Candidate Name:





2012 Preliminary Examination II

Pre-university 3

H2 CHEMISTRY

Paper 3

9647/03

14 Sept 2012

2 hours

| Additional Materials: | Writing Paper | | | |
|-----------------------|---------------|--|--|--|
| | Data Booklet | | | |
| | Graph Paper | | | |

READ THESE INSTRUCTIONS FIRST

- **1.** Do not turn over this question paper until you are told to do so.
- **2.** Write your name, class and index number in the spaces provided at the top of this page and on all the work you hand in.
- 3. Write in *dark blue* or *black pen* on both sides of the paper.
- 4. You may use a soft pencil for any diagrams or graphs.
- **5. DO NOT** use staples, paper clips, highlighters, glue or correction fluid or tape.
- 6. Answer **any four** questions.
- Give non-exact numerical answers correct to <u>3 significant figures</u>, or <u>1 decimal</u> <u>place</u> in the case of Mr and Ar, unless a different level of accuracy is specified in the_question.
- **8.** The number of marks is given in brackets [] at the end of each question or part question.
- **9.** You are reminded of the need for *good English* and *clear presentation* in your answers and to *show all working* in calculations.
- **10.** The use of a calculator is expected, where appropriate.

Answer ANY FOUR questions

 (a) When studying Hydrocarbons, we recognised the environmental consequences of carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine.

> Because of these environmental concerns, alongside with high oil prices and oil being a limited natural resource, development of cleaner alternative fuels and advanced power systems for vehicles has become a high priority for many governments and vehicle manufacturers around the world.

> An *alternative fuel vehicle* is a vehicle that runs on a fuel other than "traditional" petroleum fuels (petrol or diesel); and also refers to any technology of powering an engine that does not involve solely petroleum (e.g. electric car, hybrid electric vehicles, solar powered).

One such source of alternative fuel is the **hydrogen / oxygen fuel cell**, which is increasingly used in space crafts.

Describe, providing details, the hydrogen / oxygen fuel cell. Include the following in your answer:

- Draw a well-labeled diagram for the cell.
- Outline the reactions taking place at each electrode, assuming an alkaline medium.
- State one advantage of using this fuel cell.
- (b) Cyanogen is a highly toxic gas, composing of 46.2% carbon and 53.8% nitrogen by mass. At 25 °C and 1 atm, 1.05 g of cyanogen occupies 0.500 dm³.
- (i) Determine the molecular formula of cyanogen.
- (ii) Draw the dot-and-cross diagram for cyanogen. Hence, state its shape.
- (iii) *'Cyanogen is soluble in ethanol.'* Explain this statement with the aid of a suitable diagram.
- (c) Sketch and explain the trend observed for the atomic <u>and</u> ionic radii of the elements (from Na to C*l*) in Period 3.
- (d) Phosphine, PH₃, a gas at room temperature can be prepared by action of sodium hydroxide on phosphonium iodide, PH₄I. When 1.00 g of phosphonium iodide reacted with solid sodium hydroxide, 0.925 g of white solid was formed, together with steam and 150 cm³ of PH₃ gas.

All measurements were taken at room temperature and pressure.

Identify the white solid and use the information given to write a balanced equation with state symbols, for the preparation of PH₃.

[3]

[Total: 20 marks]

[6]

[7]

[4]

2 (a) Halogen derivatives can be used to synthesize alcohols.

The overall reaction is shown below:

 CH_3CH_2Br + NaOH \rightarrow CH₃CH₂OH + NaBr

State the type of reaction mechanism for the above reaction and illustrate how the reaction proceeds via the mechanism you stated. [3]

- (b) Describe the reactions of chloride, bromide and iodide ions with the following reagents:
 - I. Aqueous silver nitrate, followed by aqueous ammonia
 - II. Concentrated sulfuric acid

You are required to write equations where appropriate and give explanations for the differences in their reactions.

(c) When a primary aromatic amine is treated with nitrous acid in a cool solution, the product is unstable compound, known as a diazonium salt.

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| + $HNO_2 + HCl$ | \rightarrow | + H ₂ O |
|-----------------|---------------|--------------------|
| | | |

One reaction the diazonium cation under a site substitution of balides diazonium salt

The reaction is shown below, where X represents the halogen.

 $C_6 H_5 N_2{}^+ + K \textbf{X} \rightarrow C_6 H_5 \textbf{X} + K^+ + N_2 \label{eq:constraint}$ diazonium ion

Compound **P** can be synthesised from benzoic acid in the reaction shown below.

Suggest a synthetic route for the conversion of benzoic acid to compound P.

In each case, identify all the intermediate compounds and state clearly the reagents and conditions used for each transformation.

[*Note: In your proposed synthesis route, two of the stages of the synthesis requires the formation of the diazonium ion <u>and</u> the substitution of the halide.]



[5]

[3]

[7]

(d) Arrange the following halogen containing compounds according to increasing pK_a values. Explain your answer.

CH₃CHC*l*COOH, CH₃CC*l*₂COOH, CH₃CHBrCOOH

(e) Explain the following physical property trends of transition metals across the Period.
 I: relatively constant atomic radius
 II: very high melting point

[2]

[Total: 20 marks]

3 (a) An Ellingham diagram shows how the change in Gibbs free energy for a particular reaction varies with temperature.

The following shows a sketch of an Ellingham diagram for three reactions:

I:
$$2C(s) + O_2(g) \rightarrow 2CO(g)$$
 $\Delta G = (-223 - 0.18T) \text{ kJ}$
II: $2E_P(s) + O_2(g) \rightarrow 2E_PO(s)$ $\Delta G = (-525 + 0.13T) \text{ kJ}$

$$11. \quad 21 \in (3) + O_2(g) \rightarrow 21 \in O(3)$$

$$\Delta G = (-525 + 0.13T) \text{ kJ mol}^{-1}$$

 $\Delta G = (-1116 + 0.21T) \text{ kJ mol}^{-1}$

mol⁻¹

III:
$$\frac{4}{3}$$
 Al (s) + O₂ (g) $\rightarrow \frac{2}{3}$ Al₂O₃ (s) Δ G = (-1116 + 0.21T) kJ r



- Predict and explain what will happen to the value of ∆G when the pressure of the system in reaction I is reduced.
- (ii) Explain why the gradient for reaction I is negative (downward sloping), while the gradient for reactions II and III are positive (upward sloping)?
- (iii) Calculate ΔG of the following reaction at 1000K:

FeO (s)+ C (s)
$$\rightarrow$$
 Fe (s) + CO (g)

- (iv) Hence, what is the minimum temperature at which the reduction of iron (II) oxide by carbon becomes thermodynamically feasible?
- (v) Aluminium oxide and carbon have high melting points. With reference to the Ellingham diagram, explain why carbon is **not** used to line vessels that are used to contain molten steel saturated with oxygen.

[The melting point of steel is 1800 K]

- (b) The manipulation and rearrangement of the Gibbs free energy equation shows a relation between the change in Gibbs free energy and the standard electrode potential of a cell.
- (i) Define the term standard *electrode potential* of a cell.
- (ii) With the use of relevant data from the data booklet, state and illustrate how the relative stabilities of the Fe (II) / Fe (III) oxidation states are affected by the following changes:
 I. CN⁻ ligands
 II. pH

[6]

[14]

- 4 (a) Compound K is formed when phenylhydroxylamine, C₆H₅NHOH, is warmed with dilute sulfuric acid. Compound K has the following properties:
 - K is not very soluble in water, but dissolves in HCl (aq)
 - K dissolves in NaOH (aq) but not in Na₂CO₃ (aq)
 - K reacts with 1 mol of ethanoyl chloride to give compound L, C₈H₉O₂N, which is not soluble in HC*l* (aq), but is soluble in NaOH (aq).
 - **L** reacts with Br_2 (aq) to give compound **M**, $C_8H_7O_2NBr_2$.
 - K reacts with 2 mol of ethanoyl chloride to give compound N, C₁₀H₁₁O₃N, which is not soluble in HCl (aq) or NaOH (aq).
 - Suggest structures for compounds K, L, M and N.
 Present your reasoning clearly by explaining the Chemistry involved.
 - (ii) Write balanced chemical equations for each of the bullet points above to show how the reactions proceeded.
 - (b) A student was given 4 unlabelled bottles and each bottle contains one of the following organic compounds with a different functional group:
 - · 2º Alcohol
 - · Aldehyde
 - · Ketone
 - 1º Amide

Outline **a sequence** of simple chemical tests by which you could identify each of the above organic substances.

[Note: you are not allowed to identify the substances by elimination. You must give a positive test to prove the presence of each functional group present.] [8]

[Total: 20 marks]

[12]

5 (a) To study the rate of reaction between sodium and ethanol, a student added a freshly cut piece of sodium (of known mass) to a large excess of ethanol and measured the total volume of gas liberated every minute. The results obtained are given below:

| Time / min | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-----------------|---|------|------|------|------|------|------|------|------|
| Total vol. of | | | | | | | | | |
| gas produced / | 0 | 23.0 | 36.5 | 46.0 | 51.0 | 54.5 | 57.0 | 58.5 | 58.5 |
| cm ³ | | | | | | | | | |

- (i) Write an equation with state symbols for the above reaction.
- (ii) Give two reasons why sodium must be freshly cut?
- (iii) By plotting a suitable graph on graph paper, explain why the experimental results indicate that the overall kinetics is first order.
- (iv) Hence, suggest why the reaction appears to be zero order with respect to ethanol in this experiment.
- (v) The student modified the experiment by changing the concentration of ethanol.With the aid of a suitable equation, explain why water should not be used to dilute ethanol.

[8]

[7]

- (b) A solution containing ethanoic acid and sodium ethanoate functions as a buffer.
- (i) Explain what is meant by the term *buffer solution*, and write suitable equations to show how this solution functions as a buffer.
- (ii) Calculate the pH of the resulting solution when 25 cm³ of 0.10 mol dm⁻³ of ethanoic acid was added to 10 cm³ of 0.20 mol dm⁻³ of NaOH.
 [K_a of ethanoic acid = 1.8 x 10⁻⁵ mol dm⁻³]
- (c) A solution X is saturated with the soluble salts, $NaNO_3$ and $Mg(NO_3)_2$.
- (i) When solution X is heated strongly, the salts start to decompose. State which salt will begin to decomposes first, and the expected observations you will see to indicate that decomposition has taken place. Explain your answer.
- (ii) A student conducted an experiment to dissolve magnesium carbonate in solution X. She noted down her observations as follows: 'The solubility product of magnesium carbonate decreased in solution X. Only a small amount of magnesium carbonate dissolved.'

Discuss in detail the validity of this statement, making corrections to the observations where necessary.

[5]

[Total: 20 marks]

END OF PAPER