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]

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]

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]

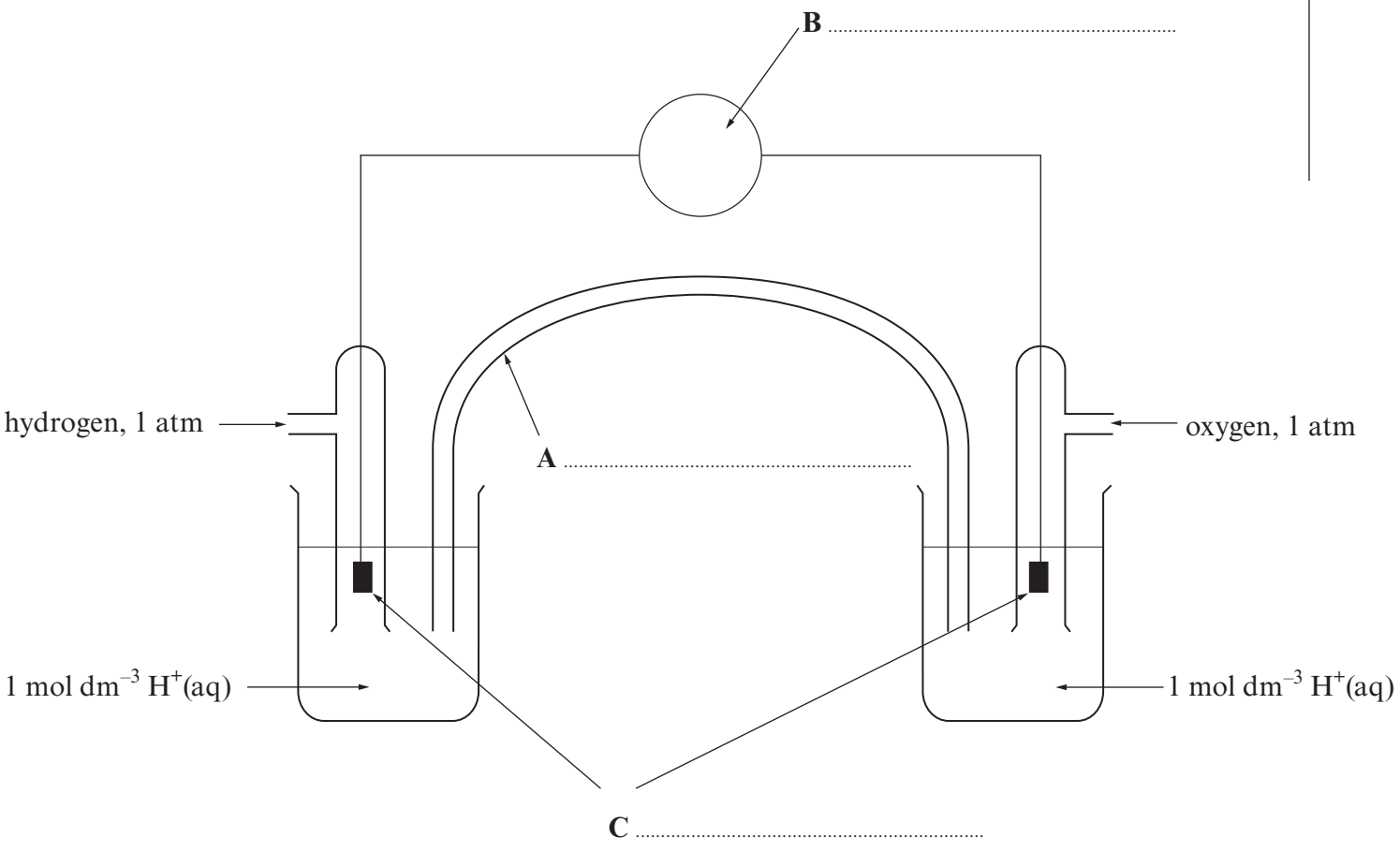
.....

(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]

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]

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]

.....

.....

.....

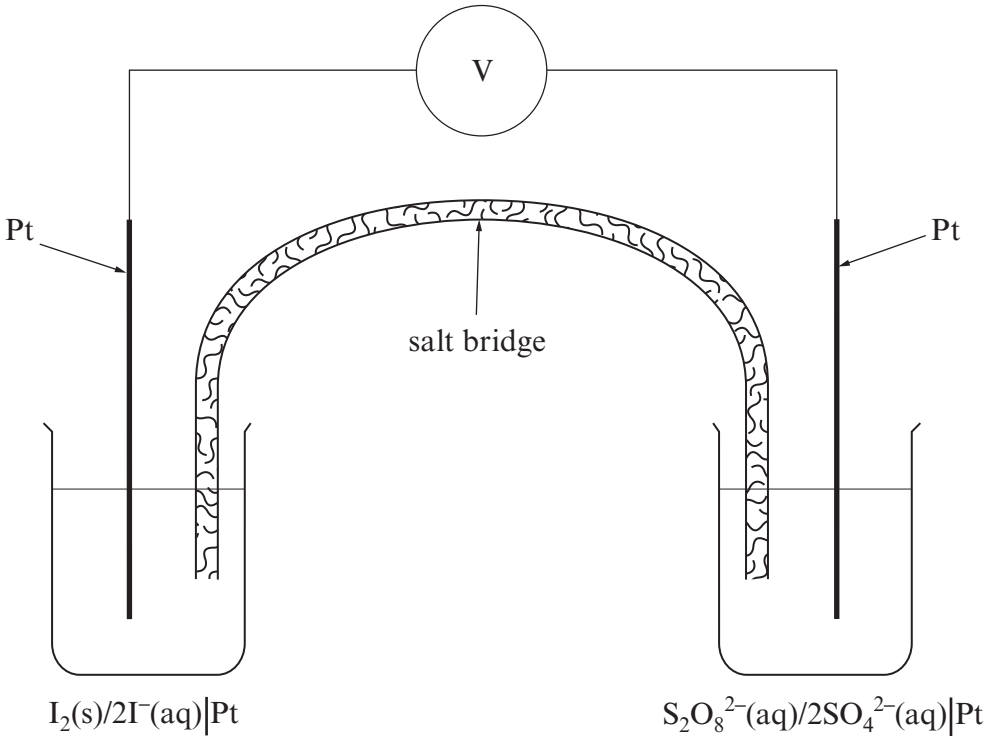
(ii) Suggest a way that the rate of decomposition of the potassium persulfate solution described in (i) could be measured. [1]

.....

.....

.....

(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]

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]

$$K_p = \frac{p_{SO_3} \times p_{NO}}{p_{SO_2} \times p_{NO_2}} = 2.5$$

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.

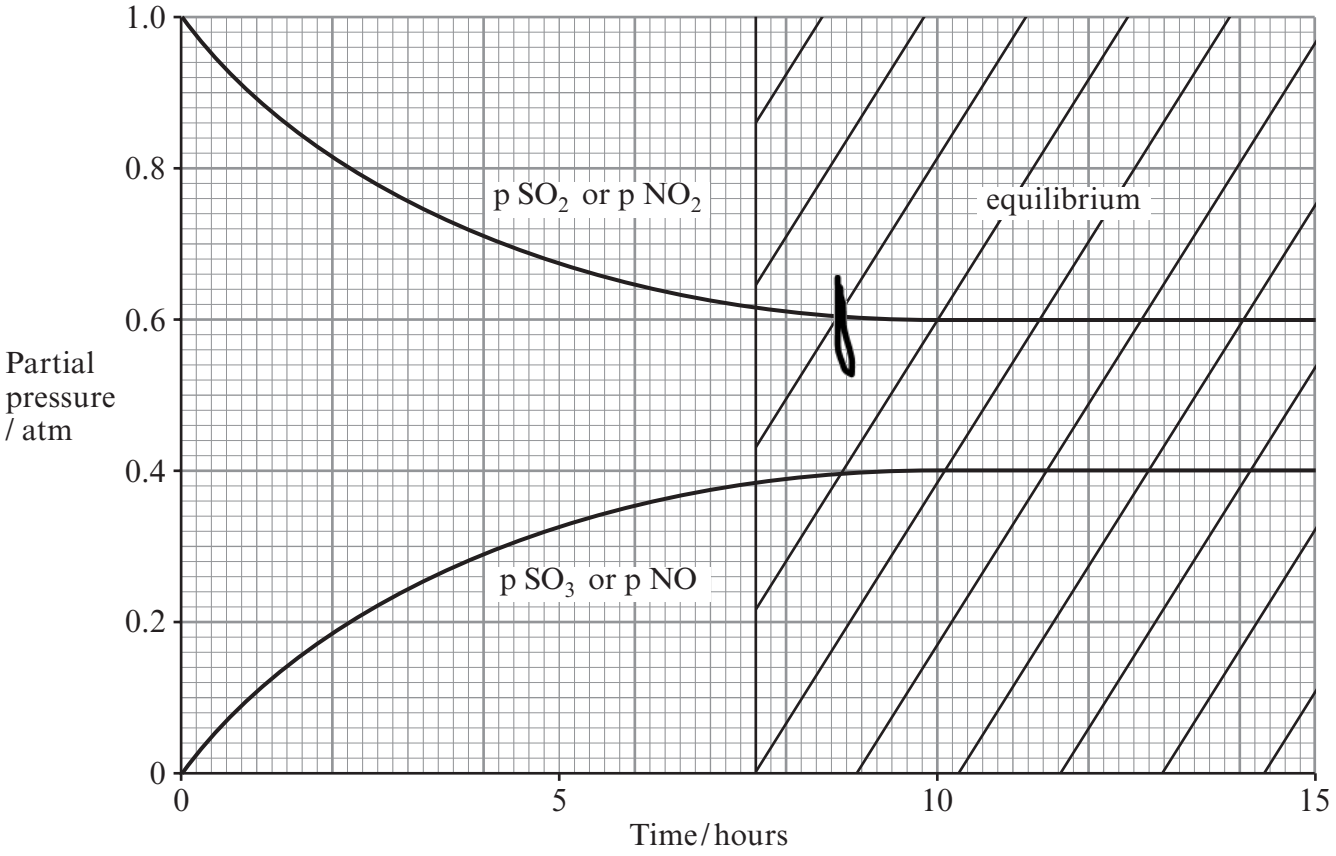
$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

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]

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]

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]

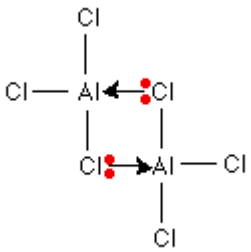
(b) +2 state becomes mores stable down the group and +4 becomes less stable. [1]

(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]

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*.

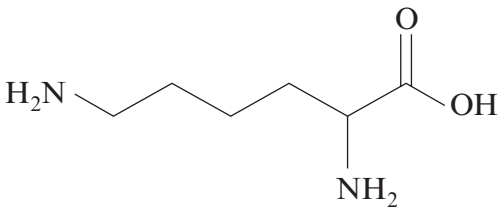
Taste continued to be an important consideration – even today many people would think of the sour taste of a lemon as being typical of an acid. However it was found that, as well as taste, these compounds had other properties in common. The dye litmus had been extracted from lichens and it was found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

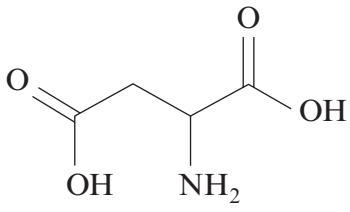
The modern classification of acids is based on the theory suggested by Lowry and Brønsted although more recent classifications, based on electron pair donation, have been suggested by Lewis.

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 -

$2H_2SO_4 + HNO_3 = 2HSO_4^- + H_3O^+ + NO_2^+$

$H_2NO_3^+$

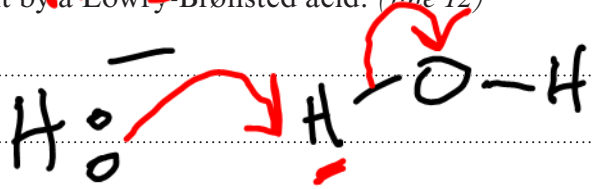
B. Acid C. Base

$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$

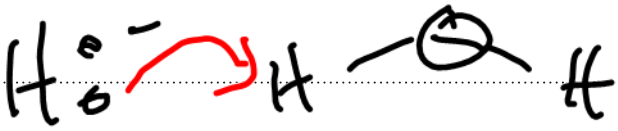
B. Acid → C. Base

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]

1 $RCOOH \rightleftharpoons RCOO^- + H^+$

2 $RCOONa \rightarrow RCOO^- + Na^+$

ACID (H^+) | ALKALI (OH^-)

$RCOO^- + H^+ = RCOOH$ | $RCOOH + OH^- =$

$RCOO^- + H_2O$

$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$

ACID (H^+) | ALKALI (OH^-)

SHIFTS TO RHS USING UP H^+ | USE UP H^+ SHIFTS TO LHS REPLACES H^+

Total [15]

Total Section A [40]

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]

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]

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

$[H^+][OH^-] = 10^{-14}$

$Ca(OH)_2$ 0·05M

Examiner only

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

$[OH^-] = 2[Ca(OH)_2] = 0.1M$

K_w =

$[H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{0.1}$

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]

.....

.....

.....

$n = cv$

$= 0.10 \times 0.01$

$= 0.001$ mol.

HCl.

(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]

$[H^+] = 0.001 \text{ mol dm}^{-3} = 10^{-3}$

In 1000 cm^3 1 dm^3

$pH = -\lg 10^{-3} = 3$

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]

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ / $CH_3COONa \longrightarrow CH_3COO^- + H^+$

$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$\frac{[SALT][H^+]}{[ACID]} = 1.78 \times 10^{-5}$

pH = ...

$-\lg[H^+]$

$-Ka$

10

pKa Ka $[H^+]$ pH

$-\lg Ka$

10^{-pH}

$[H^+] = \frac{[ACID] \times 1.78 \times 10^{-5}}{[SALT]}$

$$[H^+] = K_a \times \frac{[ACID]}{[SALT]}$$

TAKE $-\lg_{10}$ OF BOTH SIDES

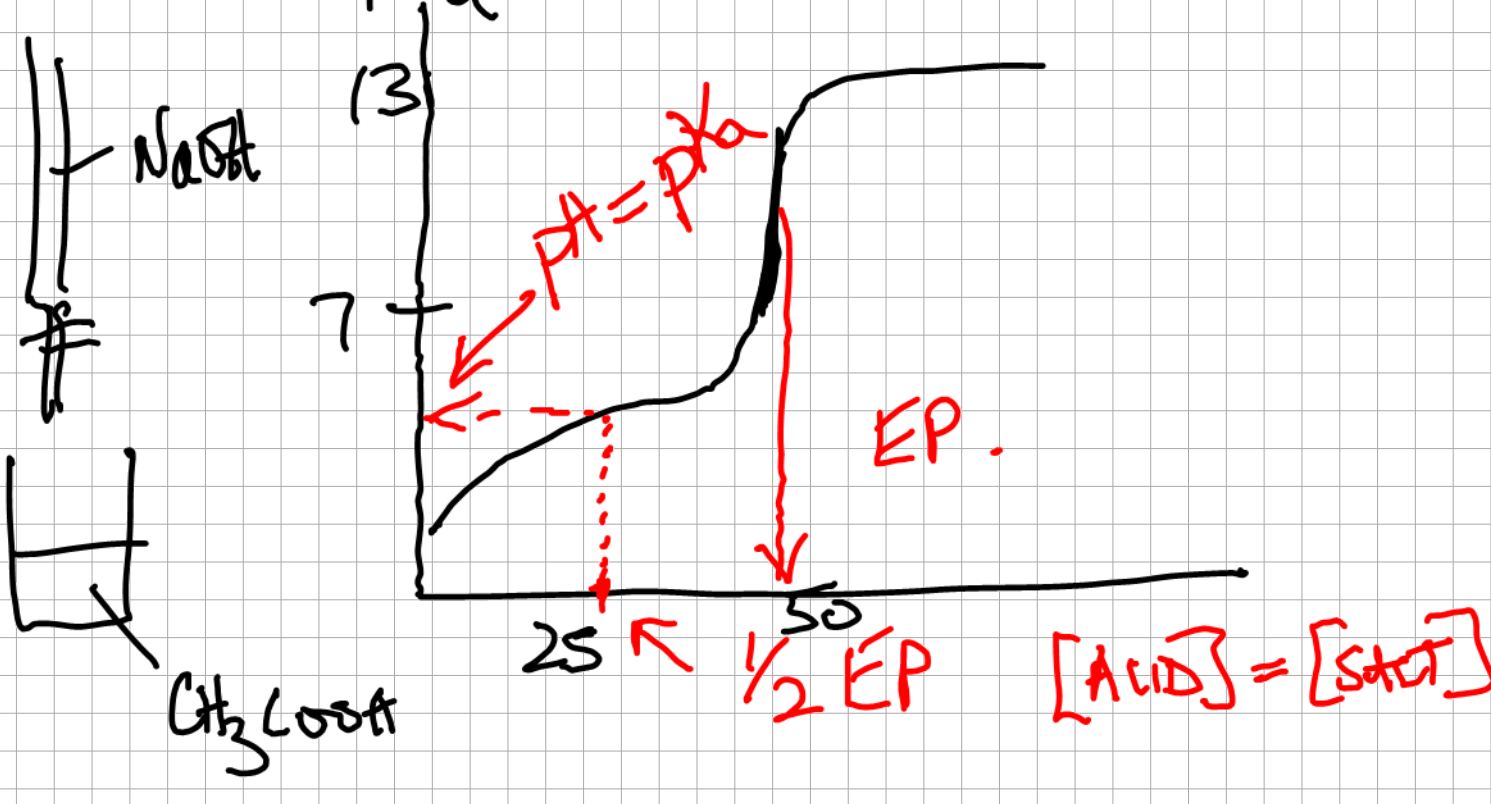
$$-\lg[H^+] = -\lg K_a + \left[-\lg \frac{[ACID]}{[SALT]}\right]$$

$$pH = pK_a - \lg \frac{[ACID]}{[SALT]}$$

IF $[ACID] = [SALT]$

$$pH = pK_a$$

$$K_a = 10^{-pK_a}$$



$CH_3COOH + NaOH = CH_3COONa + H_2O$

50cm³ 1M

25cm³ 1M → 0.025mol.

0.05 mol.

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]

5

12

Turn over.

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 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]

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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]

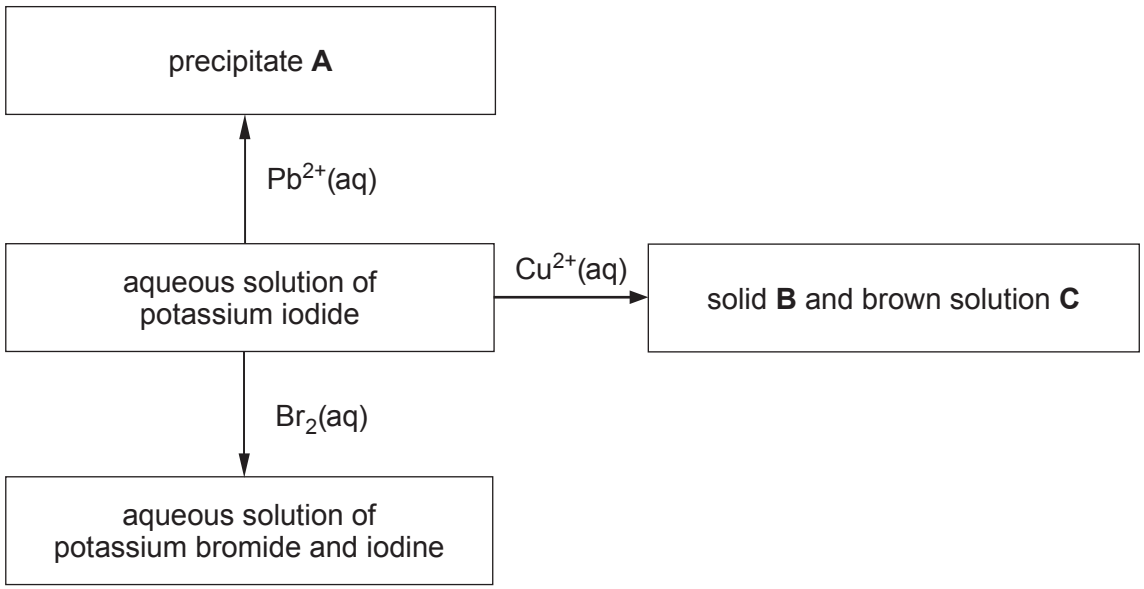
(g) Acidified potassium dichromate, $K_2Cr_2O_7$, is also an oxidising agent.

(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

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GCE A level

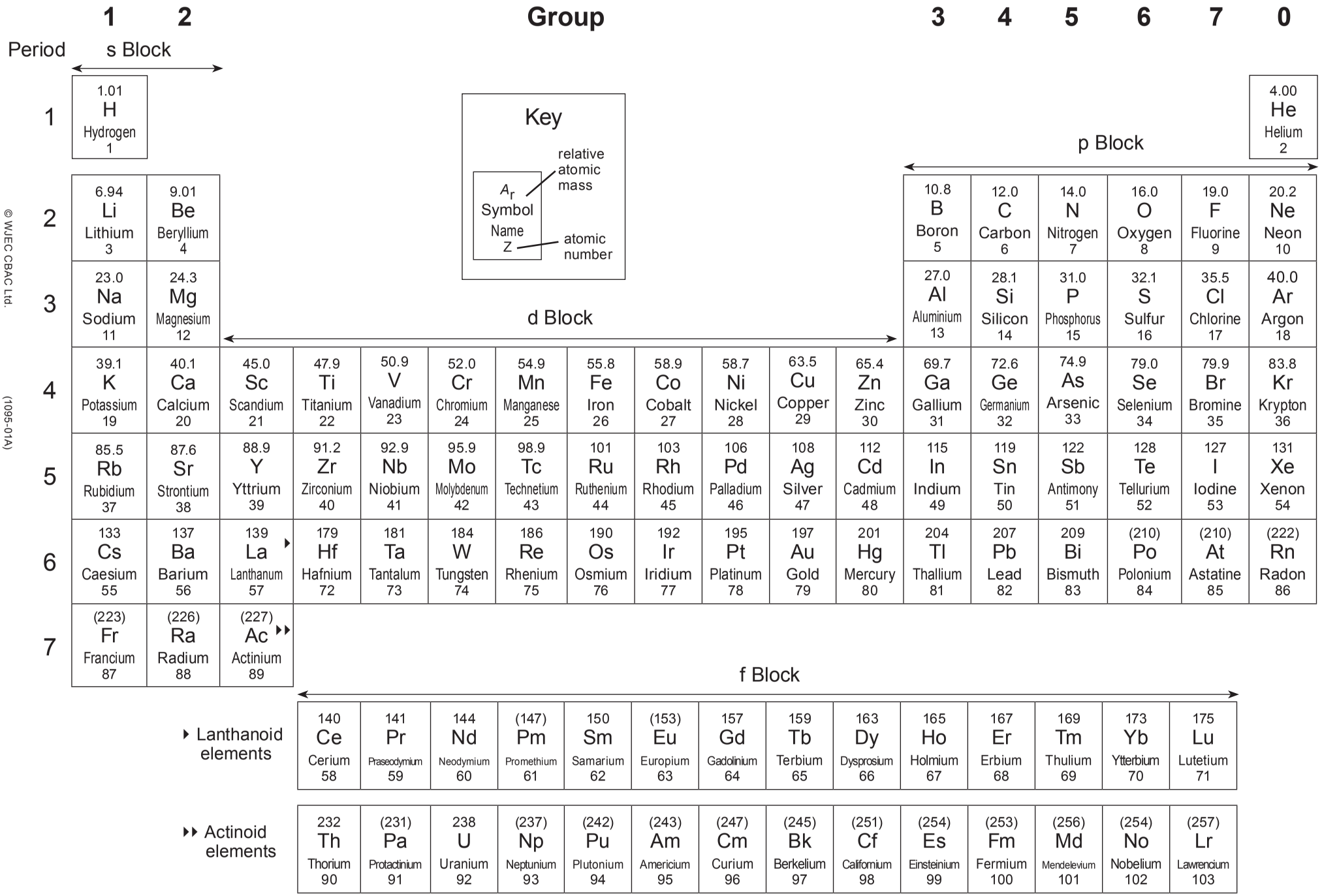
1095/01-A

S15-1095-01A

CHEMISTRY – PERIODIC TABLE
FOR USE WITH CH5

P.M. MONDAY, 15 June 2015

THE PERIODIC TABLE



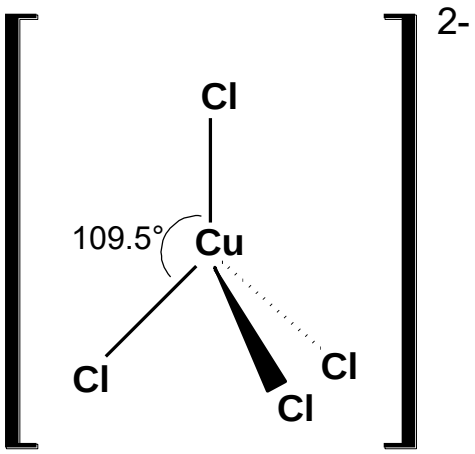
(1095-01A)

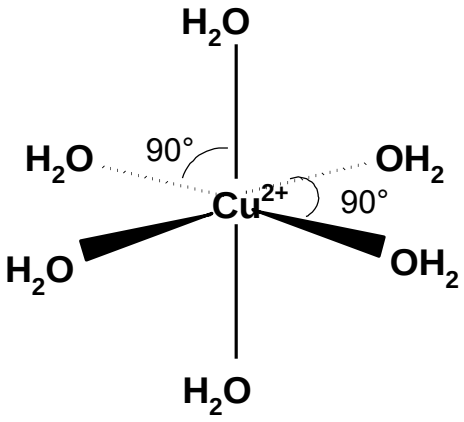
CH5

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.

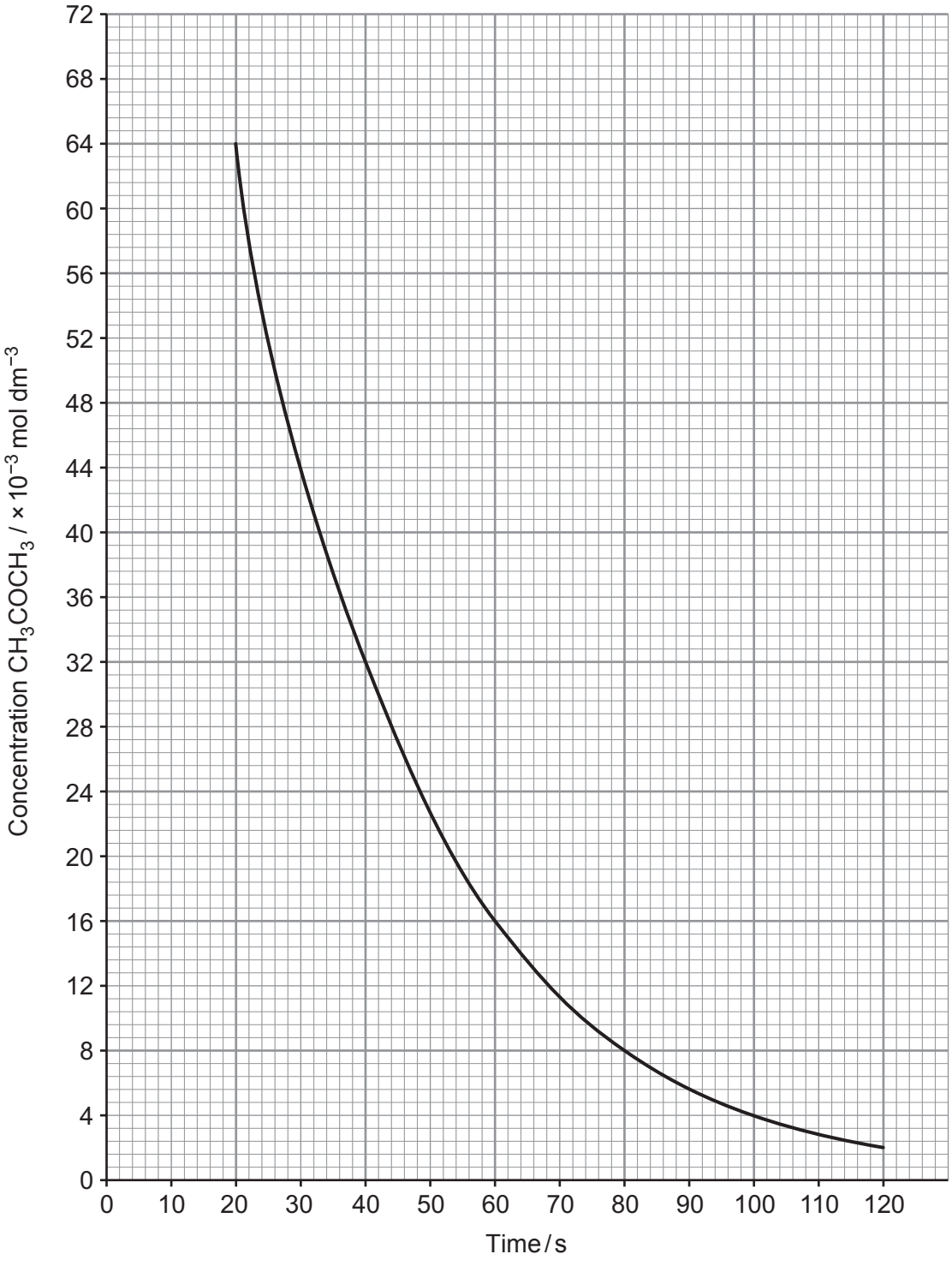
SECTION A

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

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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]

.....

.....

.....

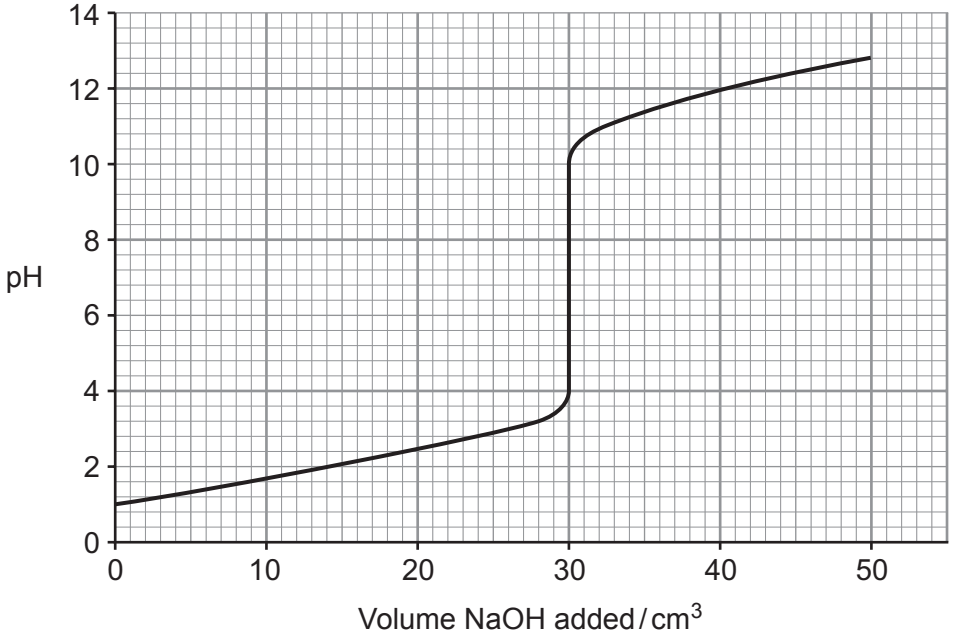
(ii) Curve **B** [3]

.....

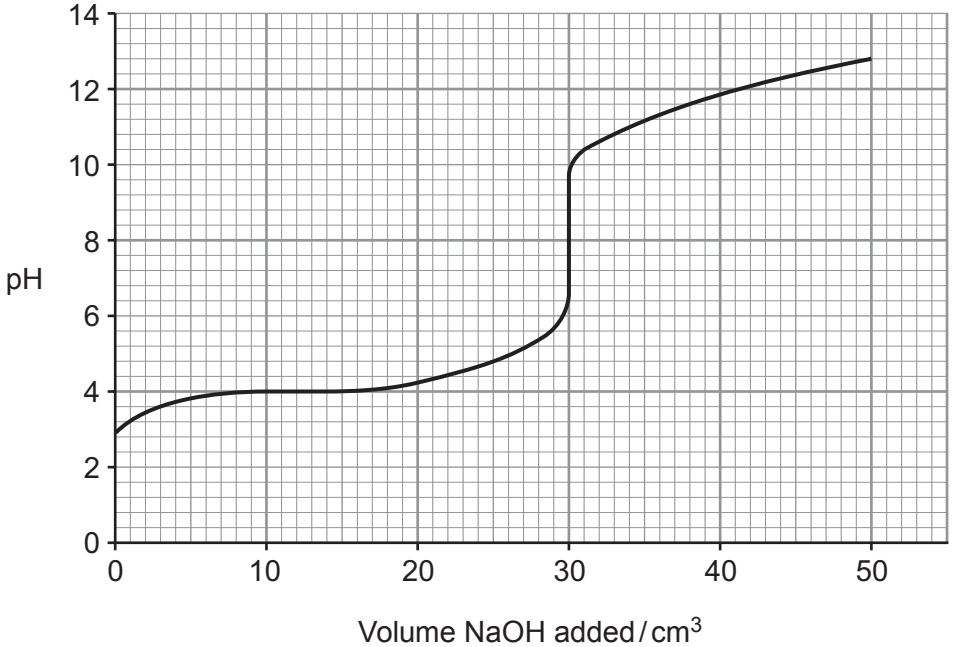
.....

.....

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

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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.

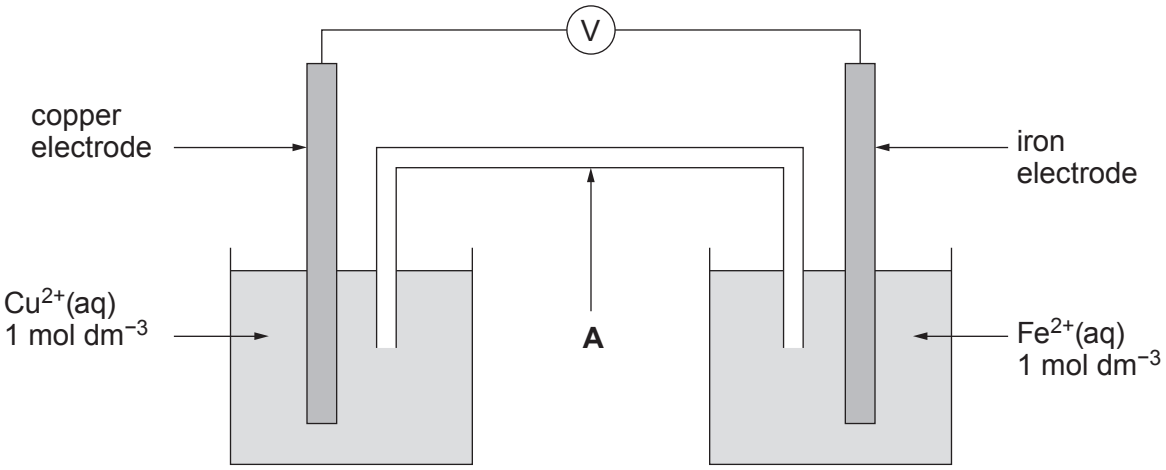
A 2.05 g brass screw was dissolved in nitric acid and the solution formed was diluted to 100 cm^3 in a volumetric flask. An excess of potassium iodide solution was added to 25.0 cm^3 of this solution and the iodine produced was titrated against a 0.200 mol dm^{-3} solution of sodium thiosulfate. The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

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GCE A level

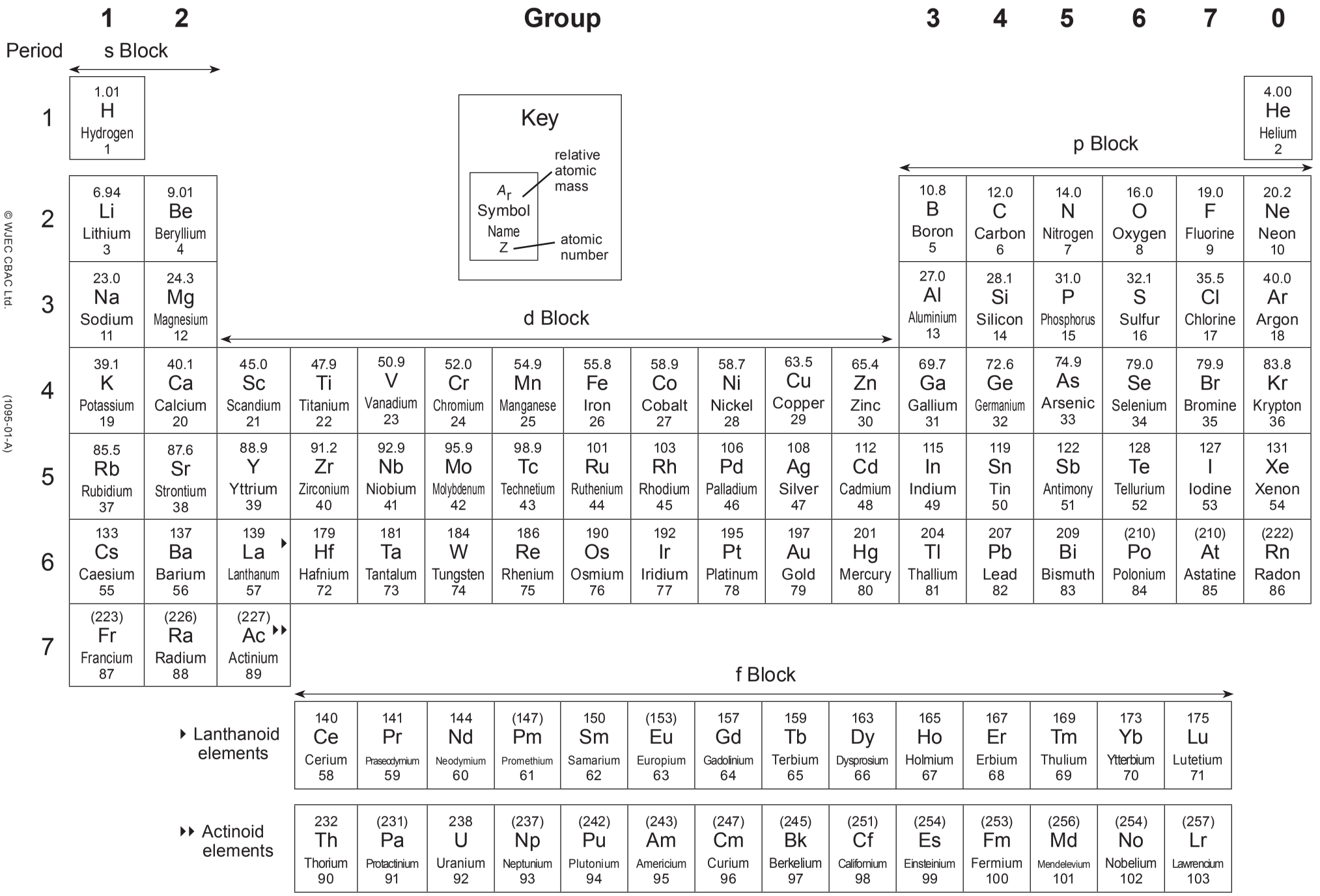
1095/01-A

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]