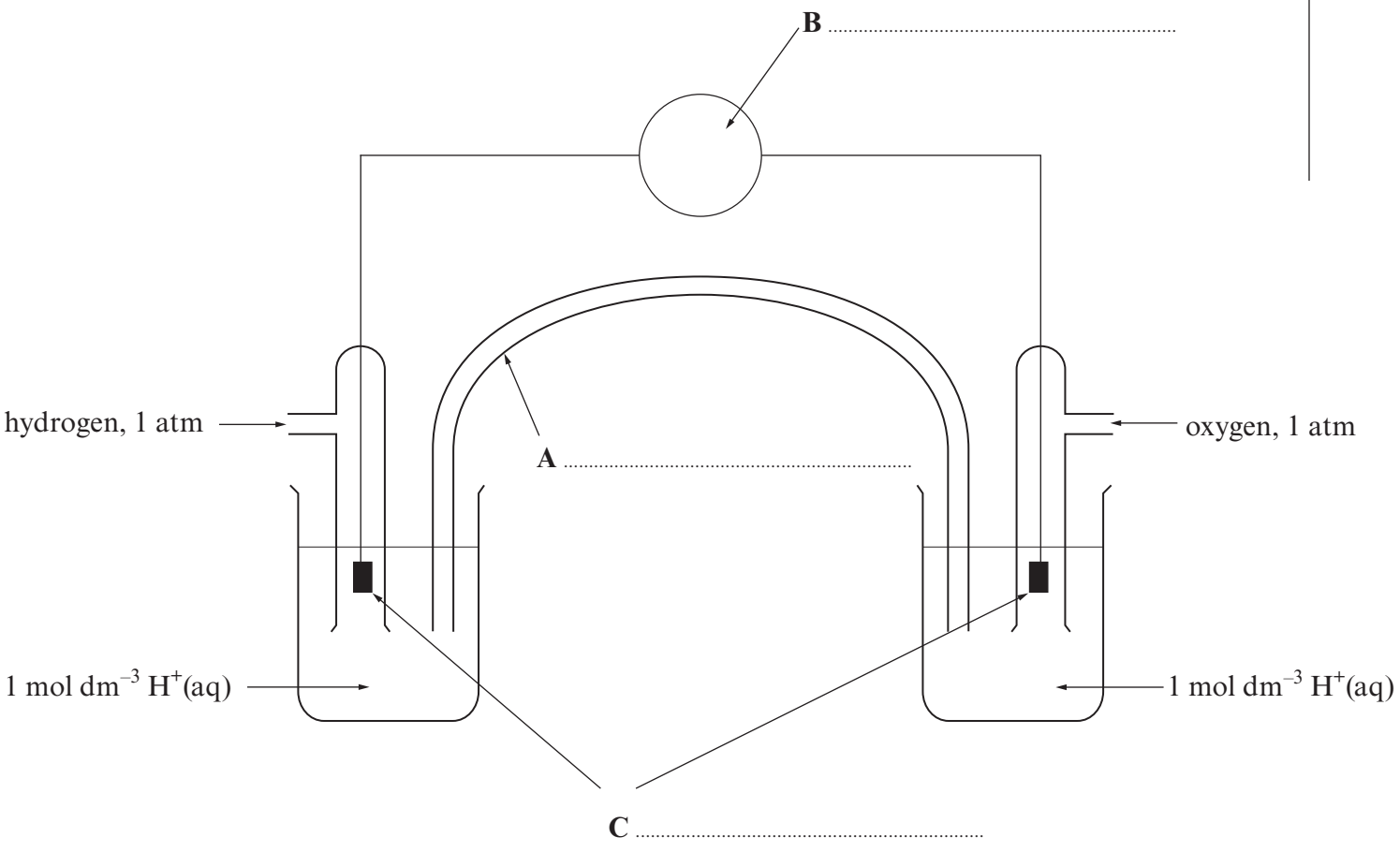
.....

(ii) Give **one** benefit of the use of fuel cells as a replacement for traditional vehicle energy sources. [1]

.....

.....

(iii) The same reaction as above can be undertaken in a traditional electrochemical cell, such as the one below. Name the parts labelled **A**-**C**. [3]



(b) A different fuel for use in fuel cells is methanol, CH_3OH, which would undergo the following reaction with oxygen.

$$CH_3OH(l) + 1\frac{1}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Compound	Standard enthalpy change of formation, $\Delta H_f^{\ominus}$ / kJ mol^{-1}
CH_3OH	–239
CO_2	–394
H_2O	–286

(i) Calculate the standard enthalpy change of combustion for methanol. [2]

.....

.....

.....

(ii) The entropy change of this reaction is calculated as follows.

ΔS = (Sum of all entropies for products) – (Sum of all entropies for reactants)

$$\Delta S = 354 - 435$$

$$\Delta S = -81 \text{ J K}^{-1} \text{ mol}^{-1}$$

The reaction was repeated using gaseous methanol, $CH_3OH(g)$, in place of the liquid methanol, $CH_3OH(l)$, used above. What effect, if any, would this have on the value of the entropy change ΔS given above? Explain your answer. [2]

.....

.....

.....

(iii) Use the values in parts (i) and (ii) of this question to calculate the value of the Gibbs free energy, ΔG, for this reaction at 298K and state what information this gives about the feasibility of the reaction. [2]

.....

.....

.....

.....

Total [11]

3. *Read the passage below and then answer questions (a) to (c) in the spaces provided.*

The oxides of nitrogen

The atmosphere around us consists principally of two elements – nitrogen gas, N_2, and oxygen gas, O_2. The relative stability of this mixture of two elements hides the fact that the elements can combine to form a number of oxides of nitrogen. Their original names are shown below.

Dinitrogen monoxide	N_2O
Nitrogen monoxide	NO
Dinitrogen trioxide	N_2O_3
Nitrogen dioxide	NO_2
Dinitrogen tetroxide	N_2O_4
Dinitrogen pentoxide	N_2O_5
Nitrogen trioxide	NO_3

Many of these oxides are useful but several can also cause environmental problems.

Dinitrogen monoxide, N_2O

This gas was one of the first gaseous compounds to be identified and is probably one of the best known of the oxides of nitrogen. Commonly called 'laughing gas', due to the behaviour of those exposed to the gas, this oxide has since been used as an anaesthetic. It was initially used for the relief of pain during dental treatment and it remained one of the dentist's most useful aids for over a century. It was also commonly used to relieve the pain of childbirth due to the rarity of any adverse reactions to the gas.

Nitrogen dioxide, NO_2

Nitrogen dioxide is a brown gas with a notable sharp odour. It can prove toxic by inhalation. The properties of the pure material are difficult to identify due to the existence of the following equilibrium, which leads to the presence of N_2O_4 in any sample of NO_2.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Nitrogen dioxide is a key intermediate in the production of nitric acid. The nitrogen dioxide is produced by the oxidation of ammonia and this is then combined with water in a disproportionation reaction.

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

Nitrogen dioxide, NO_2, along with nitrogen monoxide, NO, is considered to be a key air pollutant and these two oxides are grouped together as NO_x when air quality measurements are undertaken. Both gases are produced during combustion using air as a source of oxygen, such as in the combustion of fuel in vehicle engines. They contribute to the production of atmospheric nitric acid, a key component of acid rain.

Dinitrogen pentoxide, N_2O_5

Dinitrogen pentoxide is a colourless solid at temperatures around 0 °C, however when warmed to 32 °C the oxide sublimes to form $N_2O_5(g)$. In the gas phase the dinitrogen pentoxide is unstable and decomposes, producing nitrogen dioxide.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

colourless gas — brown gas — colourless gas

Solutions of dinitrogen pentoxide dissolved in trichloromethane, $CHCl_3$, have been used as nitration agents to introduce the $—NO_2$ grouping into organic compounds. The use of this reagent requires a great deal of care as it is a strong oxidising agent and forms explosive mixtures with a range of organic materials.

– End of passage –

Examiner only

Dinitrogen pentoxide, N_2O_5, decomposes in the gas phase according to the equation shown in *line 38*.

(a) Suggest **two** methods of studying the kinetics of this reaction. [2]

1. .....

.....

2. .....

.....

(b) The initial rates of this reaction for different concentrations of N_2O_5 were measured and are given in the table below.

Concentration of N_2O_5 / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
4.00×10^{-3}	3.00×10^{-5}
6.00×10^{-3}	4.50×10^{-5}
8.00×10^{-3}	6.00×10^{-5}

The rate equation for this reaction is:

$$\text{Rate} = k[N_2O_5]^1$$

(i) Show that the rate equation is consistent with the data above. [2]

.....

.....

.....

(ii) Calculate the value of the rate constant under these conditions. Give your answer to **three** significant figures and state its units. [3]

.....

.....

.....

Units .....

Examiner only

(iii) Two possible mechanisms have been suggested for this reaction. These are shown below.

Mechanism A	*Mechanism B*
$N_2O_5 \rightarrow NO_2 + NO_3^{\bullet}$	$2N_2O_5 \rightarrow 2NO_3^{\bullet} + N_2O_4$
$NO_3^{\bullet} \rightarrow NO^{\bullet} + O_2$	$NO_3^{\bullet} + N_2O_4 \rightarrow NO^{\bullet} + 2NO_2 + O_2$
$NO^{\bullet} + N_2O_5 \rightarrow 3NO_2$	$NO^{\bullet} + NO_3^{\bullet} \rightarrow 2NO_2$

Giving your reasons, state which of the mechanisms is compatible with the rate equation. [2]

.....

.....

.....

(c) The nitrogen dioxide, NO_2, produced in this reaction exists in dynamic equilibrium with dinitrogen tetroxide, N_2O_4. *(line 24)*

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2 \text{ kJ mol}^{-1}$$

(i) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

(ii) State and explain the effect of increasing the temperature on the value of K_p. [2]

.....

.....

.....

(iii) At a temperature of 373 K, the partial pressure of a pure sample of NO_2 was 3.00×10^5 Pa. When the mixture was allowed to reach equilibrium, the partial pressure of the remaining NO_2 was 2.81×10^5 Pa.

Calculate the value of K_p, stating its units. [3]

.....

.....

.....

Units .....

Total [15]

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* (i) State what is meant by the term *transition element*. [1]

(ii) Explain why both iron and copper are classed as transition elements, whilst zinc is not. [1]

(b) Transition elements such as copper frequently form coloured complexes. Copper(II) complexes are usually blue, but the exact colour can vary, with $[Cu(H_2O)_6]^{2+}$ being pale blue and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ being royal blue. Copper(I) complexes are usually colourless.

Explain why transition metal complexes are usually coloured. Your answer should include details of:

- The origin of colour in transition metal complexes;
- Why the copper(II) species above are coloured blue;
- Why the colours seen in different copper(II) complexes are different;
- Why copper(I) complexes do not form coloured compounds. [6]

(QWC) [2]

(c) Iron is usually extracted from iron(III) oxide, Fe_2O_3, in a blast furnace using carbon monoxide, CO, as a reducing agent, releasing metallic iron and the gas carbon dioxide.

(i) Write the overall equation for this reaction. [1]

(ii) Explain in terms of oxidation states why carbon monoxide is considered to be the reducing agent in this reaction. [2]

(iii) Explain why carbon monoxide, CO, can be used as a reducing agent but the corresponding oxide of lead, PbO, cannot. [2]

(d) The iron content of an alloy can be determined by a redox titration using acidified potassium dichromate(VI) solution, $K_2Cr_2O_7$. A piece of alloy of mass 1.870 g was dissolved completely in acid to form Fe^{2+} ions, and the solution made up to 250.0 cm^3. A 25.00 cm^3 sample of this solution was titrated against acidified $K_2Cr_2O_7$. This required 23.80 cm^3 of $K_2Cr_2O_7$ solution of concentration 0.0200 mol dm^{-3} for complete reaction.

(i) The half-equations for the processes occurring are:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

Write an **ionic** equation for the reaction between Fe^{2+} ions and $Cr_2O_7^{2-}$ ions in acid solution. [1]

(ii) Calculate the number of moles of Fe^{2+} ions present in the 25.00 cm^3 sample used in the titration. [2]

(iii) Calculate the percentage of iron in the original alloy sample. [2]

Total [20]

5. *(a)* Give a current use for a named compound of chlorine. [1]

(b) Chlorine gas, Cl_2, is used in the industrial preparation of bromine, Br_2. Sea water contains small amounts of bromide ions and by bubbling chlorine gas through the sea water these can be converted to Br_2.

(i) Write an ionic equation for the reaction occurring. [1]

(ii) Use the standard electrode potentials, $E^{\ominus}$, listed below to explain why chlorine can react with bromide ions but iodine cannot react with bromide ions. [3]

Half-equation	$E^{\ominus}$ / V
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.09
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

(c) Sodium chloride and sodium iodide are both compounds which contain halide ions.

(i) Silver nitrate solution may be used to differentiate between solutions of sodium chloride and sodium iodide. Give the observations that would be expected in **both** cases. [1]

(ii) Both sodium chloride and sodium iodide react with concentrated sulfuric acid. The observations made during both reactions are very different. Discuss the reactions occurring. Your answer should include

- the observations made during both reactions,
- the identities of any products,
- the reasons for any differences in the reactions that occur. [5]

(QWC) [1]

(d) Chlorine produces a range of oxoacids, including chloric(I) acid, HOCl, and chloric(VII) acid, $HClO_4$. Chloric(I) acid is considered to be a weak acid whilst chloric(VII) acid is considered to be a strong acid.

(i) What is meant by the term *strong acid*? [1]

(ii) Write an expression for the acid dissociation constant, K_a, of chloric(I) acid, HOCl. [1]

(iii) The pH of a solution of chloric(I) acid of concentration 0.100 mol dm^{-3} was found to be 4.23. Calculate the concentration of hydrogen ions in this solution. [2]

(iv) Using the information from part (iii), calculate the value of the acid dissociation constant, K_a, for chloric(I) acid. [2]

(v) When the weak acid HOCl reacts with the strong base sodium hydroxide it forms the salt sodium chlorate(I), NaOCl. Suggest a pH value for a solution of NaOCl, giving a reason for your answer. [2]

Total [20]

WJEC
CBAC

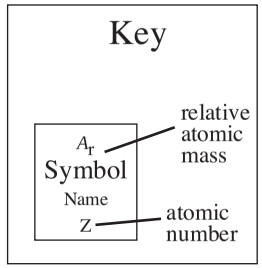
GCE A level

1095/01-A

CHEMISTRY CH5
PERIODIC TABLE

A.M. FRIDAY, 24 June 2011

THE PERIODIC TABLE



Period	1	2										3	4	5	6	7	0
	s Block											p Block					
1	1.01 H Hydrogen 1																4.00 He Helium 2
2	6.94 Li Lithium 3	9.01 Be Beryllium 4										10.8 B Boron 5	12.0 C Carbon 6	14.0 N Nitrogen 7	16.0 O Oxygen 8	19.0 F Fluorine 9	20.2 Ne Neon 10
3	23.0 Na Sodium 11	24.3 Mg Magnesium 12	d Block									27.0 Al Aluminium 13	28.1 Si Silicon 14	31.0 P Phosphorus 15	32.1 S Sulfur 16	35.5 Cl Chlorine 17	40.0 Ar Argon 18
4	39.1 K Potassium 19	40.1 Ca Calcium 20	45.0 Sc Scandium 21	47.9 Ti Titanium 22	50.9 V Vanadium 23	52.0 Cr Chromium 24	54.9 Mn Manganese 25	55.8 Fe Iron 26	58.9 Co Cobalt 27	58.7 Ni Nickel 28	63.5 Cu Copper 29	65.4 Zn Zinc 30	69.7 Ga Gallium 31	72.6 Ge Germanium 32	74.9 As Arsenic 33	79.0 Se Selenium 34	79.9 Br Bromine 35	83.8 Kr Krypton 36
5	85.5 Rb Rubidium 37	87.6 Sr Strontium 38	88.9 Y Yttrium 39	91.2 Zr Zirconium 40	92.9 Nb Niobium 41	95.9 Mo Molybdenum 42	98.9 Tc Technetium 43	101 Ru Ruthenium 44	103 Rh Rhodium 45	106 Pd Palladium 46	108 Ag Silver 47	112 Cd Cadmium 48	115 In Indium 49	119 Sn Tin 50	122 Sb Antimony 51	128 Te Tellurium 52	127 I Iodine 53	131 Xe Xenon 54
6	133 Cs Caesium 55	137 Ba Barium 56	139 La ▶ Lanthanum 57	179 Hf Hafnium 72	181 Ta Tantalum 73	184 W Tungsten 74	186 Re Rhenium 75	190 Os Osmium 76	192 Ir Iridium 77	195 Pt Platinum 78	197 Au Gold 79	201 Hg Mercury 80	204 Tl Thallium 81	207 Pb Lead 82	209 Bi Bismuth 83	(210) Po Polonium 84	(210) At Astatine 85	(222) Rn Radon 86
7	(223) Fr Francium 87	(226) Ra Radium 88	(227) Ac ▶▶ Actinium 89															

f Block

▶ Lanthanoid elements	140 Ce Cerium 58	141 Pr Praseodymium 59	144 Nd Neodymium 60	(147) Pm Promethium 61	150 Sm Samarium 62	(153) Eu Europium 63	157 Gd Gadolinium 64	159 Tb Terbium 65	163 Dy Dysprosium 66	165 Ho Holmium 67	167 Er Erbium 68	169 Tm Thulium 69	173 Yb Ytterbium 70	175 Lu Lutetium 71
▶▶ Actinoid elements	232 Th Thorium 90	(231) Pa Protactinium 91	238 U Uranium 92	(237) Np Neptunium 93	(242) Pu Plutonium 94	(243) Am Americium 95	(247) Cm Curium 96	(245) Bk Berkelium 97	(251) Cf Californium 98	(254) Es Einsteinium 99	(253) Fm Fermium 100	(256) Md Mendelevium 101	(254) No Nobelium 102	(257) Lr Lawrencium 103

GCE MARKING SCHEME

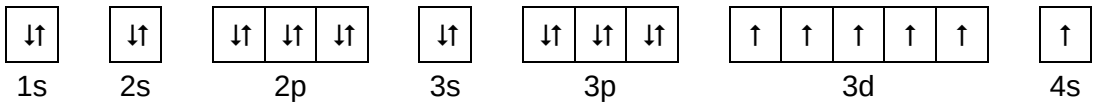
CHEMISTRY
AS/Advanced

SUMMER 2011

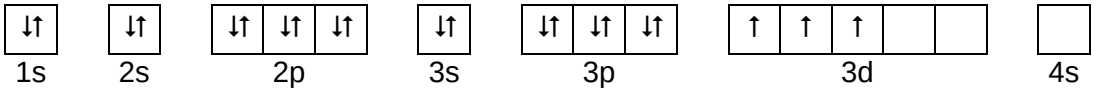
CHEMISTRY - CH5

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

(b) Chromium atom, Cr [1]



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



(c) (i) Orange → yellow [1]

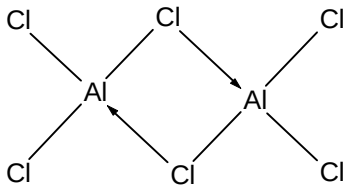
(ii) Cr +6 (1) in both reactant and product - do not accept 6+
no change in oxidation states so not a redox reaction. (1) [2]

(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)



[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) $\Delta H = 2 \times \Delta H (H_2O) + \Delta H (CO_2) – \Delta H(CH_3OH)$
$= 2 \times -286 + (-394) –(-239)$ (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) $\Delta G = -727000 – (298 \times -81) = -703$ 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) $k = \text{Rate} \div [N_2O_5]$ 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) $K_p = \frac{P_{N_2O_4}}{P_{NO_2}^2}$ [1]

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

(iii) $P_{N2O4} = 9.5 \times 10^3$ 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 <u>absorb light</u> (frequencies) to move to <u>higher</u> 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 $Cr_2O_7^{2-} = 23.80 \times 0.0200 \div 1000 = 4.76 \times 10^{-4}$ moles (1)
Moles $Fe^{2+} = 4.76 \times 10^{-4} \times 6 = 2.86 \times 10^{-3}$ 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) $Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$ [1]

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

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

(iv) $K_a = \frac{[H^+][OCl^-]}{[HOCl]} = \frac{(5.88 \times 10^{-5})^2}{0.100}$ (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]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1095/01

CHEMISTRY CH5

P.M. TUESDAY, 19 June 2012

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a copy of the **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

SECTION A

Answer **all** *questions in the spaces provided.*

1. Potassium peroxodisulfate(VI) (persulfate) is a white crystalline compound of formula $K_2S_2O_8$. It is a powerful oxidising agent and has uses as a food additive, in hair dyes and as a nappy steriliser.

(a) Unusually for potassium compounds, it is not very soluble in water.

Temperature / °C	Solubility / g per 100 g H_2O
0	1.75
20	5.29

1 dm^3 of a saturated solution of potassium persulfate at 20 °C was cooled to 0 °C. Calculate the mass of solid potassium persulfate that crystallised from the solution. [2]

.....

.....

(b) (i) A hot solution of potassium persulfate slowly decomposes, giving oxygen as one of the products.

$$2K_2S_2O_8(aq) + 2H_2O(l) \longrightarrow 4KHSO_4(aq) + O_2(g)$$

Calculate the maximum volume of oxygen gas that can be produced at 80 °C when a solution containing 0.100 mol of potassium persulfate decomposes as shown above. [2]

[At 80 °C 1 mol of oxygen has a volume of 29.0 dm^3]

.....

.....

.....

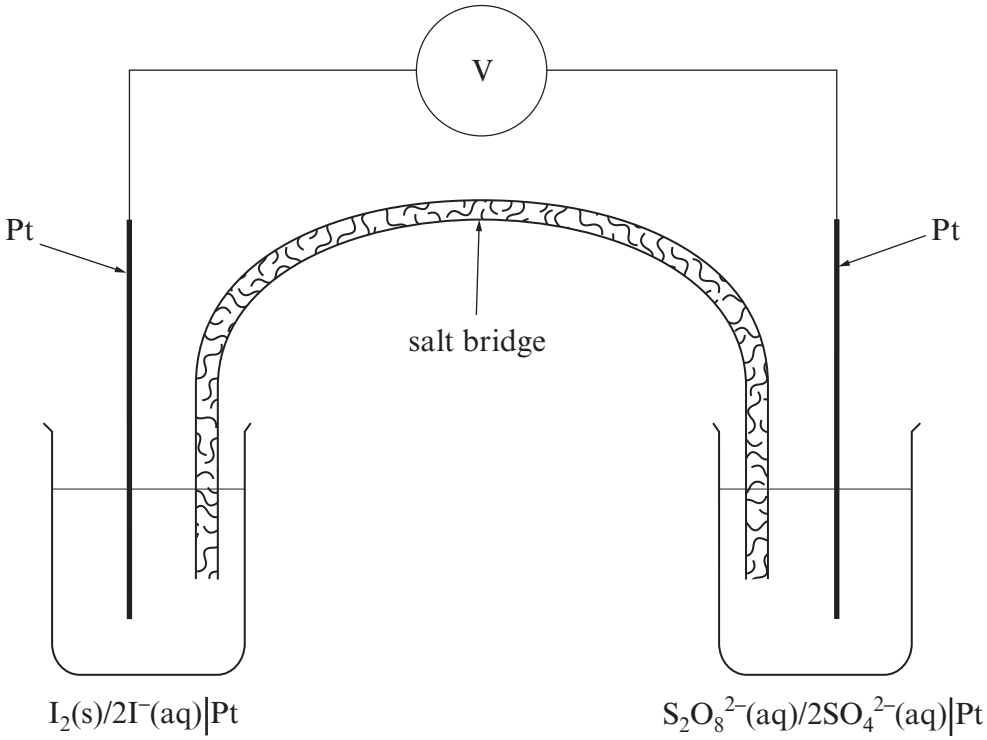
(ii) Suggest a way that the rate of decomposition of the potassium persulfate solution described in (i) could be measured. [1]

.....

.....

.....

(c) The diagram below shows a cell that uses persulfate ions in aqueous solution.



(i) State the role of the platinum electrodes in this cell. [1]

.....

(ii) Use the information given in the equations to state and explain the direction of electron flow in the external circuit. [2]

$$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq) \qquad E^{\ominus} = +2.01\ V$$

$$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq) \qquad E^{\ominus} = +0.54\ V$$

.....

.....

.....

Examiner only

(d) The reaction between persulfate ions and iodide ions in aqueous solution is

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

In an experiment to follow the rate of this reaction, the values below were obtained.

Experiment	Initial rate / mol $dm^{-3}s^{-1}$	Initial concentration of $S_2O_8^{2-}$ / mol dm^{-3}	Initial concentration of I^- / mol dm^{-3}
1	8.64×10^{-6}	0.0400	0.0100
2	3.46×10^{-5}	0.0800	0.0200

(i) The reaction is first order with respect to iodide ions. Use both the initial rate values and the concentrations to show that the order with respect to persulfate ions is also first order. [2]

.....

.....

.....

(ii) Write the rate equation for this reaction and use it to calculate the value of the rate constant, *k*, giving its units. [3]

.....

.....

.....

..... *Units* .....

(iii) It is suggested that this reaction occurs in two steps.

Step 1 $S_2O_8^{2-} + I^- + H_2O \longrightarrow 2SO_4^{2-} + HOI + H^+$

Step 2 $HOI + H^+ + I^- \longrightarrow H_2O + I_2$

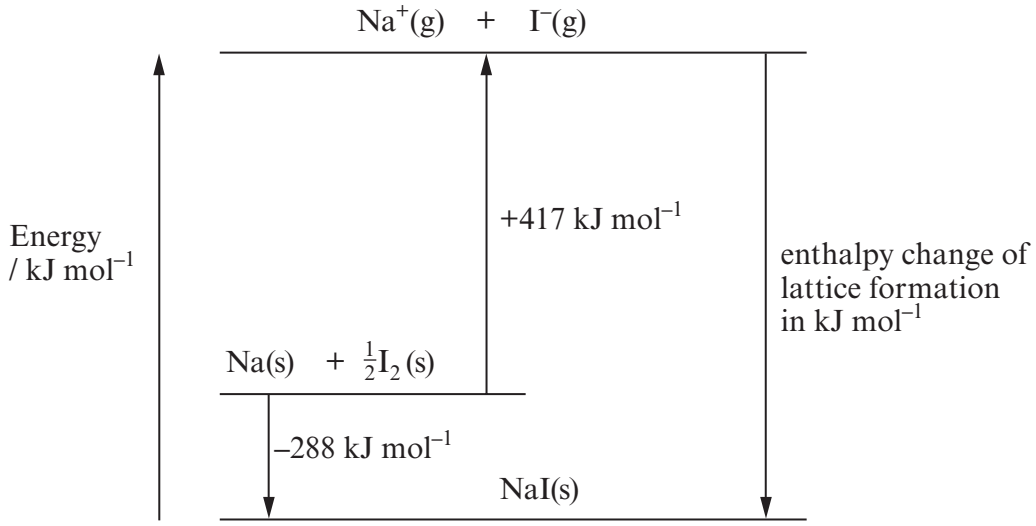
State, using your answer to (ii), why Step 1 is the rate-determining step. [1]

.....

.....

Total [14]

2. *(a)* The diagram shows an outline of the Born-Haber cycle for the formation of sodium iodide (NaI) from its elements.



Use the information given to calculate the enthalpy change of lattice formation (in kJ mol^{-1}) of sodium iodide. [2]

.....

.....

(b) Sodium iodide is very soluble in water at room temperature.

(i) Complete the sentence below using the relevant enthalpy terms.

For a compound to be very soluble in water the value of the enthalpy of

..... will be greater than the enthalpy of .....

[1]

(ii) Aqueous solutions of sodium iodide become yellow in the presence of oxygen due to the slow production of iodine.
One suggested reason for this is that a low concentration of hydrogen ions in the solution produces iodine according to the equation below.

$$4H^+(aq) + 4I^-(aq) + O_2(aq) \rightleftharpoons 2I_2(aq) + 2H_2O(l)$$

Use Le Chatelier's principle to suggest a reagent that you could add, apart from water, to decrease the amount of yellow iodine present. Explain your choice. [2]

.....

.....

.....

.....

Examiner only

(c) Sodium chloride and sodium iodide both react with concentrated sulfuric acid to give the corresponding hydrogen halide e.g.

$$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$

However, the reaction with sodium iodide continues, giving hydrogen sulfide and iodine as two of the products. This further type of reaction does not occur when sodium chloride is used in place of sodium iodide.

(i) Describe what is **seen** when solid sodium iodide is added to concentrated sulfuric acid. [2]

.....

.....

.....

(ii) The following equations show the standard electrode potentials for the Cl_2/Cl^- and I_2/I^- systems.

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \qquad E^{\ominus} = +1.36\,V$$

$$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^{\ominus} = +0.54\,V$$

Use these values to explain why only hydrogen iodide (represented as I^- in the equation) is able to further react with concentrated sulfuric acid in this way. [2]

.....

.....

.....

.....

(d) The reaction of chlorine with sodium hydroxide solution gives aqueous sodium chlorate(I) as one of the chlorine-containing products.

(i) Give the equation for this reaction. [1]

.....

(ii) State **one** use for a solution of sodium chlorate(I). [1]

.....

Total [11]

BLANK PAGE

1095
010007

Examiner only

3. *Read the passage below and then answer the questions (a) to (e) in the spaces provided.*

Copper – an essential element

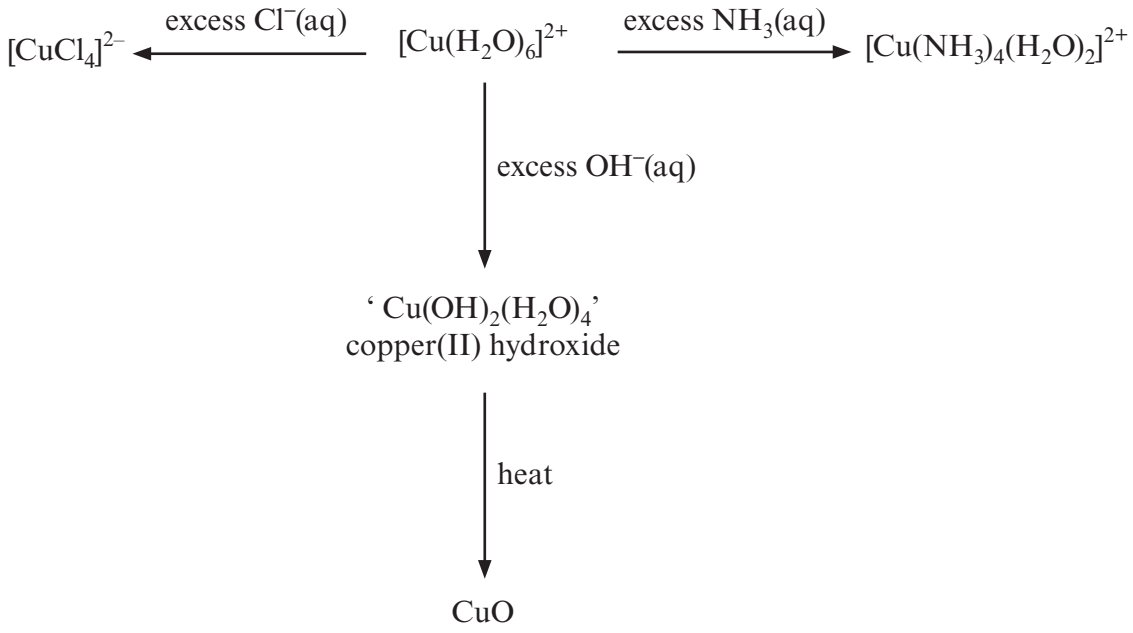
There is an ever-increasing world demand for copper and this has driven its cost upwards. This has led to the extraction of copper from sources once thought to be uneconomic. One such source of copper is the spoil heaps from old mines. The spoil heap material is crushed and then sprayed with acidified water in the presence of the bacterium *Thiobacillus ferrooxidans*. These bacteria convert any iron present to aqueous iron(III) ions, which then oxidise sulfide ions to aqueous sulfate(VI) ions, SO_4^{2-}. A solution containing copper(II) sulfate is produced that is then treated with iron to leave copper.

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$$

The concentration of copper in this copper(II) sulfate solution can be found by a variety of methods, which include

- precipitating the copper and weighing it
- reacting the solution with an excess of iodide ions and titrating the liberated iodine with aqueous sodium thiosulfate
- titrating the copper(II) ions with ethylenediaminetetra-acetic acid (EDTA)
- using instrumental methods such as atomic absorption and X-ray fluorescence spectroscopy

Copper(II) sulfate continues to be a familiar and commonly used substance in schools and colleges and its reactions are typical of many transition metal compounds. For example, in aqueous solution the copper ions are present as the complex cation, $[Cu(H_2O)_6]^{2+}$. The water molecules in this complex ion can be replaced by other ligands.



Examiner only

Copper is a relatively unreactive metal and is easy to obtain by the smelting of its ores, as was carried out in the Bronze Age. Small quantities of many transition metals can be produced by strongly heating the oxide with aluminium or magnesium. One application of this is the reaction of aluminium with iron(III) oxide to give molten iron that can be used to weld together lengths of railway track. A similar reaction occurs when magnesium is strongly heated with copper(II) oxide.

$$Mg(s) + CuO(s) \longrightarrow Cu(l) + MgO(s) \qquad \Delta H = -431\,kJ\,mol^{-1}$$

Transition metals also have important uses as catalysts and copper can be used as an economical catalyst in a number of organic processes, for example in the production of methanal.

$$CH_3OH \xrightarrow[600\ K]{Cu} \begin{matrix} H \\ \diagdown \\ C{=}O \\ \diagup \\ H \end{matrix}$$

- End of passage -

(a) The percentage of copper in a sample from a spoil heap was found by a titration using ethylenediaminetetra-acetic acid (EDTA).
19.20 cm^3 of an EDTA solution of concentration 0.010 mol dm^{-3} reacted with 50.00 cm^3 of a solution containing copper(II) ions.
EDTA reacts with copper(II) ions in a 1:1 mole ratio.

(i) Calculate the number of moles of EDTA solution used in the titration. [1]

.....

.....

(ii) State the number of moles of copper(II) ions present in 50.00 cm^3 of the copper-containing solution. [1]

.....

(iii) Calculate the concentration of copper in the solution in **g dm^{-3}**. [2]

.....

.....

.....

Examiner only

(iv) The mass of the copper-containing sample was 11.56 g. All the copper in this sample was present in a solution of volume 1.00 dm^3.
Calculate the percentage of copper in the sample. [1]

.....

.....

(b) Both copper and zinc are d-block elements. Explain, using electron configurations, why copper is described as a transition metal and zinc (whose compounds contain Zn^{2+} ions) is not. [2]
(QWC) [1]

.....

.....

.....

.....

(c) The passage shows the formulae of some copper-containing species formed by ligand exchange *(line 20)*.
Complete the table below, stating the approximate shape and colour of the complex ions shown. [2]

Complex ion	Shape	Colour
$[CuCl_4]^{2-}$		
$[Cu(NH_3)_4(H_2O)_2]^{2+}$		

(d) Standard enthalpy of formation values, $\Delta H_f^{\ominus}$, can be used to calculate enthalpy changes, such as the reduction of copper(II) oxide by magnesium, described in the article *(line 27)*.
Some $\Delta H_f^{\ominus}$ values are given in the table below.

Metal oxide	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
CuO	–157
PbO	–217

State and explain how the $\Delta H_f^{\ominus}$ values for these two oxides give an indication of their relative stability. [2]

.....

.....

.....

(e) Many transition metals and their compounds act as catalysts. The article describes copper acting as a catalyst in the oxidation of methanol *(line 30)*.

(i) Give **two** reasons why transition metals and their compounds can act as catalysts. [2]

.....

.....

(ii) Give a reason, in terms of Green Chemistry, why scientists often seek new catalysts for established chemical processes. [1]

.....

.....

Total [15]

Total Section A [40]

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* In the reaction below carbon monoxide is acting as a reducing agent.

$$5CO + I_2O_5 \longrightarrow 5CO_2 + I_2$$

Use oxidation states (numbers) to show that carbon monoxide is acting as a reducing agent in this reaction. [2]

(b) State how the stabilities of the +II and +IV oxidation states vary down Group 4. [1]

(c) You are given two solutions. One contains aqueous aluminium ions, Al^{3+}, and the other contains aqueous lead(II) ions, Pb^{2+}.

(i) Describe a reaction to show that both of these ions exhibit amphoteric behaviour. Your answer should state the reagent(s) used, the names of any precipitates and any relevant observations. *Chemical equations are not required.* [4]
QWC [1]

(ii) Describe what is **seen** when iodide ions are added to an aqueous solution of Pb^{2+} ions. Give the **ionic** equation for the reaction that occurs. [2]

(d) Monomeric aluminium chloride is described as containing an electron-deficient species.

(i) Explain, using monomeric covalent aluminium chloride, what is meant by *electron deficient* and why this leads to the ready formation of the Al_2Cl_6 dimer.
You should show the structure of this dimer as part of your answer. [3]

(ii) The electron-deficient nature of the aluminium chloride monomer results in the compound having an affinity for chlorine-containing species. This is important in catalysis and also in the production of specialised solvents.
Give **one** example of the use of the monomer in either of these ways. [1]

(iii) On heating, gaseous dimeric aluminium chloride molecules dissociate into the monomer.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

I State **one** reason why the entropy of this gaseous system is increasing. [1]

II Use the equation

$$\Delta G = \Delta H - T\Delta S$$

to calculate the temperature at which the dissociation of gaseous Al_2Cl_6 molecules into gaseous $AlCl_3$ molecules just occurs spontaneously.
The entropy change for this reaction, ΔS, is 88 J mol^{-1} K^{-1} and the enthalpy change, ΔH, is 60 kJ mol^{-1}. [2]

(e) Solutions containing aqueous aluminium ions are weakly acidic because of the dissociation of one of the coordinated water molecules.

$$[Al(H_2O)_6]^{3+}(aq) \quad \rightleftharpoons \quad [Al(H_2O)_5(OH)]^{2+}(aq) \quad + \quad H^+(aq)$$

The acidity of this solution has been used to stop bleeding from minor cuts.

The expression for the equilibrium constant, in terms of concentrations, for the above system is shown below.

$$K_c \quad = \quad \frac{\left[\,[Al(H_2O)_5(OH)\,]^{2+}(aq)\right]\left[H^+(aq)\right]}{\left[\,[Al(H_2O)_6]^{3+}(aq)\right]}$$

Use this expression to calculate the pH of a solution of aluminium ions of concentration 0.10 mol dm^{-3}. The equilibrium constant, K_c, for this system is 1.26×10^{-5} mol dm^{-3}. [3]

Total [20]

5. *(a)* A student obtained some measurements of the partial pressures of reactants and products for the reaction between sulfur(IV) oxide and nitrogen(IV) oxide.

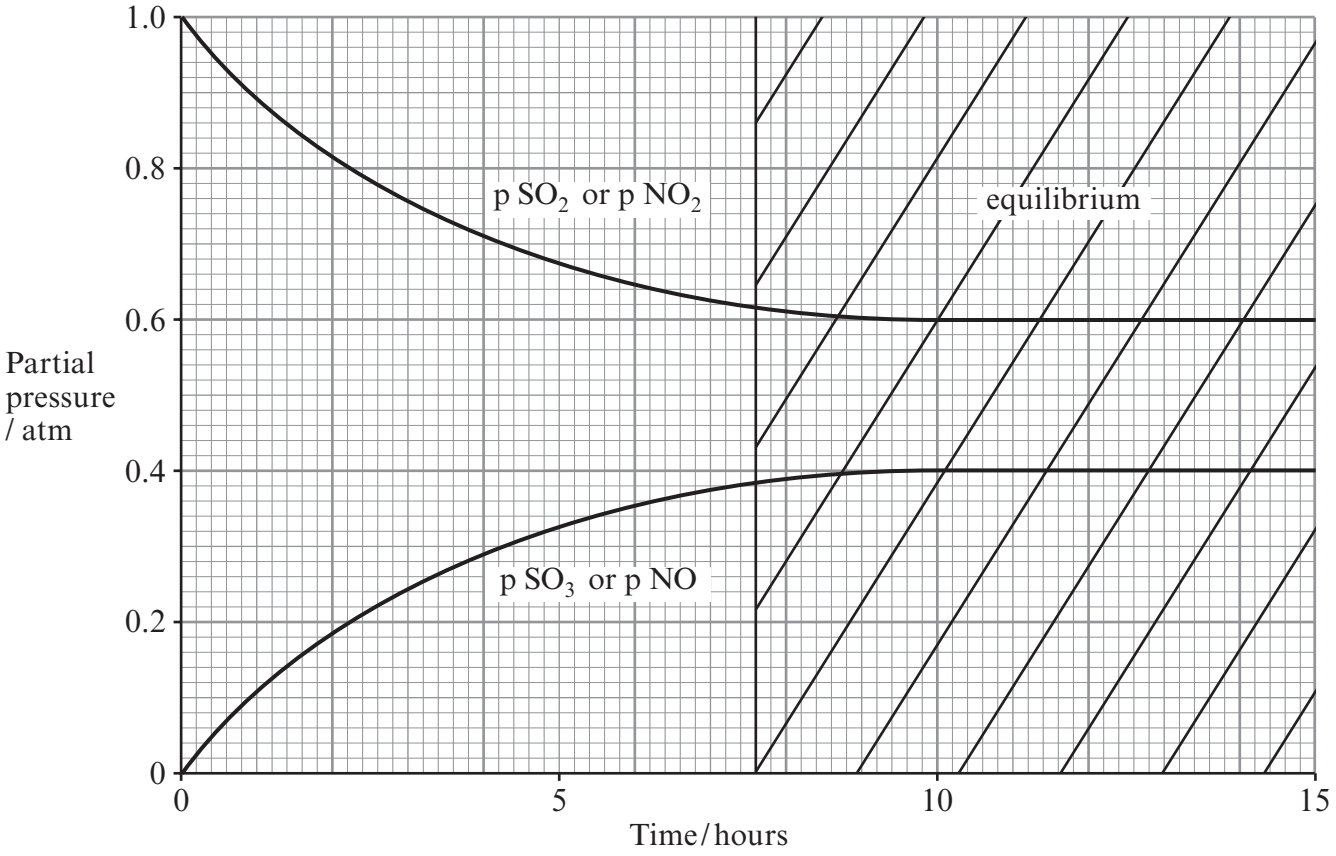
$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

The numerical value of K_p for this reaction is 2.5.

(i) Give the expression for the equilibrium constant in terms of partial pressures, K_p, stating its units (if any). [2]

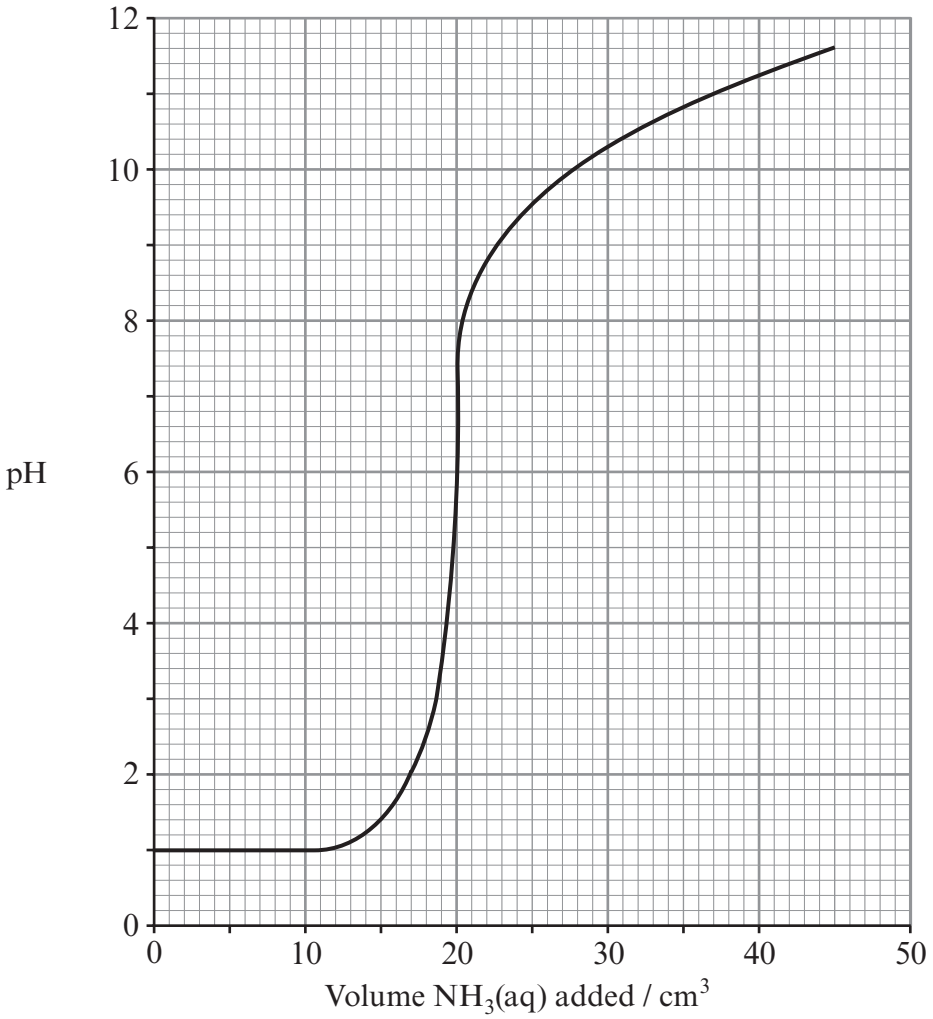
(ii) He decided to present his results in the form of the diagram below.

State the **two** things that are wrong with this diagram, explaining your answer. [4]



(iii) The enthalpy change for this reaction is –41 kJ mol^{-1}. State and explain how the value of the equilibrium constant would change (if at all) when the reaction is run at a higher temperature. [2]

(b) The acid-base titration curve for the reaction between aqueous solutions of nitric acid, HNO_3, and ammonia, both of concentration 0.100 mol dm^{-3}, is shown in the diagram. In this strong acid-weak base system, aqueous ammonia was added to 20.0 cm^3 of aqueous nitric acid.



(i) Describe and explain the shape of the curve obtained when aqueous ammonia is added to the aqueous nitric acid. [3]
QWC [1]

(ii) Deduce, using information obtained from the graph, the mole ratio of the two reactants in this titration. Explain your reasoning. [2]

(iii) I Explain why the pH of a solution of ammonium nitrate is not 7. [1]
II Use the graph to state the pH of the ammonium nitrate solution obtained at the equivalence point. [1]

(iv) Use your answer to (iii) to state the colour obtained if a few drops of the acid-base indicator bromophenol blue are added to the ammonium nitrate solution, giving the reason for your answer. [1]

pH	Colour
$\leqslant 2.8$	yellow
$\geqslant 4.7$	blue

(c) Ammonium nitrate ($M_r = 80$) is used in 'cold packs' to give a cooling effect for sports injuries. The solid crystals are added to water producing an endothermic reaction.

A typical 'cold pack' contains 40 g of ammonium nitrate that is dissolved in water to make 200 g of the solution. Calculate the molar concentration of the ammonium nitrate solution and hence the drop in temperature that occurs when this pack is used.

[1 mole of ammonium nitrate dissolved in water to make 1 kg of solution produces a drop in temperature of 6.2 °C] [3]

Total [20]

Total Section B [40]

WJEC CBAC

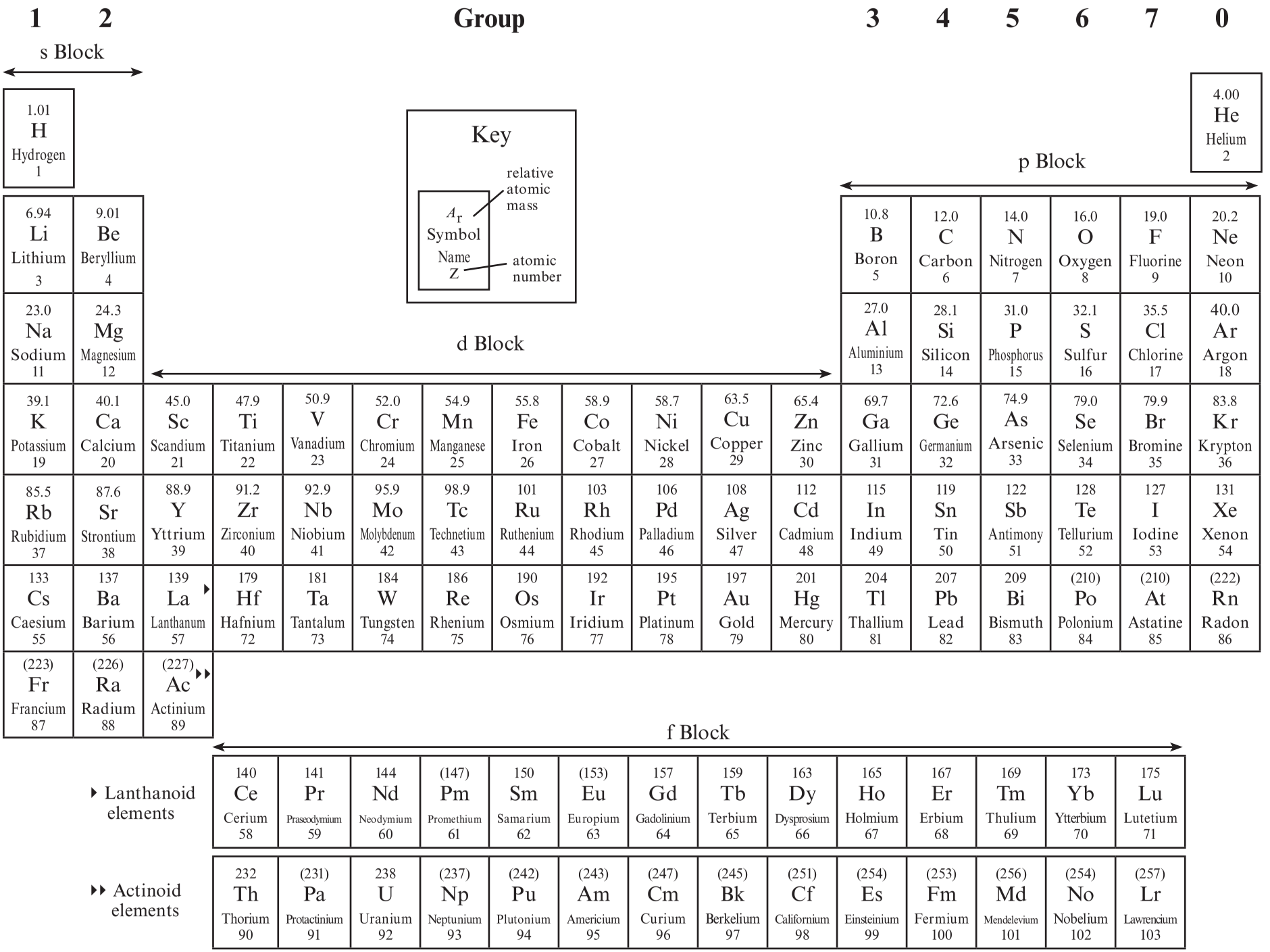
GCE A level

1095/01-A

CHEMISTRY – PERIODIC TABLE
FOR USE WITH CH5

P.M. TUESDAY, 19 June 2012

THE PERIODIC TABLE



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)
∴ 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)
∴ 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)

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

= 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)

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

- error carried forward throughout (a)

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

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

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

(iv) $$\%\text{ Cu} = \frac{0.244 \times 100}{11.56} = 2.11$$ [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) $CO \rightarrow C$ +2 $CO_2 \rightarrow$ +4 (1)

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

OR

$I_2O_5 \rightarrow I$ +5 $I_2 \rightarrow I_2$ 0 (1)

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

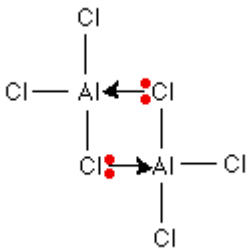
(b) +2 state becomes mores stable down the group and +4 becomes less stable. [1]

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

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

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

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

- error carried forward

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

Total [20]

5. (a) (i) $K_p = \frac{pSO_3(g) \times pNO(g)}{pSO_2(g) \times pNO_2(g)}$ (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)

∴ 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)

∴ Temperature drop $= 2.5 \times 6.2 = 15.5°C$ (1) [3]

Total [20]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1095/01

CHEMISTRY – CH5

A.M. WEDNESDAY, 19 June 2013

1¾ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a copy of the **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

1095
010001

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

SECTION A

Answer **all** *questions in the spaces provided.*

1. Halogens and their compounds take part in a wide variety of reactions.

(a) Give the chemical name of a chlorine-containing compound of commercial or industrial importance. State the use made of this compound. [1]

.....

.....

(b) Hydrogen reacts with iodine in a reversible reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

An equilibrium was established at 300 K, in a vessel of volume 1 dm^3, and it was found that 0.311 mol of hydrogen, 0.311 mol of iodine and 0.011 mol of hydrogen iodide were present.

(i) Write the expression for the equilibrium constant in terms of concentration, K_c. [1]

(ii) Calculate the value of K_c at 300 K. [1]

K_c = ...

(iii) What are the units of K_c, if any? [1]

.....

(iv) Equilibria of H_2, I_2 and HI were set up at 500 K and 1000 K and it was found that the numerical values of K_c were 6.25×10^{-3} and 18.5×10^{-3} respectively.

Use these data to deduce the sign of ΔH for the forward reaction. Explain your reasoning. [3]

.....

.....

.....

.....

Examiner only

(c) When concentrated hydrochloric acid is added to a pink aqueous solution of cobalt(II) chloride, the colour changes to blue.

Cobalt takes part in an equilibrium reaction.

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

(i) What is the oxidation state of cobalt in $[CoCl_4]^{2-}$? [1]

.....

(ii) What type of bonding is present in $[CoCl_4]^{2-}$? [1]

.....

(iii) Use the equation to identify the ions responsible for the pink and blue colours described above. Explain why the colour change occurs when concentrated hydrochloric acid is added to the pink solution. [3]

.....

.....

.....

.....

(iv) Draw diagrams to clearly show the shape of the $[Co(H_2O)_6]^{2+}$ ion and the $[CoCl_4]^{2-}$ ion. [2]

$[Co(H_2O)_6]^{2+}$ $[CoCl_4]^{2-}$

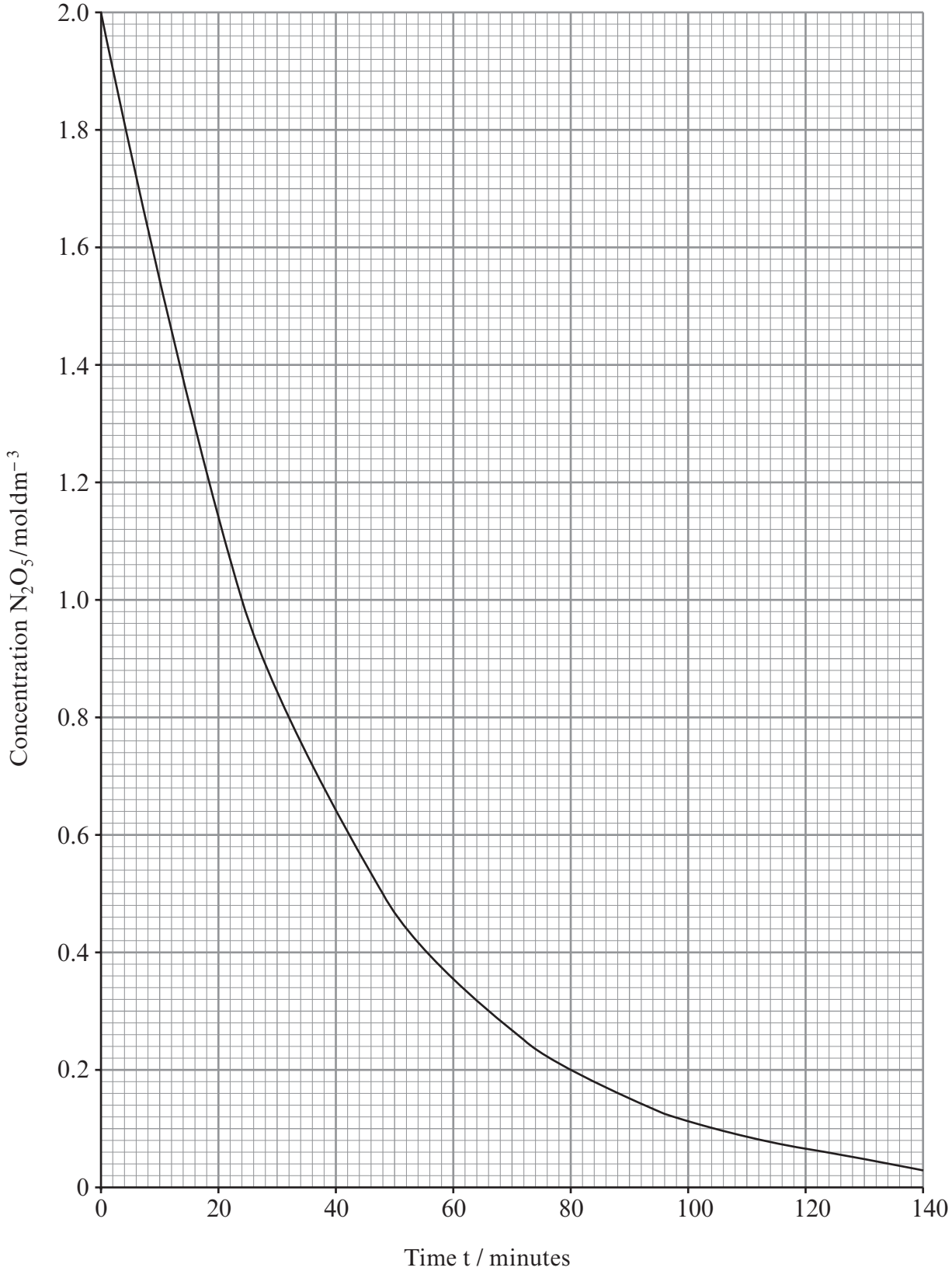
Total [14]

Examiner only

2. Nitrogen forms a variety of oxides including dinitrogen pentoxide, N_2O_5, which can decompose as shown in the equation.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

The rate at which this decomposition occurs can be followed by measuring the change in concentration of N_2O_5. A graph of the results of this decomposition is shown below.



Examiner only

(a) (i) Use the graph to determine the rate of reaction, in $mol\,dm^{-3}\,min^{-1}$, after 40 minutes. Show clearly on the graph, how you determined your answer. [2]

Rate after 40 minutes = ... $mol\,dm^{-3}\,min^{-1}$

(ii) Explain why the rate of reaction is lower at t = 60 minutes than it was at t = 40 minutes. [1]

.....

.....

.....

(b) (i) Use the graph to show that the reaction is first order with respect to N_2O_5. Explain how you reached your conclusion. [2]

.....

.....

.....

(ii) Write the rate equation for the reaction. [1]

.....

(iii) Find the value of k in the rate equation and state its units. [2]

Value of k = ...

Units = ...

Examiner only

(iv) Two students suggested possible mechanisms for the decomposition of N_2O_5.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

Student A

$$N_2O_5 \xrightarrow{\text{slow}} NO_2 + NO + O_2$$

$$NO + O_2 \xrightarrow{\text{fast}} NO_2 + \tfrac{1}{2}O_2$$

Student B

$$2N_2O_5 \xrightarrow{\text{slow}} 4NO + 3O_2$$

$$4NO + 2O_2 \xrightarrow{\text{fast}} 4NO_2$$

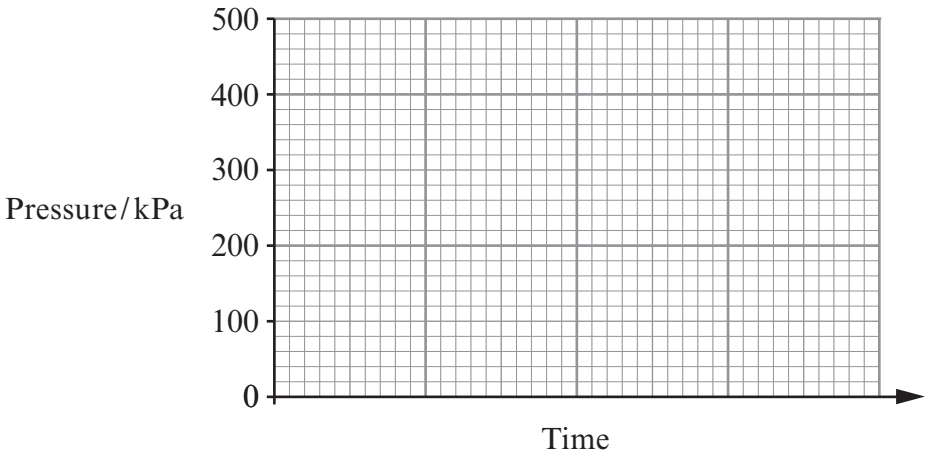
State, with a reason, which student's suggested mechanism is more likely to be correct. [1]

.....

.....

.....

(c) The progress of the reaction could have been followed by monitoring changes in pressure. On the axes below sketch the results expected if the initial pressure of the N_2O_5 was 100 kPa and the reaction reached completion. [2]



Total [11]

BLANK PAGE

1095
010007

3. *Read the passage below and then answer the questions in the spaces provided.*

Acids Through The Ages

The ancient Greeks started to classify materials as salt-tasting, sweet-tasting, sour-tasting and bitter-tasting. In this classification acids were those considered to be sour-tasting – the name comes from the Latin *acere*.

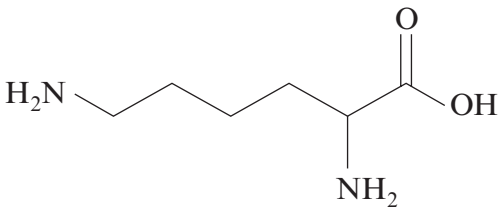
Taste continued to be an important consideration – even today many people would think of the sour taste of a lemon as being typical of an acid. However it was found that, as well as taste, these compounds had other properties in common. The dye litmus had been extracted from lichens and it was found that acids changed the colour of this to red. They also corroded metals.

Many acids were identified – citric acid could be extracted from citrus fruit and methanoic acid could be extracted, by distillation, from red ants. Methanoic acid used to be called formic acid since the biological term for an ant is *formica*.

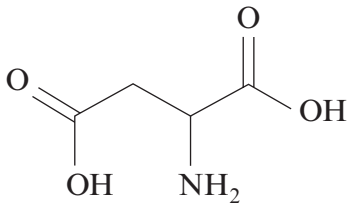
The modern classification of acids is based on the theory suggested by Lowry and Brønsted although more recent classifications, based on electron pair donation, have been suggested by Lewis.

Using the Lowry-Brønsted classification both citric acid and methanoic acid are described as being weak. For methanoic acid, HCOOH, the value of the acid dissociation constant, K_a, is 1.75×10^{-4} mol dm^{-3}.

Acids have a wide variety of uses in modern chemistry. They can, for example, be used as catalysts in hydrolysis reactions and work is currently being done to investigate the possibility of obtaining biofuels by the hydrolysis of farm waste such as straw. In some situations however acids can destroy catalytic effects. The tertiary structure and therefore the shape of the active sites of some enzyme catalysts can be maintained by ionic attractions. This could arise, for example, when the enzyme involves the amino acids lysine and aspartic acid. The NH_2 on the lysine can be protonated to give a positive ion, whilst the COOH can be deprotonated to give a negative ion. Attraction between oppositely charged ions holds the shape but if the pH is altered and one of the charges is lost the shape can change and the enzyme becomes denatured.



lysine



aspartic acid

The possible alteration of the shapes of molecules in biological systems means that it is important that the pH of, for example shampoos, is maintained within a small range. For best results shampoo should stay at a pH just below 7.

- End of passage -

Examiner only

(a) State what is meant by a Lowry-Brønsted acid. *(line 12)* [1]

.....

.....

(b) Define pH. [1]

.....

.....

(c) David and Peter were discussing acids and bases. David said that you could decide whether an acid was strong or weak by measuring the pH of the acid solution. He said that the strong acid would have a lower pH. Peter said that he felt that the strength of the acid was not the only factor that affected pH.

Discuss the factors that affect pH. [4]
QWC [1]

.....

.....

.....

.....

.....

.....

.....

(d) Methanoic acid is a weak acid.

(i) Write the expression for the acid dissociation constant, K_a, of methanoic acid. [1]

(ii) Using the information in *lines 16* and *17* of the article, calculate the pH of 0.10 mol dm^{-3} methanoic acid. [3]

pH = ...

Examiner only

(e) The article *(line 29)* states that it is important to maintain the pH of shampoo within a small range.

(i) What name is given to a system designed to maintain pH within a small range? [1]

.....

(ii) The pH of a shampoo is maintained within a small range by using a weak acid, RCOOH, and its sodium salt, RCOONa.

Explain how this mixture maintains pH within a small range. [3]

.....

.....

.....

.....

.....

.....

Total [15]

Total Section A [40]

BLANK PAGE

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* Electrochemical cells are used as power sources in many everyday applications. To decide what to use in a cell, it is necessary to know the standard electrode potential for electrodes. This is measured using a standard hydrogen electrode as a reference standard.

Draw a labelled diagram of the apparatus you would use to measure the standard electrode potential of an Fe^{3+}/Fe^{2+} electrode. [5]

(b) Vanadium is a transition metal that can form compounds with a variety of oxidation states. Zinc however forms compounds with an oxidation state of +2 only.

(i) Why can transition elements form compounds with a variety of oxidation states? [1]

(ii) Give the electronic structure of Zn. [1]

(iii) State why zinc forms Zn^{2+}. [1]

You will need the standard electrode potentials in the table below to answer part *(c)*.

Oxidation state of vanadium at start of reaction	Reaction	$E^{\ominus}$/V
+5	$VO_3^-(aq) + 4H^+(aq) + e \rightleftharpoons VO^{2+}(aq) + 2H_2O(l)$	+1.00
+4	$VO^{2+}(aq) + 2H^+(aq) + e \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
+3	$V^{3+}(aq) + e \rightleftharpoons V^{2+}(aq)$	–0.26
+2	$V^{2+}(aq) + 2e \rightleftharpoons V(s)$	–1.13
	$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	–0.76
	$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$	+0.34

(c) Vanadium(V)(aq), as VO_3^-, is yellow and can be reduced by zinc and aqueous acid producing a series of coloured solutions until the reduction stops with the formation of a violet solution. The reducing agent involves the $Zn^{2+}(aq)/Zn(s)$ equilibrium.

(i) State the identity of the violet vanadium-containing solution produced in this reduction. Use standard electrode potentials to explain your answer. [3]

(ii) What is the standard potential of a cell formed from a standard $Zn^{2+}(aq)/Zn(s)$ electrode and a standard $Cu^{2+}(aq)/Cu(s)$ electrode? [1]

(iii) Write the equilibrium equation for the change occurring at the zinc electrode showing the direction in which the reaction proceeds. [1]

(iv) Use Le Chatelier's principle to predict the effect on the electrode potential of the zinc electrode of increasing the concentration of $Zn^{2+}(aq)$ in the electrode. Explain your answer. [2]

(d) Halogens can also form compounds with a variety of oxidation states. Some of these including compounds of iodate(V), IO_3^-, behave as oxidising agents.

A student was investigating the reaction that occurs when iodate(V) oxidises iodide ions to produce iodine. Two possible equations were suggested.

$$IO_3^- + 6H^+ + 5I^- \longrightarrow 3I_2 + 3H_2O \qquad \textbf{equation 1}$$

$$IO_3^- + 4H^+ + 4I^- \longrightarrow IO^- + 2H_2O + 2I_2 \qquad \textbf{equation 2}$$

He prepared a solution of potassium iodate(V) by dissolving 0.978 g of KIO_3 in 250 cm^3 of solution. He pipetted 25.0 cm^3 of this solution into a conical flask, added excess potassium iodide and titrated the iodine produced with 0.100 mol dm^{-3} sodium thiosulfate solution, $Na_2S_2O_3$. A volume of 27.40 cm^3 of this solution was needed to react with the iodate(V).

The equation for the reaction of thiosulfate with iodine is shown below.

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

(i) Calculate the number of moles of thiosulfate used to react with the iodine. [1]

(ii) Deduce the number of moles of iodine present in the 25.0 cm^3 sample. [1]

(iii) Calculate the number of moles of KIO_3 present in 250 cm^3 of the original solution and hence the number of moles present in 25.0 cm^3. [1]

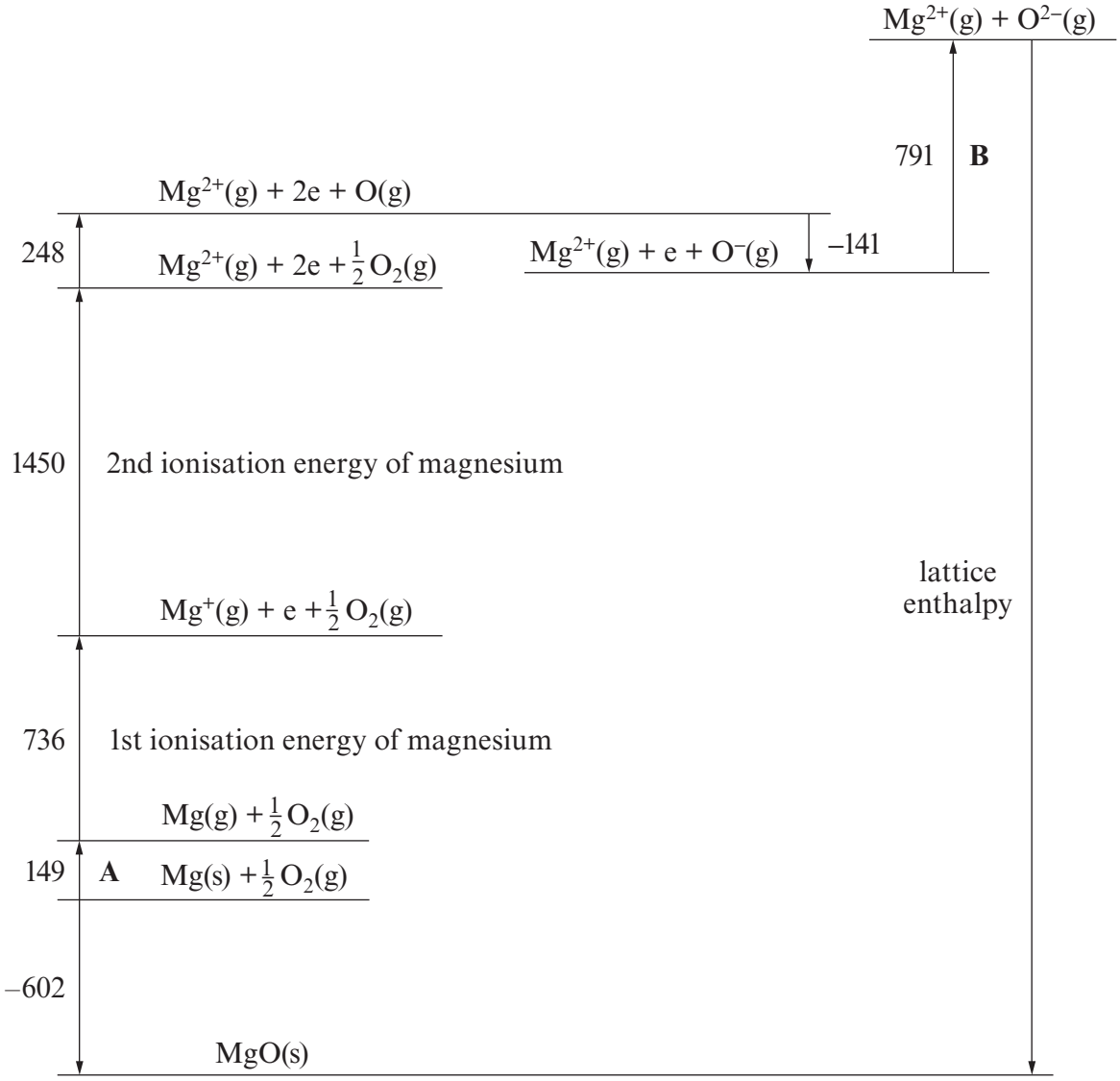
(iv) Use your results from (ii) and (iii) to deduce which of **equation 1** and **equation 2** suggested above, correctly shows what happens when iodate(V) ions oxidise iodide ions. Show, by calculation, how you came to this conclusion. [2]

Total [20]

5. Magnesium oxide, MgO, is a white solid with a very high melting temperature and it is used as the refractory lining in furnaces.

(a) The following Born-Haber cycle shows the enthalpy changes involved in the formation of magnesium oxide.

All enthalpy changes are in kJ mol^{-1}. The cycle is not drawn to scale.



(i) What is the name given to the enthalpy change labelled **A**? [1]

(ii) State why the second ionisation energy of magnesium is greater than its first ionisation energy. [1]

(iii) Suggest why the second electron affinity of oxygen, labelled **B**, is positive. [1]

(iv) Calculate the value of the lattice enthalpy for magnesium oxide. [2]

(b) Many metal oxides can be reduced to the metal by carbon monoxide. The equation for the reduction of magnesium oxide is given below.

$$MgO(s) + CO(g) \longrightarrow Mg(s) + CO_2(g)$$

The conditions under which reactions will occur can be predicted using enthalpy and entropy changes. The entropies of the substances involved in this reaction are shown in the table.

Substance	MgO(s)	CO(g)	Mg(s)	$CO_2(g)$
Entropy / $JK^{-1}mol^{-1}$	26.9	197.7	32.7	213.7

(i) Suggest a reason why the entropies of carbon monoxide and carbon dioxide are much higher than those of magnesium and magnesium oxide. [1]

(ii) Calculate the entropy change in this reaction. [1]

(iii) The enthalpy change, ΔH, for the reduction of magnesium oxide is $318.0\,kJ\,mol^{-1}$. Calculate the minimum temperature at which this reduction could occur. [3]

(c) Magnesium oxide, MgO, lead(II) oxide, PbO, and aluminium oxide, Al_2O_3, all react with dilute acids to form aqueous ions – $Mg^{2+}(aq)$, $Pb^{2+}(aq)$ and $Al^{3+}(aq)$.

Suggest tests that would enable you to distinguish between solutions containing one of each of these ions. You should include the expected result for **each** test and are advised to record your tests and expected results in a table. [5]

QWC [2]

(d) Aluminium chloride, $AlCl_3$, can be used to produce compounds including the chloroaluminate(III) ion, $AlCl_4^-$.

(i) Draw a dot and cross diagram to show the electron arrangement in the $AlCl_4^-$ ion. You should show outer electrons only. [1]

(ii) Give **one** industrially important use in which the $AlCl_4^-$ ion is involved. State the role of the ion in this use. [2]

Total [20]

Total Section B [40]

END OF PAPER

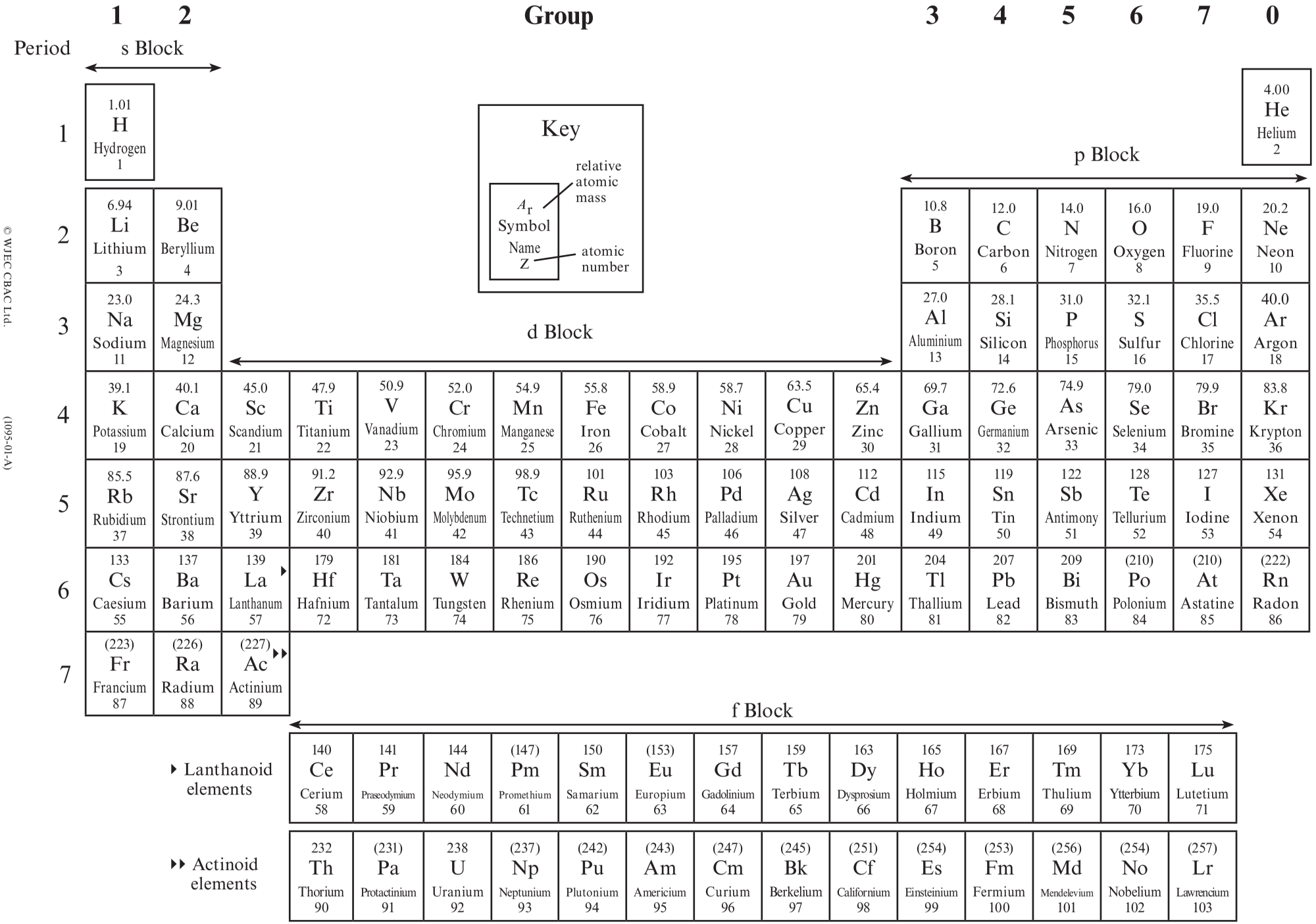
GCE A level

1095/01-A

CHEMISTRY – CH5
Periodic Table

A.M. WEDNESDAY, 19 June 2013

THE PERIODIC TABLE



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 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) $K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$ **[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)

$Fe^{2+}(aq)$ 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 $KIO_3 = 0.978/ 214.1 = 4.57 \times 10^{-3}$ 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(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]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1095/01

CHEMISTRY – CH5

P.M. TUESDAY, 17 June 2014

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1.**	**10**	
	2.	**12**	
	3.	**18**	
Section B	**4.**	**20**	
	5.	**20**	
	Total	**80**	

1095 010001

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a copy of the **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

Examiner only

SECTION A

Answer **all** *questions in the spaces provided.*

1. Ammonium salts are very important chemicals as they are used as a nitrogen source in fertilisers.

(a) When cold aqueous sodium hydroxide is added to an ammonium salt, the following equilibrium exists.

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$

Identify the **two** acid-base conjugate pairs in the equilibrium. [2]

.....

.....

(b) Ammonium chloride and sodium nitrite react together in aqueous solution to produce nitrogen gas. This can be represented by the ionic equation:

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$$

The rate equation for the reaction is given below.

$$\text{Rate} = k[NH_4^+][NO_2^-]$$

(i) Complete the table of data for the above reaction. All experiments were carried out at the same temperature. [3]

	$[NH_4^+(aq)]$ / 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		0.010	2.00×10^{-7}
3	0.200		1.20×10^{-6}
4	0.100	0.020	

(ii) Calculate the value of the rate constant, *k*, giving its units. [2]

Value of k = ...

Units .....

Examiner only

(iii) State how the value of *k* will alter, if at all, if the concentration of NH_4^+ ions is increased. [1]

.....

(iv) State, giving a reason, how the value of *k* will alter, if at all, if the temperature is increased. [2]

.....

.....

.....

Total [10]

10

1095 010003

Examiner only

2. *(a)* Write an expression for the ionic product of water, K_w, giving its units, if any. [2]

K_w =

Units .....

(b) (i) The value for K_w at 298 K is 1.0×10^{-14}. Explain why the pH of pure water at this temperature has a value of 7. [2]

.....

.....

.....

(ii) Calculate the pH of the final solution if 10 cm^3 of 0.10 mol dm^{-3} hydrochloric acid is added to 990 cm^3 of pure water. [2]

pH = ...

(c) Calculate the pH of a solution which is 0.010 mol dm^{-3} with respect to ethanoic acid and 0.020 mol dm^{-3} with respect to sodium ethanoate at 298 K. [3]

[K_a for ethanoic acid = 1.78×10^{-5} mol dm^{-3} at 298 K]

pH = ...

Examiner only

(d) If 10 cm^3 of 0.10 mol dm^{-3} hydrochloric acid is added to 990 cm^3 of the solution described in *(c)* the change in pH is only 0.06. Explain why this change in pH is much smaller than that in *(b)*(ii). [3]

.....

.....

.....

.....

.....

.....

Total [12]

12

1095 010005

3. *Read the passage below and then answer the questions in the spaces provided.*

Hydrogen Peroxide

If a non-scientist knows only one chemical formula it is most likely to be H_2O for water but how much do you know about another hydrogen oxide, hydrogen peroxide? A molecule of hydrogen peroxide has the molecular formula H_2O_2.

Most chemistry students first meet hydrogen peroxide as a colourless solution that is used to prepare oxygen. Bottles of hydrogen peroxide from a pharmacist are often labelled '20 volume'. This means that one volume of solution decomposes to give 20 volumes of oxygen gas. The equation for the decomposition is:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

$$1\,dm^3 \qquad\qquad 20\,dm^3$$

This reaction is very slow at room temperature. However the addition of a suitable catalyst increases the rate of decomposition phenomenally. Manganese(IV) oxide, potatoes and blood are all effective. Potatoes and blood both contain the enzyme catalase and one catalase molecule decomposes 50 000 molecules of H_2O_2 per second!

Is hydrogen peroxide an oxidising agent or a reducing agent?

Both in the laboratory and at home hydrogen peroxide is most commonly used as an oxidising agent (so the hydrogen peroxide itself is reduced). The half-equation is:

Reduction $\qquad H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$

Since some colouring matter is bleached by oxidation and the product of hydrogen peroxide's reduction is water, it is used as a safe bleaching agent particularly in hair treatment. A peroxide blonde is someone with almost white hair, usually as a result of treatment with hydrogen peroxide.

However, if hydrogen peroxide reacts with a more powerful oxidising agent such as potassium manganate(VII), the hydrogen peroxide will act as a reducing agent and will itself be oxidised. The half-equation is:

Oxidation $\qquad H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$

Therefore hydrogen peroxide can act as both oxidising agent and reducing agent. In fact, it can react with itself so that alternate molecules are oxidised and reduced. The overall equation is obtained by adding the half-equations for the reduction and oxidation, giving

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

which is the standard decomposition equation!

- End of passage -

Examiner only

(a) Using outer electrons only, draw a dot and cross diagram to show the bonding in a hydrogen peroxide molecule *(line 3)*. [1]

(b) Use the equation for the decomposition of hydrogen peroxide *(line 8)* to calculate the concentration, in mol dm^{-3}, of aqueous hydrogen peroxide solution in a bottle of '20 volume hydrogen peroxide' at 25 °C. [2]

[1 mol of oxygen occupies 24 dm^3 at 25 °C]

Concentration = ... mol dm^{-3}

(c) Manganese(IV) oxide *(line 10)* and potassium manganate(VII) *(lines 20-21)* are typical transition metal compounds.

(i) Give **two** reasons why transition metal compounds can act as catalysts. [2]

.....

.....

.....

(ii) Explain why transition metal complex ions appear coloured. [4]
QWC [1]

.....

.....

.....

.....

.....

.....

.....

.....

Examiner only

(d) In an acidic solution, hydrogen peroxide is oxidised to oxygen by potassium manganate (VII) *(lines 20-23)*.

(i) Write the half-equation for the reduction of MnO_4^- to Mn^{2+} ions in acidic solution. [1]

.....

(ii) Use your answer to (i) and the half-equation given in *line 23* to deduce the overall equation for this reaction. [2]

.....

.....

.....

(iii) 20.0 cm^3 of an acidified solution of hydrogen peroxide required 14.80 cm^3 of a 0.020 mol dm^{-3} solution of potassium manganate(VII) for complete reaction. Calculate the concentration, in mol dm^{-3}, of the hydrogen peroxide solution. [3]

Concentration = ... mol dm^{-3}

(e) Explain, using oxidation states, why the decomposition of hydrogen peroxide *(line 27)* can be classified as a redox reaction. [2]

.....

.....

.....

Total [18]

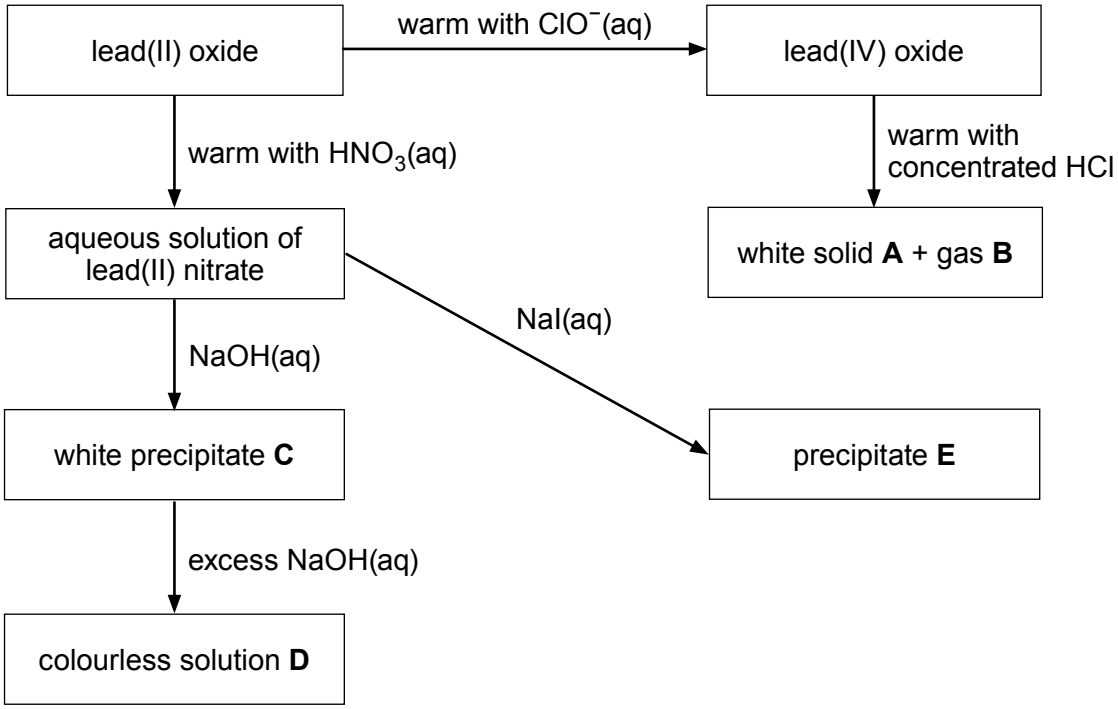
18

Total Section A [40]

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* The diagram shows some of the reactions of lead compounds.



(i) State the role of lead(IV) oxide in the reaction with concentrated hydrochloric acid. [1]

(ii) Name white solid **A** and gas **B**. [2]

(iii) Give the formula of the lead-containing species present in colourless solution **D**. [1]

(iv) Give the colour of precipitate **E**. [1]

(v) Write the equation for the formation of lead(II) nitrate from lead(II) oxide. [1]

(b) Carbon is the first element in Group 4. Two of its allotropes are diamond and graphite. A compound that forms structures corresponding to diamond and graphite is boron nitride.

(i) Describe the structure of graphite and explain why **hexagonal** boron nitride can adopt the same structure yet have different electrical conductivity properties. [4]
QWC [1]

(ii) State **one** use for the **cubic** boron nitride structure. [1]

(c) Another element in Group 4 is tin. At low temperatures tin exists as its grey form. At higher temperatures the white form is stable. The change can be represented by the equation:

$$Sn_{(grey)} \longrightarrow Sn_{(white)} \qquad \Delta H^{\ominus} = 1.92\,kJ\ mol^{-1}$$

The standard entropy values are $44.8\,J\,K^{-1}\,mol^{-1}$ for grey tin and $51.5\,J\,K^{-1}\,mol^{-1}$ for white tin.

(i) Calculate the minimum temperature needed to cause grey tin to change to white tin. [3]

(ii) During Napoleon's disastrous campaign in Russia from June to December in 1812 the tin buttons on his infantry's uniforms disintegrated. Suggest a reason why this might have happened. [1]

(d) An important technological development in recent years has been the hydrogen fuel cell. This uses electrochemical methods to get energy from hydrogen.

(i) Write the half-equations for the processes occurring at the electrodes and an equation for the overall reaction. [3]

(ii) Give **one** disadvantage of using hydrogen fuel cells to power vehicles. [1]

Total [20]

5. *(a)* Chlorine reacts with aqueous sodium hydroxide in one of two ways, depending on the temperature used.

(i) Write the equation for the reaction of chlorine with

I cold aqueous sodium hydroxide, [1]

II hot aqueous sodium hydroxide. [1]

(ii) Classify this type of redox reaction. [1]

(b) Chlorine reacts with many elements to form chlorides. Explain why phosphorus forms two chlorides, PCl_3 and PCl_5, but nitrogen only forms NCl_3. [2]

(c) Most ionic chlorides, e.g. sodium chloride, are soluble in water. However some, e.g. silver chloride, are insoluble.

The enthalpy change of solution of an ionic compound and its solubility depend on the balance between two enthalpy changes. Name these enthalpy changes and state if they are endothermic or exothermic. Explain how the enthalpy change of solution of a compound and its solubility depend on the balance between them. [4]

QWC [1]

(d) Some standard electrode potentials, $E^{\ominus}$, are given below.

System	$E^{\ominus}$/V
$\frac{1}{2}I_2(s) + e^- \rightleftharpoons I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$\frac{1}{2}Br_2(l) + e^- \rightleftharpoons Br^-(aq)$	+1.09
$\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$	+1.36
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.45

(i) Using the information from the table, state which of the **halides** will reduce Fe^{3+} to Fe^{2+}. Give a reason for your answer. [2]

(ii) Write the cell diagram of the cell formed by combining the $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ and $Ce^{4+}(aq)$, $Ce^{3+}(aq)$ half cells and calculate the standard e.m.f. of this cell. [2]

QUESTION 5 CONTINUES ON PAGE 12

(e) A flask containing an initial mixture of 0.100 mol of ethanoic acid and 0.083 mol of methanol was kept at 25 °C until the following equilibrium had been established.

$$CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O \qquad \Delta H = -3\,kJ\ mol^{-1}$$

The ethanoic acid present at equilibrium required 32.0 cm^3 of a 1.25 mol dm^{-3} solution of sodium hydroxide for complete reaction.

(i) Write an expression for the equilibrium constant, K_c, giving the units, if any. [2]

(ii) Calculate the number of moles of ethanoic acid present at equilibrium. [1]

(iii) Calculate the value of the equilibrium constant, K_c, for this reaction. [2]

(iv) State, giving a reason, what happens to the value of the equilibrium constant, K_c, if the temperature is increased. [1]

Total [20]

Total Section B [40]

END OF PAPER

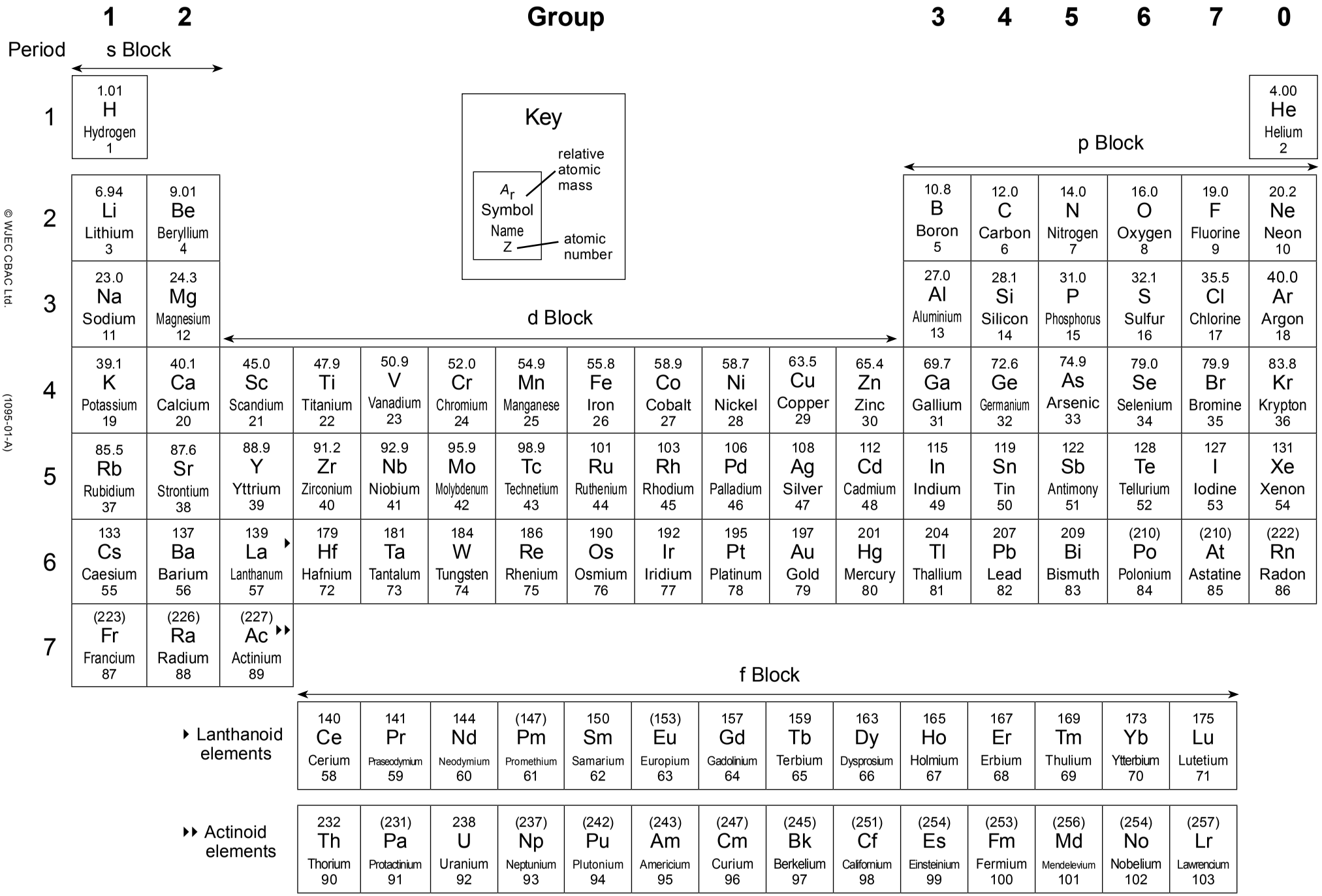
GCE A level

1095/01-A

CHEMISTRY – CH5
Periodic Table

P.M. TUESDAY, 17 June 2014

THE PERIODIC TABLE



(1095-01-A)

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 = $\frac{0.1 \times 10}{1000} = 0.001$ (1)

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

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

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

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)

[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 $MnO_4^- = \frac{0.02 \times 14.8}{1000} = 2.96 \times 10^{-4}$ (1)

Moles $H_2O_2 = 7.40 \times 10^{-4}$ (1)

Concentration $H_2O_2 = \frac{7.40 \times 10^{-4}}{0.020} = 0.037$ 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)

$T = \frac{1.92}{0.0067}$ (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]
(2^{nd} 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]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1095/01

S15-1095-01

CHEMISTRY – CH5

P.M. MONDAY, 15 June 2015

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1.**	**16**	
	2.	**9**	
	3.	**15**	
Section B	**4.**	**20**	
	5.	**20**	
	Total	**80**	

1095 010001

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a copy of the **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The *QWC* label alongside particular part-questions indicates those where the Quality of Written Communication is assessed.

Examiner only

SECTION A

Answer **all** *questions in the spaces provided.*

1. *(a)* Copper ions combine with a range of ligands to form complex ions, including $[CuCl_4]^{2-}$ and $[Cu(H_2O)_6]^{2+}$.

(i) State what is meant by a *ligand*. [1]

.....

.....

(ii) Draw the structures of $[CuCl_4]^{2-}$ and $[Cu(H_2O)_6]^{2+}$ ions. [2]

(iii) A solution containing $[Cu(H_2O)_6]^{2+}$ ions is blue. Explain the origin of this colour. [3]

.....

.....

.....

.....

.....

.....

(iv) When excess ammonia is added to a solution containing $[Cu(H_2O)_6]^{2+}$ ions, the colour of the solution changes as a new complex ion is formed. Give the formula of the new complex ion and the colour of the solution formed. [2]

.....

.....

Examiner only

(b) Phosphorus forms two chlorides, PCl_3 and PCl_5, and there is a dynamic equilibrium between these compounds in the gas phase. This is represented by the equation below.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(i) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

(ii) A sealed vessel is filled with PCl_5 at a pressure of 3.0×10^5 Pa. Upon heating, the system comes to equilibrium to form a mixture that contains PCl_3 at a partial pressure of 1.3×10^5 Pa.

I. State the partial pressure of Cl_2 at equilibrium. [1]

.....

II. Calculate the value of the equilibrium constant, K_p, giving its units. [3]

K_p = ...

Units .....

III. As the temperature is increased the value of K_p increases. State what information this provides about the enthalpy change of this reaction, giving a reason for your answer. [1]

.....

.....

(c) Silicon(IV) chloride reacts with water whilst CCl_4 does not. Give the equation for the reaction of $SiCl_4$ with water and explain why the behaviour of CCl_4 and $SiCl_4$ with water is so different. [2]

.....

.....

.....

Total [16]

1095 010003

Examiner only

2. Iron is extracted at high temperatures from the ore haematite, which contains iron(III) oxide, Fe_2O_3. The process can be summarised by the equation below.

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H^\theta = -23\,kJ\,mol^{-1}$$

Some thermodynamic data for the substances in the reaction are shown in the following table.

Substance	Standard enthalpy change of formation, ΔH^θ_f / kJ mol^{-1}	Standard entropy, S^θ / J K^{-1} mol^{-1}
$Fe_2O_3(s)$	−826	90
Fe(s)	0	27
CO(g)		198
$CO_2(g)$	−394	213

(a) Calculate the standard enthalpy change of formation of carbon monoxide. [3]

ΔH^θ_f = ... kJ mol^{-1}

(b) Explain why the standard entropies of carbon dioxide and carbon monoxide are significantly greater than those of iron(III) oxide and iron. [1]

.....

.....

(c) The standard entropy change for this reaction, ΔS^θ, is +9 J K^{-1} mol^{-1}.

(i) Calculate the free energy change, ΔG^θ, for this reaction at 298K. [2]

ΔG^θ = ... kJ mol^{-1}

Examiner only

(ii) Explain why this reaction is feasible at all temperatures. [2]

.....

.....

.....

(iii) Many industrial processes use high temperatures even when the reaction is feasible at low temperatures. Suggest why high temperatures are used. [1]

.....

.....

Total [9]

9

1095 010005

3. *Read the passage below and then answer the questions in the spaces provided.*

The Chemistry of Boron

Boron is an element at the top of Group 3. It forms a range of compounds whose behaviour is very different from the other elements in the same group. Boron shows the properties of a non-metal, however the remaining elements, including aluminium, gallium, indium and thallium all show metallic properties. This change is similar to that seen in other groups in the p-block with Group 4 having the non-metal carbon at the top and the metal lead at the bottom. In its compounds, boron exhibits the +3 oxidation state exclusively, forming materials such as BCl_3, BF_3 and B_2O_3. No compounds with a +1 oxidation state are known. Aluminium also exists only as the +3 oxidation state, however the +1 oxidation state becomes more common as the group is descended.

Boranes

There are very many compounds formed between boron and hydrogen and these are called boranes. These boranes are grouped into series and two examples of these are:

- *Nido*-boranes with a general formula of B_nH_{n+4}. This series includes pentaborane(9), B_5H_9, and decaborane(14), $B_{10}H_{14}$.
- *Arachno*-boranes with a general formula of B_nH_{n+6}. The first member of this series is tetraborane(10), B_4H_{10}.

All of these boranes are electron deficient, which leads them to be very reactive. The majority react explosively on contact with air, which led to their proposed use as a rocket fuel. To destroy the stockpile of B_5H_9 when it was no longer needed, the US government treated it with steam to form a solution of boric acid (H_3BO_3) and hydrogen gas.

Boron nitride

Boron nitride has a giant covalent structure that has the same number of electrons as graphite and diamond. They are said to be isoelectronic. Boron nitride exists in two forms:

- Hexagonal boron nitride has a structure similar to graphite, and is sometimes called 'white graphite' because of its excellent lubricating properties. Unlike graphite, hexagonal boron nitride is an insulator and has applications which depend upon this property.
- Cubic boron nitride has a diamond structure, and is the second hardest natural material known. It has high thermal conductivity and is chemically inert.

Uses of boron compounds

Nearly all boron ore extracted from the Earth is destined for refinement into boric acid and sodium tetraborate. Most boric acid is used in the production of shock-resistant glass, whilst sodium tetraborate is used as an additive to detergents. Boron is also used in nuclear reactors, where boron shielding is used as a control, taking advantage of its high cross-section for neutron capture.

- End of passage -

Examiner only

(a) Explain why boron forms compounds with the +3 oxidation state alone, but thallium compounds are more stable with the +1 oxidation state *(lines 6-9)*. [2]

.....

.....

.....

(b) Boranes are compounds made up of boron and hydrogen only *(lines 11-16)*. A sample of a gaseous borane was found to contain 78.14 % boron and 21.86 % hydrogen by mass. A sample of this borane of mass 1.232 g occupied a volume of 1 dm^3 at 273 K and 1 atm pressure.

[The molar volume of a gas at 273 K and 1 atm pressure is 22.4 dm^3.]

(i) What is the empirical formula of this borane? [2]

Empirical formula .....

(ii) What is the molecular formula of this borane? [3]

Molecular formula .....

(c) Explain the term *electron deficient (line 17)*. [1]

.....

.....

1095 010007

Examiner only

(d) Balance the equation for the reaction of pentaborane(9), B_5H_9, with steam *(lines 18-20)*. [1]

..... B_5H_9 + ... H_2O ⟶ ..... H_3BO_3 + ... H_2

(e) The standard enthalpy change of formation of pentaborane(9) is +42.8 kJ mol^{-1}. State what information this value gives about the stability of this compound. [1]

.....

.....

(f) Hexagonal boron nitride and graphite have similar structures *(lines 24-26)*. Describe the differences between these two isoelectronic materials in terms of their bonding and structure. [3]
QWC [1]

.....

.....

.....

.....

.....

.....

(g) Boron-10 absorbs a neutron *(line 33)* to form an intermediate, which then decays by emission of an alpha particle.

Give the mass number and atomic number of the final product. [1]

Mass number ..... *Atomic number* .....

Total [15]

15

Total Section A [40]

BLANK PAGE

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. The leaves of the rhubarb plant are rich in ethanedioic acid (oxalic acid) which is a poisonous compound. A solution containing ethanedioate ions can be formed by boiling rhubarb leaves with water. It can be separated and samples titrated against acidified potassium manganate(VII) to find the concentration of the ethanedioate solution.

(a) Suggest how the ethanedioate solution could be separated from the rhubarb leaves. [1]

(b) Write an ion-electron half-equation for the reduction of acidified manganate(VII) ions, MnO_4^-. [1]

(c) The ion-electron half-equation for the oxidation of ethanedioate ions is given below.

$$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(g) + 2e^-$$

(i) Give the oxidation states for carbon at the start and end of this reaction. [1]

(ii) Write an equation for the reaction of acidified manganate(VII) ions with ethanedioate ions. [1]

(d) Give a reason why an indicator is not needed in this titration. [1]

(e) Four samples of 25.00 cm^3 of the ethanedioate solution were titrated against acidified potassium manganate(VII) solution of concentration 0.0200 mol dm^{-3}. The volumes of potassium manganate(VII) solution required for complete reaction are listed below.

	1	2	3	4
Volume of $KMnO_4(aq)$ / cm^3	28.80	27.95	28.00	27.80

Use the information given to calculate the concentration of the ethanedioate solution. [4]

(f) Heating ethanedioic acid in glycerol produces methanoic acid, HCOOH.

(i) Write the expression for the acid dissociation constant, K_a, for methanoic acid. [1]

(ii) The value of K_a for methanoic acid is 1.8×10^{-4} mol dm^{-3}.
Calculate the pH of a solution of methanoic acid of concentration 0.2 mol dm^{-3}. [3]

(iii) A mixture of methanoic acid and sodium methanoate can be used as a buffer solution. State what is meant by a *buffer solution* and explain how a mixture of methanoic acid and sodium methanoate acts as a buffer. [3]
QWC [1]

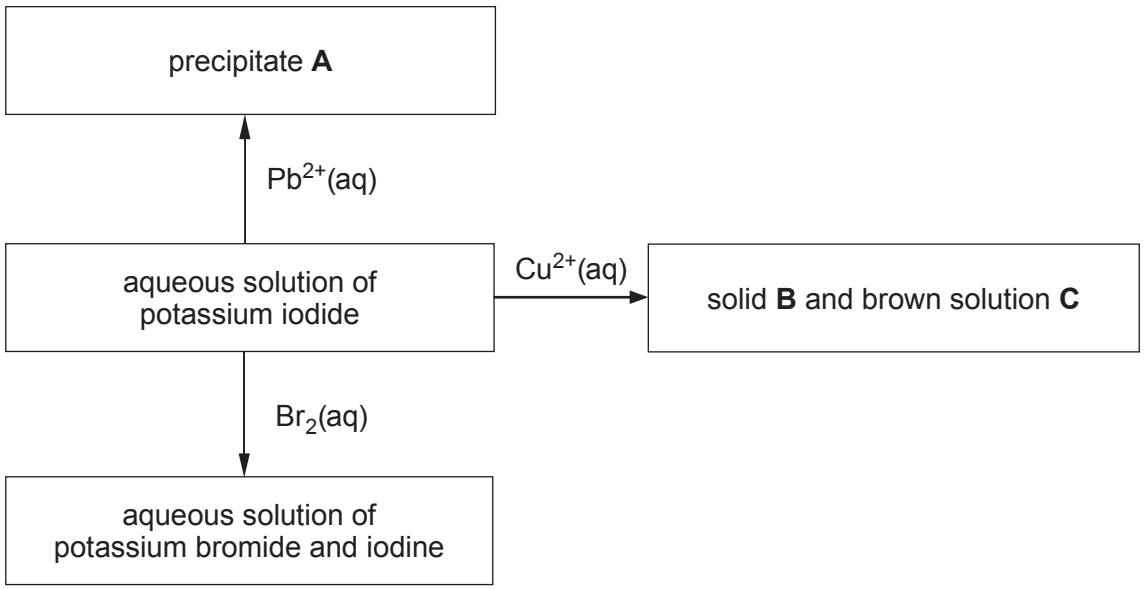
(g) Acidified potassium dichromate, $K_2Cr_2O_7$, is also an oxidising agent.

(i) Give the colour change that occurs when acidified potassium dichromate acts as an oxidising agent. [1]

(ii) When sodium hydroxide is added to a solution of potassium dichromate, a colour change occurs without a redox reaction occurring. Give the formula of the new chromium-containing ion and the colour of the solution formed. [2]

Total [20]

5. The diagram below shows some of the reactions of potassium iodide solution.



(a) Identify precipitate **A** and give its colour. [2]

(b) Write an equation for the reaction of $Cu^{2+}(aq)$ and $I^-(aq)$, clearly identifying the precipitate. [2]

(c) Bromine reacts with aqueous potassium iodide as shown above, however bromine does not react with aqueous sodium chloride. Use the standard electrode potentials below to explain these observations. [3]
QWC [1]

Half-equation	E^θ/V
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.09
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

(d) Solid potassium iodide reacts with concentrated sulfuric acid in the same way as sodium iodide.

Describe the observations made during this reaction and identify the products formed. [3]

(e) Hydrogen peroxide reacts with acidified potassium iodide according to the equation below.

$$2H^+ + 2I^- + H_2O_2 \longrightarrow I_2 + 2H_2O$$

(i) This reaction was studied using an iodine clock reaction. Describe the principles of how the rate of a clock reaction is determined. Experimental details are not required. [2]

(ii) The rate of this reaction was studied by a different method for a range of concentrations of $H_2O_2(aq)$ and $I^-(aq)$ and pH values. These are listed in the table below.

Experiment number	Initial concentration of $H_2O_2(aq)$ / mol dm^{-3}	Initial concentration of $I^-(aq)$ / mol dm^{-3}	pH	Initial rate / mol dm^{-3} s^{-1}
1	0.0010	0.10	1	2.8×10^{-6}
2	0.0020	0.10	1	5.6×10^{-6}
3	0.0020	0.10	2	5.6×10^{-6}
4	0.0010	0.40	1	11.2×10^{-6}

I. Some experiments were undertaken at pH 1 and some at pH 2. Give the difference in the concentrations of H^+ ions in these two solutions. [1]

II. Use the data in the table to deduce the rate equation for this reaction, giving your reasoning. [3]

III. Calculate the value of the rate constant, *k*, giving its units. [2]

IV. The reaction is repeated at a higher temperature. State how the increase in temperature affects the rate equation and rate constant. [1]

Total [20]

Total Section B [40]

END OF PAPER

BLANK PAGE

BLANK PAGE

GCE A level

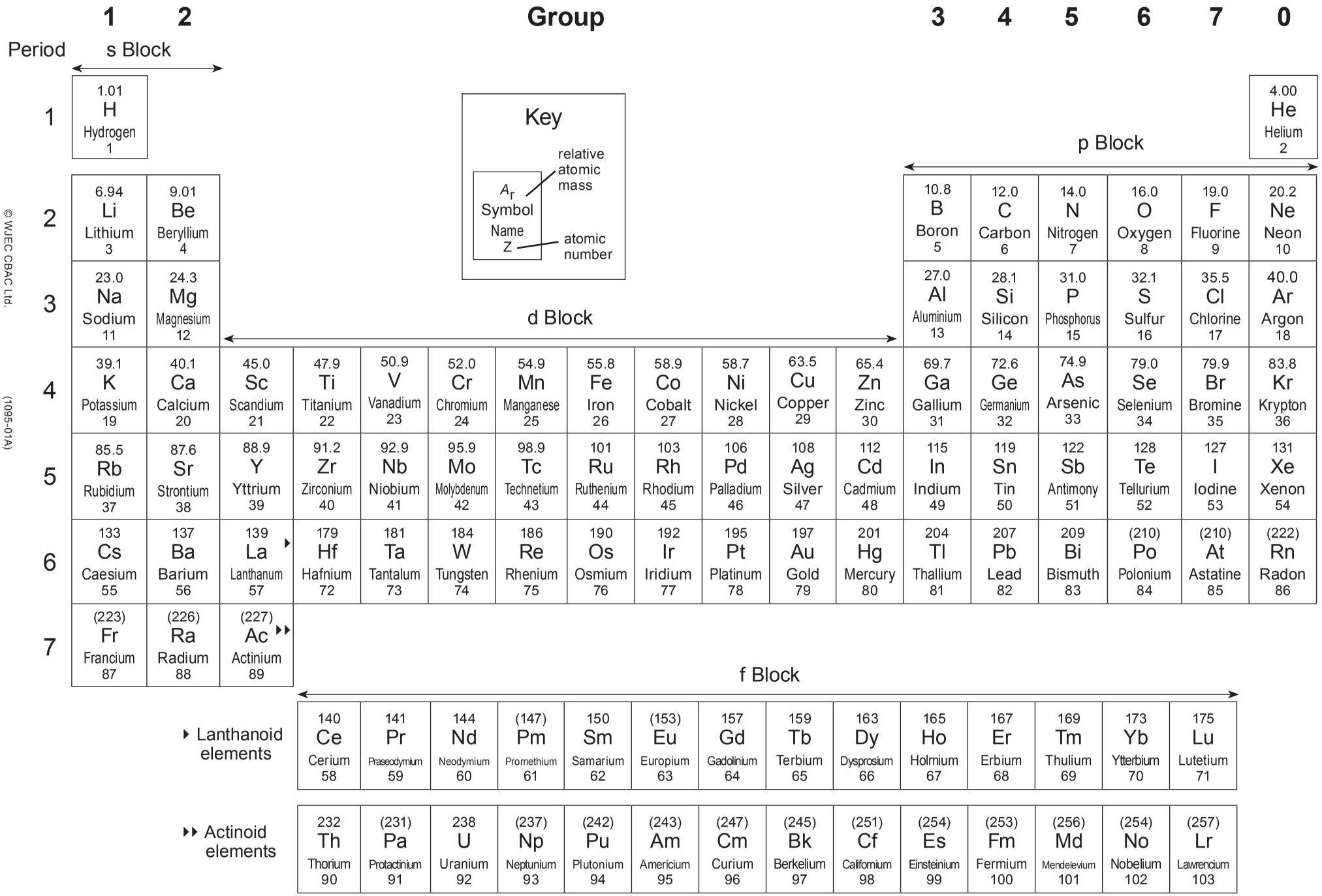
1095/01-A

S15-1095-01A

CHEMISTRY – PERIODIC TABLE
FOR USE WITH CH5

P.M. MONDAY, 15 June 2015

THE PERIODIC TABLE



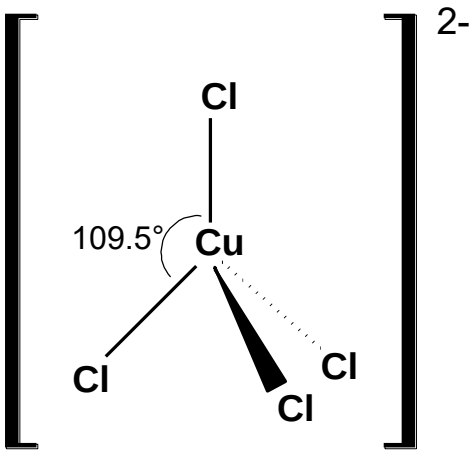
(1095-01A)

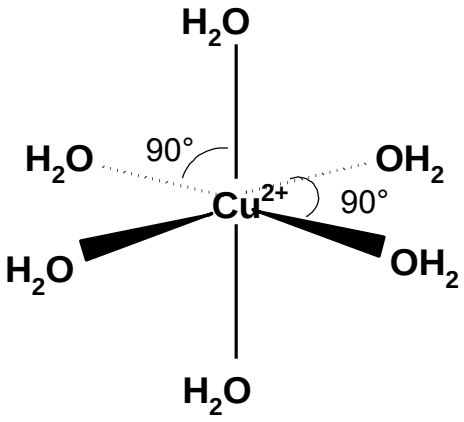
CH5

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) $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (1) Royal blue (1) [2]

(b) (i) $K_p = \frac{P_{PCl3}P_{Cl2}}{P_{PCl5}}$ do not accept if [ ] included [1]

(ii) I. 1.3×10^5 (Pa) [1]

II. $P_{PCl5} = 3.0 \times 10^5 - 1.3 \times 10^5 = 1.7 \times 10^5$ (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]

(c) $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ OR

$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$ (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) $2 \times (0) + 3 \times (-394) - (-826) - 3 \times \Delta H^{\theta}_{f}(CO) = -23$ (1)

$2 \times (\Delta H^{\theta}_{f}(Fe)) + 3 \times (\Delta H^{\theta}_{f}(CO_2)) - (\Delta H^{\theta}_{f}(Fe_2O_3)) - 3 \times \Delta H^{\theta}_{f}(CO) = -23$ (1)

$-1182 + 826 + 23 = 3 \times \Delta H^{\theta}_{f}(CO)$

$-333 = 3 \times \Delta H^{\theta}_{f}(CO)$

$-111 \text{ kJ mol}^{-1} = \Delta H^{\theta}_{f}(CO)$ (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 = 4.46×10^{-2} moles (1)

M_r = 1.232 / 4.46×10^{-2} = 27.6 (1)

Molecular formula = B_2H_6 (1) [3]

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

(d) $B_5H_9 + 15H_2O \rightarrow 5H_3BO_3 + 12H_2$ [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) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ [1]

(c) (i) Carbon O.S. at start = +3; Carbon O. S. at end = +4 [1]

(ii) $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$ [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 = $27.92 \times 0.020 / 1000 = 5.584 \times 10^{-4}$ mol (1)

Moles oxalate = $5.584 \times 10^{-4} \times 5/2 = 1.396 \times 10^{-3}$ mol (1)

Concentration = $1.396 \times 10^{-3} / 25 \times 10^{-3} = 0.0558$ mol dm^{-3} (1) [4]

(f) (i) $K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$ [1]

(ii) $[H^+]^2 = K_a \times [HCOOH] = 1.8 \times 10^{-4} \times 0.2 = 0.36 \times 10^{-4}$ (1)

$[H^+] = 6.0 \times 10^{-3}$ mol dm^{-3} (1)

$pH = -\log [H^+] = 2.22$ (1) [3]

(iii) A buffer keeps the pH almost constant when **small amounts** of acid or base are added (1)

$HCOOH \rightleftharpoons HCOO^- + H^+$ (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) $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$ (1)

The precipitate is copper(I) iodide (stated or clearly indicated by state symbols) (1) [2]

(c) Bromine has a more positive E^θ than iodine so it is a stronger oxidising agent (1)

Bromine is able to oxidise iodide (1)

Bromine has a less positive E^θ 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 ÷ 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 = $k[H_2O_2][I^-]$ (1) [3]

III. k = 0.028 (1) $mol^{-1}dm^3 s^{-1}$ (1) [ecf from rate equation] [2]

IV. Rate equation is unchanged and increasing temperature increases the value of the rate constant [1]

Total [20]

Surname	Centre Number	Candidate Number
Other Names		2

GCE A level

1095/01

S16-1095-01

CHEMISTRY – CH5

A.M. WEDNESDAY, 22 June 2016

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1.**	**10**	
	2.	**12**	
	3.	**18**	
Section B	**4.**	**20**	
	5.	**20**	
	Total	**80**	

1095 010001

ADDITIONAL MATERIALS

In addition to this examination paper, you will need:
- a calculator;
- an 8 page answer book;
- a copy of the **Periodic Table** supplied by WJEC. Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The *QWC* label alongside particular part-questions indicates those where the Quality of Written Communication is assessed.

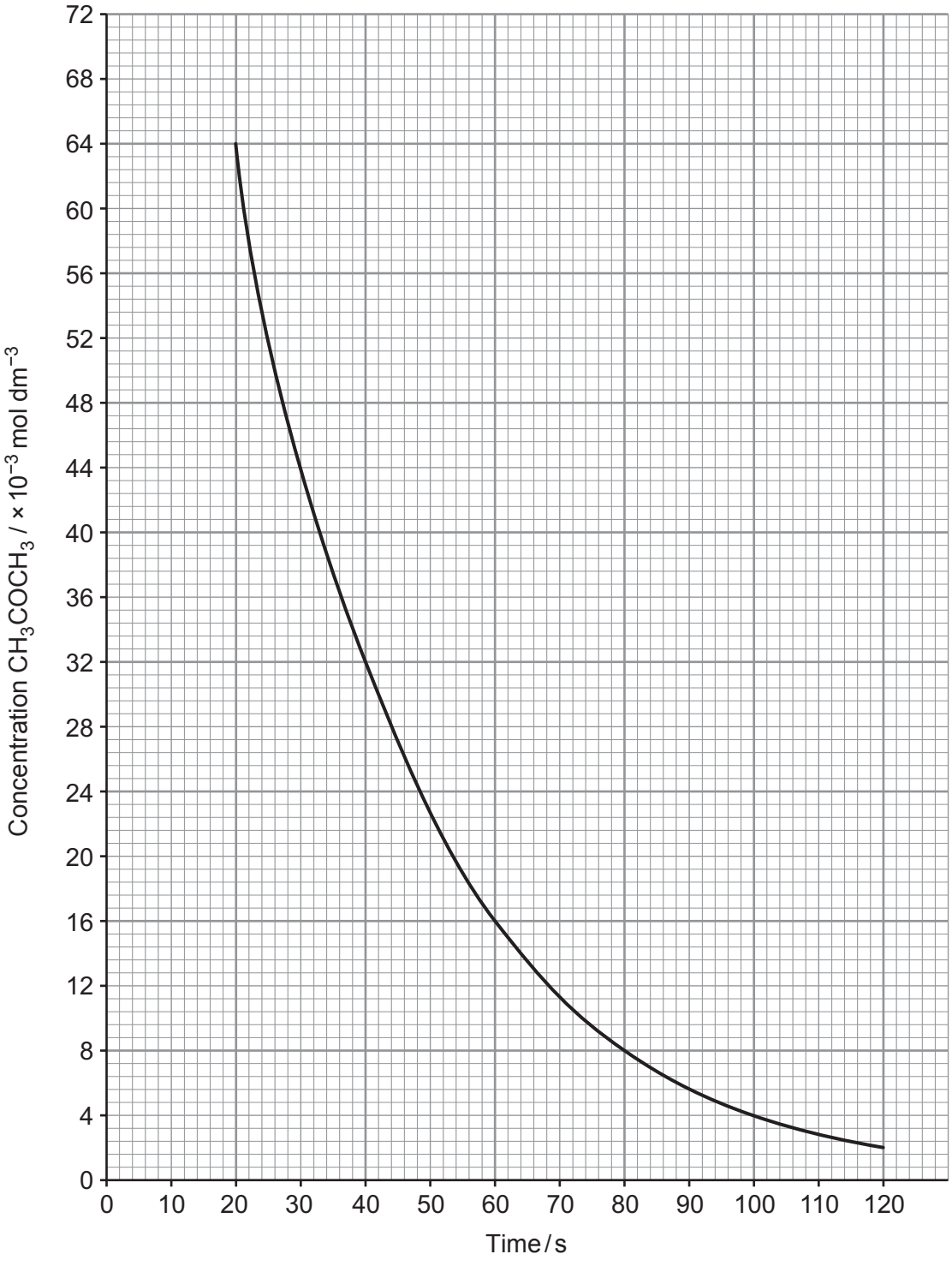
SECTION A

Answer **all** *questions in the spaces provided.*

1. *(a)* Elen carried out an investigation into the rate of reaction between propanone and iodine in an acidic solution. This is a multi-step reaction but the overall equation for the reaction is:

$$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$$

(i) In the first part of the investigation she measured how the concentration of propanone changed with time. Her results are shown in the graph below.



Examiner only

Explain how the graph shows that the reaction is first order with respect to propanone. Use values from the graph to justify your answer. [2]

.....

.....

.....

.....

(ii) In the second part of the investigation Elen investigated how different initial concentrations of iodine and acid affected the rate of reaction. The following results were obtained.

$[CH_3COCH_3]$ / mol dm^{-3}	$[I_2]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1.5×10^{-3}	0.030	0.020	2.1×10^{-9}
1.5×10^{-3}	0.060	0.040	4.2×10^{-9}
1.5×10^{-3}	0.030	0.040	4.2×10^{-9}

1095 010003

I. Determine the orders of reaction with respect to I_2 and H^+. [2]

I_2 .....

.....

H^+ .....

.....

II. Write the rate equation for the reaction. [1]

.....

III. Calculate the value of the rate constant in the rate equation and state its unit. [2]

k = ...

Unit .....

Examiner only

(b) Another multi-step reaction is the one between nitrogen dioxide and carbon monoxide. The overall equation for the reaction is:

$$NO_2 + CO \longrightarrow NO + CO_2$$

The rate equation for this reaction is as follows.

rate = $k[NO_2]^2$

The first step is the rate-determining step.

(i) Explain what is meant by the *rate-determining step*. [1]

.....

.....

(ii) Write equations to show a possible two-step mechanism for this reaction. [2]

.....

.....

Total [10]

10

BLANK PAGE

Examiner only

2. Acids can be considered to be strong or weak and concentrated or dilute.

(a) For an aqueous solution of an acid, explain the difference between the meaning of the terms *weak acid* and *dilute acid*. [2]

.....

.....

.....

.....

(b) The grids opposite show titration curves for the addition of aqueous sodium hydroxide solution to 25.0 cm^3 of aqueous acid.

From the list below, choose which acids were used to give curves **A** and **B** giving reasons for your answer.

W	0.1 mol dm^{-3} HCl
X	0.001 mol dm^{-3} HCl
Y	0.1 mol dm^{-3} CH_3COOH
Z	0.001 mol dm^{-3} CH_3COOH

(K_a for $CH_3COOH = 1.8 \times 10^{-5}$ mol dm^{-3})

(i) Curve **A** [2]

.....

.....

.....

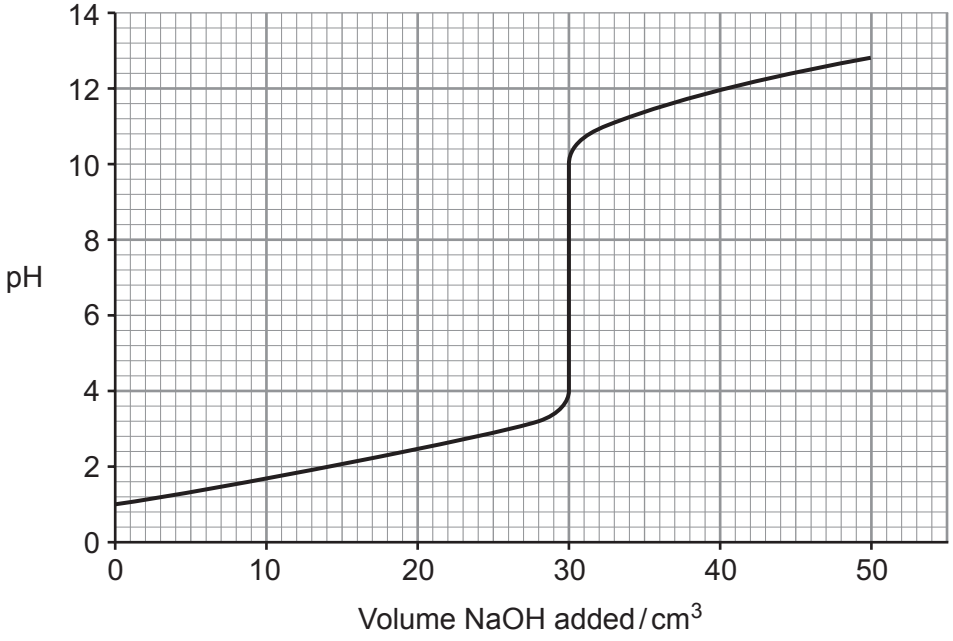
(ii) Curve **B** [3]

.....

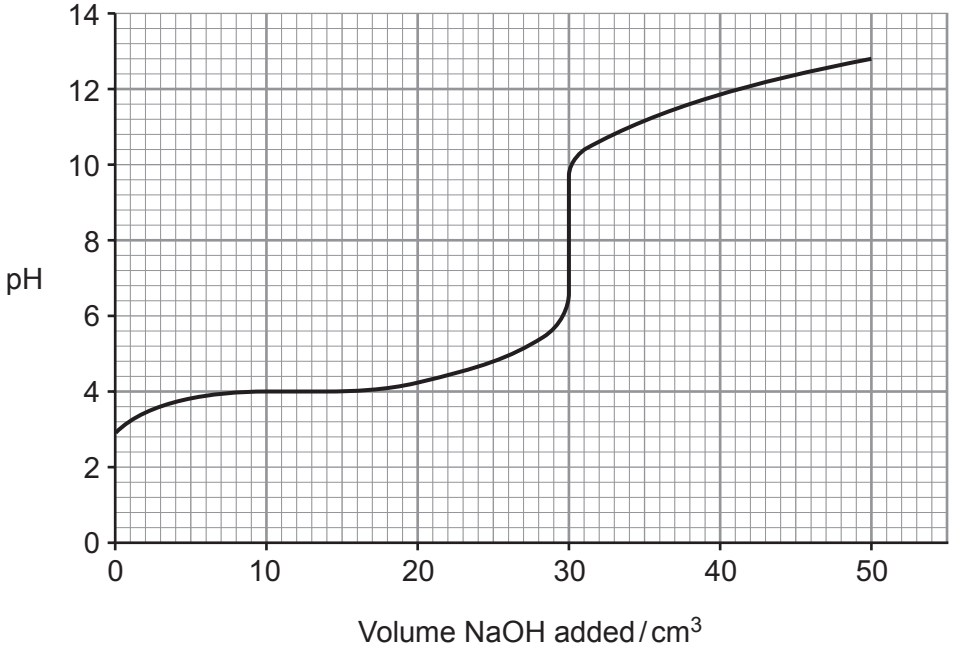
.....

.....

Titration curves of acid-alkali reactions



Curve A



Curve B

Examiner only

(iii) State, giving a reason, which of the following indicators would be **most** suitable for titration **B**. [2]

Indicator	pH range
methyl orange	3.4 – 4.8
chlorophenol red	4.8 – 6.4
thymol blue	8.0 – 9.6
brilliant cresyl blue	10.8 – 12.0

.....

.....

.....

(iv) Calculate the concentration of the aqueous sodium hydroxide solution used in titration **A**. [2]

Concentration = ... mol dm^{-3}

(c) Aqueous ammonia reacts with hydrochloric acid to form the salt ammonium chloride, NH_4Cl. Give a reason why the pH value for a solution of NH_4Cl is less than 7. [1]

.....

.....

.....

Total [12]

12

BLANK PAGE

3. *Read the passage below and then answer the questions in the spaces provided.*

Hydrogen

Hydrogen might be the simplest of all the elements in terms of atomic structure, but a look at the chemistry of hydrogen enables us to gain a better understanding of many important chemical ideas. Several chemical definitions and standards are based on hydrogen chemistry – from standard electrodes to the pH scale.

Hydrogen is the first element in the Periodic Table and is named from the Greek word *hydrogenos* which means water maker. Hydrogen is the only element that has different names for its isotopes. $^{1}_{1}H$ is hydrogen, $^{2}_{1}H$ is deuterium and $^{3}_{1}H$ is tritium.

Acidity is expressed using the pH scale first devised by the Swedish chemist Sorenson.

$$pH = -\log[H^+]$$

The scale usually runs from 0–14 because 1 mol dm^{-3} H^+ (acid) has a pH of 0 and 1 mol dm^{-3} OH^- (alkali) has a pH of 14. An aqueous solution is neutral when the concentrations of H^+ and OH^- are equal. At 25 °C, the ionic product of water, K_w, has a numerical value of 1.0×10^{-14}. Pure water has a pH of 7, and is neutral. This neutral value of pH can be calculated from K_w. Since boiling water has a larger value of K_w than water at 25 °C, it follows that a substance that is dissolved in boiling water to give a solution with a pH of 7 is slightly alkaline!

When measuring electrode potentials, it is potential differences which are measured. This means that the potential of one half-cell is compared with that of another. Again, hydrogen is the basis of the comparison. All electrode potentials are compared with that of the standard hydrogen electrode.

Looking at data for elements, we see that hydrogen often has the greatest or smallest quantity. For example when burned in air, hydrogen evolves more heat per unit mass than any other substance [$\Delta H_c^{\theta}(H_2) = -286$ kJ mol^{-1}]. Rockets such as the space shuttle, use a mixture of liquid hydrogen and liquid oxygen to propel them into orbit. Cars have been developed that run on hydrogen using fuel cells. The original airships were filled with hydrogen but its flammability led to a catastrophic fire on the Hindenburg in 1937. Modern airships use helium.

Most hydrogen today is used for the processing of fossil fuels and in the production of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Other important uses include as a hydrogenating agent in making margarines, in the production of methanol, in the manufacture of hydrochloric acid and also in cryogenics. Hydrogen – the light, flammable gas with its important industrial roles – does far more than just make water!

- End of passage -

Examiner only

(a) Write an expression for the ionic product of water, K_w, *(line 12)* giving its unit, if any. [1]

Unit .....

(b) The value for K_w at 100 °C is 5.13×10^{-13}. Use this to explain why an aqueous solution of a salt with a pH of 7 at this temperature is slightly alkaline *(line 15)*. [3]

.....

.....

(c) All electrode potentials are compared with the standard hydrogen electrode *(lines 18-19)*. With the aid of a diagram or otherwise explain what is meant by the *standard hydrogen electrode*. [2]

.....

.....

.....

Examiner only

(d) (i) Use the data given to calculate the standard enthalpy change of combustion of methane. [2]

Substance	$CH_4(g)$	$CO_2(g)$	$H_2O(l)$
Standard enthalpy change of formation, ΔH_f^θ / kJ mol^{-1}	−75	−394	−286

ΔH_c^θ = ... kJ mol^{-1}

(ii) Use this result to show that the statement in *line 21* is correct when comparing hydrogen and methane. [2]

.....

.....

(e) Cars have been developed that run on hydrogen using fuel cells *(lines 23-24)*. Explain the principles underlying the operation of the hydrogen fuel cell. [3]
QWC [1]

.....

.....

.....

.....

.....

.....

Examiner only

(f) In the production of ammonia *(lines 26-27)*, nitrogen and hydrogen were mixed in a vessel and allowed to reach equilibrium at a given temperature. The initial partial pressure of nitrogen was 26 atm and that of hydrogen was 82 atm. The equilibrium partial pressure of the remaining nitrogen was 18 atm.

(i) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

(ii) Calculate the equilibrium partial pressures of hydrogen and ammonia and use these to calculate a value for K_p at this temperature, giving the unit if any. [3]

K_p = ...

Unit .....

Total [18]

18

Total Section A [40]

SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* Copper is a typical transition metal.

Characteristics of these metals include an ability to:

- form coloured ions
- show variable oxidation states
- form complex ions

(i) State **one** *other* chemical property of transition metals. [1]

(ii) Explain why copper(I) compounds are generally white. [2]

(b) Copper compounds take part in several different types of reaction including ligand substitution and precipitation. Using copper compounds, give an example for both types of reaction, stating any observations. Give the formula for the copper-containing product for each example. [6]

QWC [1]

(c) Brass is an alloy of copper and zinc.

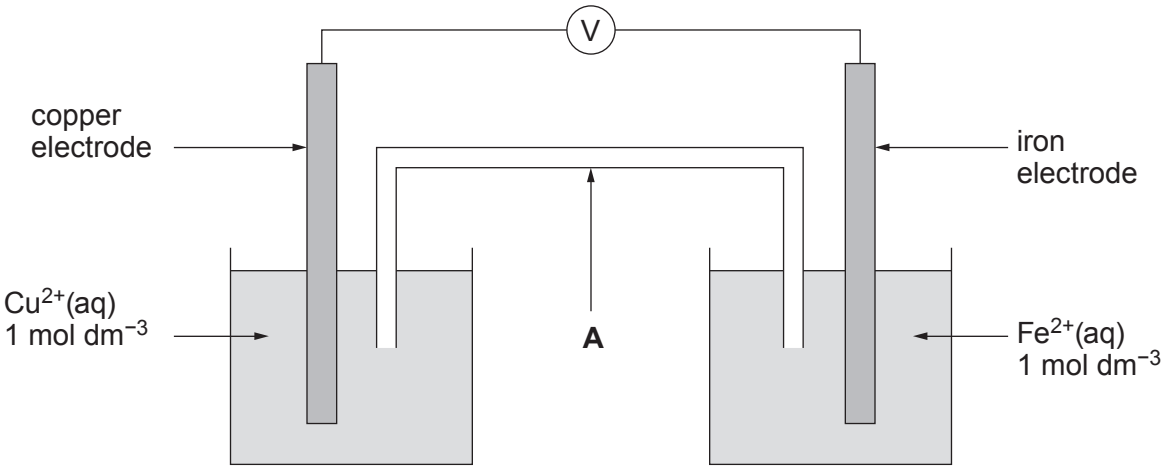
A 2.05 g brass screw was dissolved in nitric acid and the solution formed was diluted to 100 cm^3 in a volumetric flask. An excess of potassium iodide solution was added to 25.0 cm^3 of this solution and the iodine produced was titrated against a 0.200 mol dm^{-3} solution of sodium thiosulfate. The iodine required 24.00 cm^3 of the sodium thiosulfate solution for complete reaction.

(i) Name a suitable indicator for this titration. [1]

(ii) Calculate the percentage by mass of copper in the brass. Give your answer to **three** significant figures. [4]

(The ratio of $Cu^{2+} : S_2O_3^{2-}$ is 1 : 1)

(d) The diagram below shows the apparatus that was used to measure the emf of a Cu^{2+}/Cu, Fe^{2+}/Fe electrochemical cell.



Some standard electrode potentials, E^{θ}, are given below.

System	E^{θ}/V
$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$	+0.34
$Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$	−0.44
$Ni^{2+}(aq) + 2e^{-} \rightleftharpoons Ni(s)$	−0.25

(i) Name the part of the cell labelled **A** and state its purpose. [2]

(ii) State, giving a reason, which of the electrodes will be positively charged in the above cell. [1]

(iii) Calculate the standard emf, in volts, for the above cell. [1]

(iv) State whether or not you would expect nickel to react with iron(II) ions. Give a reason for your answer. [1]

Total [20]

5. *(a)* Group II elements can only show an oxidation state of II, however Group IV elements can show oxidation states of II and IV in their compounds.

(i) State how the relative stability of these oxidation states changes as Group IV is descended and give a reason for this trend. [2]

(ii) The characteristics of the Group IV elements and their compounds change significantly from carbon to lead. Show how this statement is true by comparing:

- the reactions, if any, of carbon dioxide and lead(II) oxide with acids and alkalis
- the reduction-oxidation properties of carbon monoxide and lead(IV) oxide.

Your answer should include any relevant chemical equations. [6]
QWC [1]

(b) Endothermic solid-solid reactions are rare in chemistry, but some do occur spontaneously. One such example is the reaction between barium hydroxide and ammonium chloride. The reaction can be represented as follows.

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \longrightarrow 2NH_3(g) + 8H_2O(l) + BaCl_2.2H_2O(s) \quad \Delta H = 135 \text{ kJ mol}^{-1}$$

The entropy values of the compounds involved in this reaction are given below.

Compound	$Ba(OH)_2.8H_2O(s)$	$NH_4Cl(s)$	$NH_3(g)$	$H_2O(l)$	$BaCl_2.2H_2O(s)$
Entropy / J K^{-1} mol^{-1}	427	95	192	70	203

(i) Explain why there is an increase in entropy for this reaction. [1]

(ii) Calculate the entropy change for this reaction. [1]

(iii) Calculate the free energy change, ΔG, for the reaction at 25 °C and explain why this reaction is feasible. [3]

(c) The enthalpy change of formation of barium chloride, $BaCl_2$, can be determined indirectly using a Born-Haber cycle.

Use the data given below to calculate the enthalpy change of formation of barium chloride in kJ mol^{-1}. [4]

Process	ΔH^{θ} / kJ mol^{-1}
$Ba(s) \longrightarrow Ba(g)$	176
$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	121
$Ba(g) \longrightarrow Ba^+(g) + e^-$	502
$Ba^+(g) \longrightarrow Ba^{2+}(g) + e^-$	966
$Cl(g) + e^- \longrightarrow Cl^-(g)$	−364
$Ba^{2+}(g) + 2Cl^-(g) \longrightarrow BaCl_2(s)$	−2018

(d) Write the **formulae** of the chlorine-containing species that are produced when chlorine reacts with warm aqueous sodium hydroxide. [2]

Total [20]

Total Section B [40]

END OF PAPER

BLANK PAGE

BLANK PAGE

GCE A level

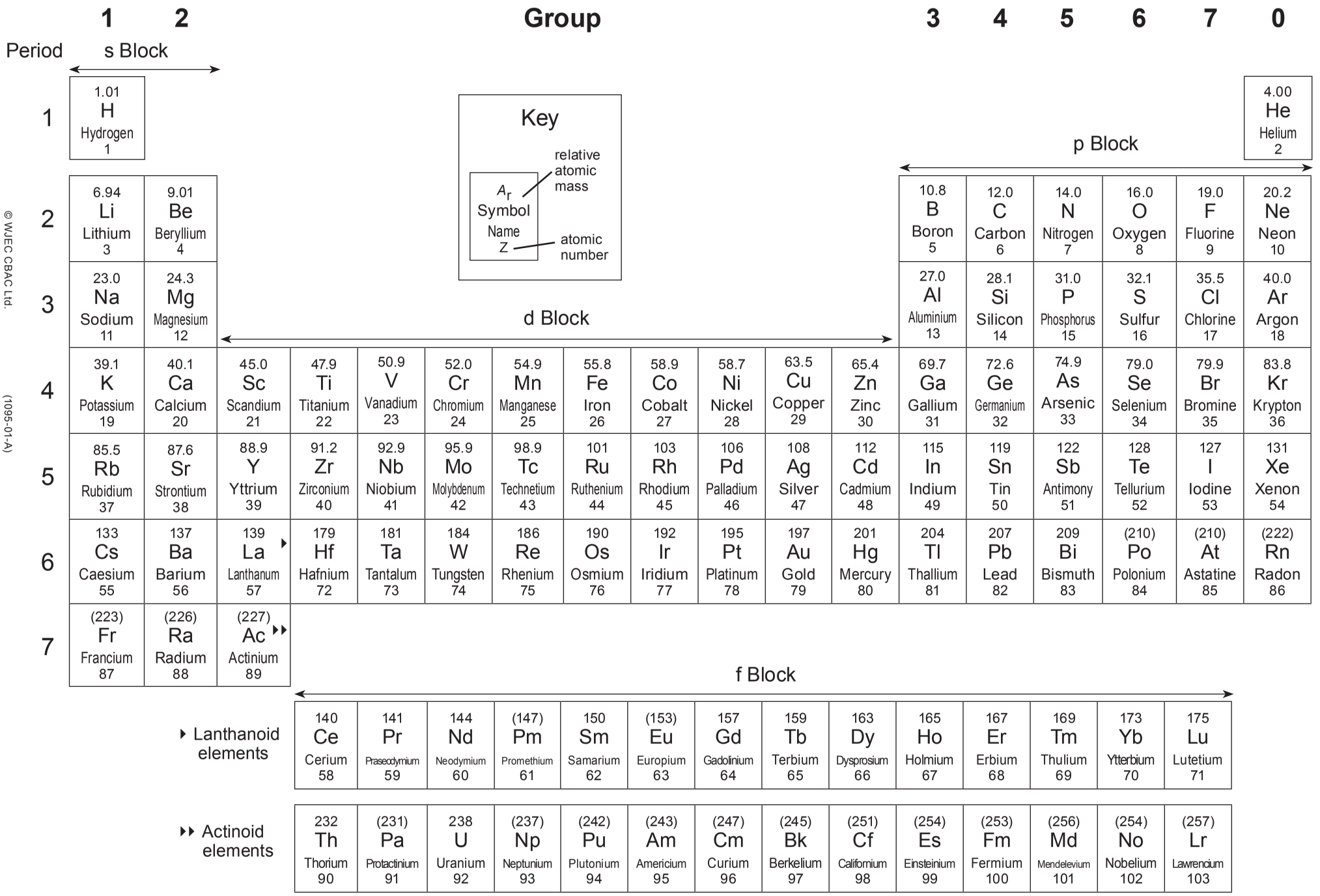
1095/01-A

S16-1095-01A

CHEMISTRY – PERIODIC TABLE
FOR USE WITH CH5

A.M. WEDNESDAY, 22 June 2016

THE PERIODIC TABLE



(1095-01-A)

GCE MARKING SCHEME

SUMMER 2016

CHEMISTRY - CH5
1095-01

INTRODUCTION

This marking scheme was used by WJEC for the 2016 examination. It was finalised after detailed discussion at examiners' conferences by all the examiners involved in the assessment. The conference was held shortly after the paper was taken so that reference could be made to the full range of candidates' responses, with photocopied scripts forming the basis of discussion. The aim of the conference was to ensure that the marking scheme was interpreted and applied in the same way by all examiners.

It is hoped that this information will be of assistance to centres but it is recognised at the same time that, without the benefit of participation in the examiners' conference, teachers may have different views on certain matters of detail or interpretation.

WJEC regrets that it cannot enter into any discussion or correspondence about this marking scheme.

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 = $k[CH_3COCH_3][H^+]$ [1]

III 7.0×10^{-5} (1)

$dm^3\ mol^{-1}\ s^{-1}$ (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. $2NO_2 \rightarrow 2NO + O_2$)

Second step has CO as reactant with products from step 1 (1)
(e.g. $2NO + O_2 + 2CO \rightarrow 2NO + 2CO_2$)

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 mol dm^{-3} 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 mol dm^{-3} CH_3COOH / **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) mol dm^{-3} (1)

Ecf from part (i) [2]

(c) Salt hydrolysis occurs $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$
(Accept NH_4^+ partially dissociates to release H^+) [1]

Total [12]

3. (a) $K_w = [H^+][OH^-]$ $mol^2\ dm^{-6}$ [1]

(b) pH = 7, therefore $[H^+] = 1.0 \times 10^{-7}$ (1)

$$[OH^-] = \frac{5.13 \times 10^{-13}}{1.0 \times 10^{-7}} = 5.13 \times 10^{-6} \quad (1)$$

$[OH^-] > [H^+]$ therefore solution is alkaline (1)

Alternative method

$[H^+] = 7.16 \times 10^{-7}$ at 100 °C (1)

pH = 6.15 (1)

pH 7 above neutral so $[OH^-] > [H^+]$ and solution is alkaline (1) [3]

(c) Half-cell where hydrogen at 1 atm (1)
Bubbles over a Pt electrode in contact with 1 mol dm^{-3} $H^+(aq)$ at 298K (1)
[2]

(d) (i) $\Delta H = (-394) + 2(-286) - (-75)$ (1)

$\Delta H = -891$ kJ mol^{-1} (1) [2]

(ii) Heat per unit mass $H_2 = \frac{286}{2.02} = 141.6$ kJ g^{-1} (1)

Heat per unit mass $CH_4 = \frac{891}{16.04} = 55.5$ kJ g^{-1} (1) [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) $K_p = \frac{(pNH_3)^2}{(pH_2)^3(pN_2)}$ do not accept [ ] [1]

(ii) $pH_2 = 58$ atm and $pNH_3 = 16$ atm (1)

$K_p = 7.3 \times 10^{-5}$ (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 $CuSO_4$/$[Cu(H_2O)_6]^{2+}$

Suitable observation (1)
e.g. formation of royal blue solution

Correct formula (1)
e.g. $[Cu(NH_3)_4(H_2O)_2]^{2+}$

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. $Cu(OH)_2$ [6]

QWC *The information is organised clearly and coherently, using specialist vocabulary where appropriate* [1]

(c) (i) Starch
[1]

(ii) Moles $S_2O_3^{2-} = 4.80 \times 10^{-3}$ (1)

Moles Cu^{2+} in original solution $= 1.92 \times 10^{-2}$ (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. $CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$ (1)

$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2$

$Pb(OH)_2 + 2OH^- \rightarrow [Pb(OH)_4]^{2-}$ (1)

or

$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$

$PbO + 2OH^- + H_2O \rightarrow [Pb(OH)_4]^{2-}$ (1)

Carbon monoxide is a reducing agent while lead(IV) is an oxidizing agent (1)

e.g. $CO + CuO \rightarrow CO_2 + Cu$ (1)

$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$ (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) $\Delta S = 530$ (J K^{-1} mol^{-1}) [1]

(iii) $\Delta G = 135 - 298(0.53)$ (1)

$\Delta G = -22.9$ (kJ mol^{-1}) (1)

ΔG is negative so the reaction is feasible (1) [3]

(c) $\Delta H_f = \Delta H_{at}Ba + I.E.Ba + \Delta H_{at}Cl_2 + E.A.Cl + \Delta H_{lat}BaCl_2$ (1)

Doubling value for forming 2Cl and $2Cl^-$ (1)
(These marks can be obtained from Born-Haber cycle)

$\Delta H_f\ BaCl_2 = 176 + 1468 + 242 - 728 - 2018$ (1)

$\Delta H_f\ BaCl_2 = -860$ (kJ mol^{-1}) (1) [4]

(d) $NaCl / Cl^-$ (1)

$NaClO_3 / ClO_3^-$ (1) [2]

Total [20]