| Surname | Centre <br> Number | Candidate <br> Number |
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| Other Names |  |  |
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P.M. MONDAY, 15 June 2015

1 hour 45 minutes

## ADDITIONAL MATERIALS

|  |  |  |  |
| :---: | :---: | :---: | :---: |
|  | For Examiner's use only |  |  |
| Section A | Question | Maximum <br> Mark | Mark <br> Awarded |
| Section B | 1. | 16 |  |
|  | 2. | 9 |  |
|  | 3. | 15 |  |
|  | 4. | 20 |  |
|  | 5. | 20 |  |
|  | Total | 80 |  |
|  |  |  |  |

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) Copper ions combine with a range of ligands to form complex ions, including $\left[\mathrm{CuCl}_{4}\right]^{2-}$ and $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$.
(i) State what is meant by a ligand.
$\qquad$
(ii) Draw the structures of $\left[\mathrm{CuCl}_{4}\right]^{2-}$ and $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ ions.
(iii) A solution containing $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ ions is blue. Explain the origin of this colour. [3]
$\qquad$
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$\qquad$
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$\qquad$
(iv) When excess ammonia is added to a solution containing $\left[\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ 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.
(b) Phosphorus forms two chlorides, $\mathrm{PCl}_{3}$ and $\mathrm{PCl}_{5}$, and there is a dynamic equilibrium between these compounds in the gas phase. This is represented by the equation below.

$$
\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})
$$

(i) Write an expression for the equilibrium constant, $K_{\mathrm{p}}$, for this reaction.
(ii) A sealed vessel is filled with $\mathrm{PCl}_{5}$ at a pressure of $3.0 \times 10^{5} \mathrm{~Pa}$. Upon heating, the system comes to equilibrium to form a mixture that contains $\mathrm{PCl}_{3}$ at a partial pressure of $1.3 \times 10^{5} \mathrm{~Pa}$.
I. State the partial pressure of $\mathrm{Cl}_{2}$ at equilibrium.
II. Calculate the value of the equilibrium constant, $K_{p}$, giving its units.

$$
K_{p}=
$$

$\qquad$
Units
III. As the temperature is increased the value of $K_{\mathrm{p}}$ increases. State what information this provides about the enthalpy change of this reaction, giving a reason for your answer.
(c) Silicon(IV) chloride reacts with water whilst $\mathrm{CCl}_{4}$ does not. Give the equation for the reaction of $\mathrm{SiCl}_{4}$ with water and explain why the behaviour of $\mathrm{CCl}_{4}$ and $\mathrm{SiCl}_{4}$ with water is so different.
,

$\qquad$

## 


2. Iron is extracted at high temperatures from the ore haematite, which contains iron(III) oxide, $\mathrm{Fe}_{2} \mathrm{O}_{3}$. The process can be summarised by the equation below.

$$
\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+3 \mathrm{CO}(\mathrm{~g}) \longrightarrow 2 \mathrm{Fe}(\mathrm{~s})+3 \mathrm{CO}_{2}(\mathrm{~g}) \quad \Delta H^{\theta}=-23 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

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

| Substance | Standard enthalpy <br> change of formation, <br> $\Delta H_{\mathrm{f}} / \mathrm{kJ} \mathrm{mol}$ |  |
| :---: | :---: | :---: |
| $\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})$ | -826 | Standard entropy, <br> $\mathrm{S}^{\theta} / \mathrm{J} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$ |
| $\mathrm{Fe}(\mathrm{s})$ | 0 | 90 |
| $\mathrm{CO}(\mathrm{g})$ |  | 27 |
| $\mathrm{CO}_{2}(\mathrm{~g})$ | -394 | 198 |

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

$$
\Delta H_{\mathrm{f}}^{\theta}=
$$

$\qquad$ $\mathrm{kJ} \mathrm{mol}^{-1}$
(b) Explain why the standard entropies of carbon dioxide and carbon monoxide are significantly greater than those of iron(III) oxide and iron.
(c) The standard entropy change for this reaction, $\Delta S^{\theta}$, is $+9 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$.
(i) Calculate the free energy change, $\Delta G^{\theta}$, for this reaction at 298 K .
Examiner [2]
(ii) Explain why this reaction is feasible at all temperatures.
(iii) Many industrial processes use high temperatures even when the reaction is feasible at low temperatures. Suggest why high temperatures are used.
$\qquad$
$\qquad$
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 $\mathrm{BCl}_{3}$, $\mathrm{BF}_{3}$ and $\mathrm{B}_{2} \mathrm{O}_{3}$. 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 $\mathrm{B}_{\mathrm{n}} \mathrm{H}_{\mathrm{n}+4}$. This series includes
pentaborane $(9), \mathrm{B}_{5} \mathrm{H}_{9}$, and decaborane(14), $\mathrm{B}_{10} \mathrm{H}_{14}$.
- Arachno-boranes with a general formula of $\mathrm{B}_{\mathrm{n}} \mathrm{H}_{\mathrm{n}+6}$. The first member of this series is tetraborane(10), $\mathrm{B}_{4} \mathrm{H}_{10}$.

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 $\mathrm{B}_{5} \mathrm{H}_{9}$ when it was no longer needed, the US government treated it with steam to form a solution of boric acid $\left(\mathrm{H}_{3} \mathrm{BO}_{3}\right)$ 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.

[^0] compounds are more stable with the +1 oxidation state (lines 6-9).
(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 $1 \mathrm{dm}^{3}$ at 273 K and 1 atm pressure.
[The molar volume of a gas at 273 K and 1 atm pressure is $22.4 \mathrm{dm}^{3}$.]
(i) What is the empirical formula of this borane?
(ii) What is the molecular formula of this borane?
(c) Explain the term electron deficient (line 17).
$\qquad$
$\qquad$

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

Mass number Atomic number $\qquad$

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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.
(b) Write an ion-electron half-equation for the reduction of acidified manganate(VII) ions, $\mathrm{MnO}_{4}{ }^{-}$.
(c) The ion-electron half-equation for the oxidation of ethanedioate ions is given below.

$$
\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}(\mathrm{aq}) \longrightarrow 2 \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{e}^{-}
$$

(i) Give the oxidation states for carbon at the start and end of this reaction.
(ii) Write an equation for the reaction of acidified manganate(VII) ions with ethanedioate ions.
(d) Give a reason why an indicator is not needed in this titration.
(e) Four samples of $25.00 \mathrm{~cm}^{3}$ of the ethanedioate solution were titrated against acidified potassium manganate(VII) solution of concentration $0.0200 \mathrm{moldm}^{-3}$. The volumes of potassium manganate(VII) solution required for complete reaction are listed below.

|  | 1 | 2 | 3 | 4 |
| :---: | :---: | :---: | :---: | :---: |
| Volume of $\mathrm{KMnO}_{4}(\mathrm{aq}) / \mathrm{cm}^{3}$ | 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, $K_{\mathrm{a}}$, for methanoic acid. [1]
(ii) The value of $K_{\mathrm{a}}$ for methanoic acid is $1.8 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$.

Calculate the pH of a solution of methanoic acid of concentration $0.2 \mathrm{~mol} \mathrm{dm}^{-3}$. [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.
(g) Acidified potassium dichromate, $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$, is also an oxidising agent.
(i) Give the colour change that occurs when acidified potassium dichromate acts as an oxidising agent.
(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.
5. The diagram below shows some of the reactions of potassium iodide solution.

(a) Identify precipitate $\mathbf{A}$ and give its colour.
(b) Write an equation for the reaction of $\mathrm{Cu}^{2+}(\mathrm{aq})$ and $\mathrm{I}^{-}(\mathrm{aq})$, clearly identifying the precipitate.
(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.

| Half-equation | $E^{\theta} / \mathrm{V}$ |
| :---: | :---: |
| $\mathrm{I}_{2}+2 \mathrm{e}^{-} \rightleftharpoons 2 \mathrm{I}^{-}$ | +0.54 |
| $\mathrm{Br}_{2}+2 \mathrm{e}^{-} \rightleftharpoons 2 \mathrm{Br}^{-}$ | +1.09 |
| $\mathrm{Cl}_{2}+2 \mathrm{e}^{-} \rightleftharpoons 2 \mathrm{Cl}^{-}$ | +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.
(e) Hydrogen peroxide reacts with acidified potassium iodide according to the equation below.

$$
2 \mathrm{H}^{+}+2 \mathrm{I}^{-}+\mathrm{H}_{2} \mathrm{O}_{2} \longrightarrow \mathrm{I}_{2}+2 \mathrm{H}_{2} \mathrm{O}
$$

(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.
(ii) The rate of this reaction was studied by a different method for a range of concentrations of $\mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{aq})$ and $\mathrm{I}^{-}(\mathrm{aq})$ and pH values. These are listed in the table below.

| Experiment <br> number | Initial concentration of <br> $\mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{aq}) / \mathrm{mol} \mathrm{dm}^{-3}$ | Initial concentration of <br> $\mathrm{I}^{-}(\mathrm{aq}) / \mathrm{mol} \mathrm{dm}^{-3}$ | pH | Initial rate/ <br> $\mathrm{mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 0.0010 | 0.10 | 1 | $2.8 \times 10^{-6}$ |
| 2 | 0.0020 | 0.10 | 1 | $5.6 \times 10^{-6}$ |
| 3 | 0.0020 | 0.10 | 2 | $5.6 \times 10^{-6}$ |
| 4 | 0.0010 | 0.40 | 1 | $11.2 \times 10^{-6}$ |

I. Some experiments were undertaken at pH 1 and some at pH 2 . Give the difference in the concentrations of $\mathrm{H}^{+}$ions in these two solutions.
II. Use the data in the table to deduce the rate equation for this reaction, giving your reasoning.
III. Calculate the value of the rate constant, $k$, giving its units.
IV. The reaction is repeated at a higher temperature. State how the increase in temperature affects the rate equation and rate constant.

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P.M. MONDAY, 15 June 2015
THE PERIODIC TABLE


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[^0]:    - End of passage -

