| Surname | Centre <br> Number | Candidate <br> Number |
| :--- | :--- | :--- | :--- |
| Other Names |  |  |
| 2 |  |  |

A.M. WEDNESDAY, 22 June 2016

1 hour 45 minutes

## ADDITIONAL MATERIALS

|  |  |  |  |
| :---: | :---: | :---: | :---: |
|  | For Examiner's use only |  |  |
| Section A | Question | Maximum <br> Mark | Mark <br> Awarded |
| Section B | 1. | 10 |  |
|  | 2. | 12 |  |
|  | 3. | 18 |  |
|  | 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) 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:

$$
\mathrm{CH}_{3} \mathrm{COCH}_{3}+\mathrm{I}_{2} \longrightarrow \mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{I}+\mathrm{HI}
$$

(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.


Explain how the graph shows that the reaction is first order with respect to propanone.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(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.

| $\left[\mathrm{CH}_{3} \mathrm{COCH}_{3}\right]$ <br> $/ \mathrm{mol} \mathrm{dm}^{-3}$ | $\left[\mathrm{I}_{2}\right] / \mathrm{mol} \mathrm{dm}^{-3}$ | $\left[\mathrm{H}^{+}\right] / \mathrm{mol} \mathrm{dm}^{-3}$ | Initial rate <br> $/ \mathrm{mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}$ |
| :---: | :---: | :---: | :---: |
| $1.5 \times 10^{-3}$ | 0.030 | 0.020 | $2.1 \times 10^{-9}$ |
| $1.5 \times 10^{-3}$ | 0.060 | 0.040 | $4.2 \times 10^{-9}$ |
| $1.5 \times 10^{-3}$ | 0.030 | 0.040 | $4.2 \times 10^{-9}$ |

I. Determine the orders of reaction with respect to $\mathrm{I}_{2}$ and $\mathrm{H}^{+}$.
$I_{2}$ $\qquad$
$\qquad$
$\mathrm{H}^{+}$ $\qquad$
II. Write the rate equation for the reaction.
III. Calculate the value of the rate constant in the rate equation and state its unit.
(b) Another multi-step reaction is the one between nitrogen dioxide and carbon monoxide. The overall equation for the reaction is:

$$
\mathrm{NO}_{2}+\mathrm{CO} \longrightarrow \mathrm{NO}+\mathrm{CO}_{2}
$$

The rate equation for this reaction is as follows.

$$
\text { rate }=k\left[\mathrm{NO}_{2}\right]^{2}
$$

The first step is the rate-determining step.
(i) Explain what is meant by the rate-determining step.
$\qquad$
$\qquad$
(ii) Write equations to show a possible two-step mechanism for this reaction.

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

From the list below, choose which acids were used to give curves $\mathbf{A}$ and $\mathbf{B}$ giving reasons for your answer.

| $\mathbf{W}$ | $0.1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HCl}$ |
| :---: | :--- |
| $\mathbf{X}$ | $0.001 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HCl}$ |
| $\mathbf{Y}$ | $0.1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{CH}_{3} \mathrm{COOH}$ |
| $\mathbf{Z}$ | $0.001 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{CH}_{3} \mathrm{COOH}$ |

$$
\left(\mathrm{K}_{\mathrm{a}} \text { for } \mathrm{CH}_{3} \mathrm{COOH}=1.8 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}\right)
$$

(i) Curve $\mathbf{A}$
$\qquad$
$\qquad$
$\qquad$
(ii) Curve $\mathbf{B}$

Titration curves of acid-alkali reactions


Curve A

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

| 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 $\mathbf{A}$.
$\qquad$ $\mathrm{mol} \mathrm{dm}^{-3}$
(c) Aqueous ammonia reacts with hydrochloric acid to form the salt ammonium chloride, $\mathrm{NH}_{4} \mathrm{Cl}$. Give a reason why the pH value for a solution of $\mathrm{NH}_{4} \mathrm{Cl}$ is less than 7 .

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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. ${ }_{1}^{1} \mathrm{H}$ is hydrogen, ${ }_{1}^{2} \mathrm{H}$ is deuterium and ${ }_{1}^{3} \mathrm{H}$ is tritium.
Acidity is expressed using the pH scale first devised by the Swedish chemist Sorenson.

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]
$$

The scale usually runs from $0-14$ because $1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{H}^{+}$(acid) has a pH of 0 and $1 \mathrm{~mol} \mathrm{dm}^{-3}$ $\mathrm{OH}^{-}$(alkali) has a pH of 14. An aqueous solution is neutral when the concentrations of $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$are equal. At $25^{\circ} \mathrm{C}$, the ionic product of water, $K_{\mathrm{w}}$, has a numerical value of $1.0 \times 10^{-14}$. Pure water has a pH of 7 , and is neutral. This neutral value of pH can be calculated from $K_{\mathrm{w}}$. Since boiling water has a larger value of $K_{w}$ than water at $25^{\circ} \mathrm{C}$, 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 $\left[\Delta H_{c}{ }^{\theta}\left(\mathrm{H}_{2}\right)=-286 \mathrm{~kJ} \mathrm{~mol}^{-1}\right]$. 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.

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

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 -
(a) Write an expression for the ionic product of water, $K_{w}$, (line 12) giving its unit, if any. [1] ${ }^{\text {Examiner }}$ only

Unit
(b) The value for $K_{w}$ at $100^{\circ} \mathrm{C}$ is $5.13 \times 10^{-13}$. Use this to explain why an aqueous solution of a salt with a pH of 7 at this temperature is slightly alkaline (line 15).
(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.

| (d) (i) Use the data given to calculate the standard enthalpy change of combustion of |
| :--- |
| methane. |
| Substance |
| Standard enthalpy change of formation, <br> $\Delta H_{\mathrm{f}}^{\theta} / \mathrm{kJ} \mathrm{mol}^{-1}$ |
| -75$)$ |
| $\mathrm{CO}_{2}(\mathrm{~g})$ | methane.

(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.
(ii) Calculate the equilibrium partial pressures of hydrogen and ammonia and use these
$K_{\mathrm{p}}=$
Unit
Total [18]
Examiner


#### Abstract

to calculate a value for $K_{p}$ at this temperature, giving the unit if any.


## 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.
(ii) Explain why copper(I) compounds are generally white.
(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.
(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 $100 \mathrm{~cm}^{3}$ in a volumetric flask. An excess of potassium iodide solution was added to $25.0 \mathrm{~cm}^{3}$ of this solution and the iodine produced was titrated against a $0.200 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of sodium thiosulfate. The iodine required $24.00 \mathrm{~cm}^{3}$ of the sodium thiosulfate solution for complete reaction.
(i) Name a suitable indicator for this titration.
(ii) Calculate the percentage by mass of copper in the brass. Give your answer to three significant figures.

$$
\text { (The ratio of } \mathrm{Cu}^{2+}: \mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-} \text { is } 1: 1 \text { ) }
$$

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


Some standard electrode potentials, $E^{\theta}$, are given below.

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

(i) Name the part of the cell labelled $\mathbf{A}$ and state its purpose.
(ii) State, giving a reason, which of the electrodes will be positively charged in the above cell.
(iii) Calculate the standard emf, in volts, for the above cell.
(iv) State whether or not you would expect nickel to react with iron(II) ions. Give a reason for your answer.
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.
(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.
(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.

$$
\mathrm{Ba}(\mathrm{OH})_{2} \cdot 8 \mathrm{H}_{2} \mathrm{O}(\mathrm{~s})+2 \mathrm{NH}_{4} \mathrm{Cl}(\mathrm{~s}) \longrightarrow 2 \mathrm{NH}_{3}(\mathrm{~g})+8 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{BaCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~s}) \quad \Delta H=135 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

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

| Compound | $\mathrm{Ba}(\mathrm{OH})_{2} \cdot 8 \mathrm{H}_{2} \mathrm{O}(\mathrm{s})$ | $\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s})$ | $\mathrm{NH}_{3}(\mathrm{~g})$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ | $\mathrm{BaCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{s})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Entropy <br> $/ \mathrm{J} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$ | 427 | 95 | 192 | 70 | 203 |

(i) Explain why there is an increase in entropy for this reaction.
(ii) Calculate the entropy change for this reaction.
(iii) Calculate the free energy change, $\Delta G$, for the reaction at $25^{\circ} \mathrm{C}$ and explain why this reaction is feasible.
(c) The enthalpy change of formation of barium chloride, $\mathrm{BaCl}_{2}$, 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 $\mathrm{kJ} \mathrm{mol}^{-1}$.

| Process | $\Delta H^{\theta} / \mathrm{kJ} \mathrm{mol}^{-1}$ |
| :--- | :---: |
| $\mathrm{Ba}(\mathrm{s}) \longrightarrow \mathrm{Ba}(\mathrm{g})$ | 176 |
| $1 / 2 \mathrm{Cl}(\mathrm{g}) \longrightarrow \mathrm{Cl}(\mathrm{g})$ | 121 |
| $\mathrm{Ba}(\mathrm{g}) \longrightarrow \mathrm{Ba}^{+}(\mathrm{g})+\mathrm{e}^{-}$ | 502 |
| $\mathrm{Ba}^{+}(\mathrm{g}) \longrightarrow \mathrm{Ba}^{2+}(\mathrm{g})+\mathrm{e}^{-}$ | 966 |
| $\mathrm{Cl}(\mathrm{g})+\mathrm{e}^{-} \longrightarrow \mathrm{Cl}^{-}(\mathrm{g})$ | -364 |
| $\mathrm{Ba}^{2+}(\mathrm{g})+2 \mathrm{Cl}^{-}(\mathrm{g}) \longrightarrow \mathrm{BaCl}_{2}(\mathrm{~s})$ | -2018 |

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

## END OF PAPER

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| $\begin{gathered} 6.94 \\ \mathrm{Li} \\ \text { Lithium } \\ 3 \\ \hline \end{gathered}$ | $\begin{gathered} 9.01 \\ \text { Be } \\ \text { Beryllium } \\ 4 \end{gathered}$ |  |
| :---: | :---: | :---: |
| $\begin{aligned} & 23.0 \\ & \mathrm{Na} \end{aligned}$ <br> Sodium 11 | $24.3$ <br> Mg <br> Magnesium 12 | $<$ |
| $\substack{39.1 \\ \mathrm{~K} \\ \text { Potassium } \\ 19}$ | $\begin{gathered} 40.1 \\ \text { Ca } \\ \text { Calcium } \\ 20 \end{gathered}$ | $\begin{array}{r} 45 \\ \text { Sc } \\ \text { Scand } \\ 21 \end{array}$ |
| $\begin{gathered} 85.5 \\ \mathrm{Rb} \\ \text { Rubidium } \\ 37 \end{gathered}$ | 87.6 Sr <br> Strontium 38 | $\begin{array}{r} 88 . \\ Y \\ \text { Yttril } \\ 39 \end{array}$ |
| $\begin{gathered} 133 \\ \text { Cs } \\ \text { Caesium } \\ 55 \end{gathered}$ | 137 Ba Barium 56 | Lantha 57 |
| $\begin{gathered} \text { (223) } \\ \text { Fr } \\ \text { Francium } \\ 87 \end{gathered}$ | (226) <br> Ra <br> Radium 88 | $\begin{array}{r} (227 \\ \text { Ac } \\ \text { Actini } \\ 89 \end{array}$ |

d Block

| 45.0 Sc <br> Scandium <br> 21 | $\begin{gathered} 47.9 \\ \mathrm{Ti} \\ \text { Titanium } \\ 22 \end{gathered}$ | $\begin{gathered} 50.9 \\ V \\ \begin{array}{c} 5 a n a d i u m \\ 23 \end{array} \end{gathered}$ |  |  | $\begin{gathered} 55.8 \\ \text { Fe } \\ \text { Iron } \\ 26 \end{gathered}$ |  | $\begin{gathered} 58.7 \\ \mathrm{Ni} \\ \text { Nickel } \\ 28 \end{gathered}$ | $\begin{gathered} 63.5 \\ \text { Cu } \\ \text { Copper } \\ 29 \end{gathered}$ | $\begin{gathered} 65.4 \\ \text { Zn } \\ \text { Zinc } \\ 30 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 88.9 | 91.2 | 92.9 | 95.9 | 98.9 | 101 | 103 | 106 | 108 | 112 |
| Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| $\underset{39}{\text { Yttrium }}$ | $\begin{aligned} & \text { Zirconium } \\ & 40 \end{aligned}$ | $\begin{gathered} \text { Niobium } \\ 41 \end{gathered}$ | $\begin{aligned} & \text { Moybderum } \\ & 42 \end{aligned}$ | $\begin{aligned} & \text { Technetium } \\ & 43 \end{aligned}$ | $\begin{aligned} & \text { Ruthenium } \\ & 44 \end{aligned}$ | $\begin{gathered} \text { Rhodium } \\ 45 \end{gathered}$ | $P_{46} P_{46}$ | $\begin{gathered} \text { Silver } \\ 47 \end{gathered}$ | $\begin{gathered} \text { Cadmium } \\ 48 \end{gathered}$ |
| 139 | 179 | 181 | 184 | 186 | 190 | 192 | 195 | 197 | 201 |
| La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |
| ${ }_{5}^{\text {Lanthanum }}$ | Hafnium | Tantalum | Tungsten | Rhenium | Osmium | Iridium | Platinum | Gold | Mercury |


|  |  |  |
| :---: | :---: | :---: |
|  |  |  |
|  | ® ¢ ¢ ¢ ¢ |  |
|  |  |  |



