

# NATIONAL JUNIOR COLLEGE **PRELIMINARY EXAMINATIONS**

Higher 2

CANDIDATE NAME		
SUBJECT CLASS	REGISTRATION NUMBER	

## CHEMISTRY

Paper 3 Free response

9647/03 Tues 18 Sep 2012

2 hours

## READ THESE INSTRUCTIONS FIRST

Answer any *four* questions.

Start your answer to each question on a fresh piece of paper.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

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

At the end of the examination, fasten all your work securely behind the cover page.

This paper consists of **13** printed pages including **1** blank page.

#### Answer any **four** questions.

**1 (a)** The graph below shows the variation of pV versus p for NH<sub>3</sub>, which exists as a gas under normal room conditions.



Explain the shape of the graph, commenting on the behaviour of  $NH_3$  gas as an ideal gas at **A**, **B**, **C** and **D**.

[3]

(b) Ammonia is manufactured by the Haber Process, using gaseous nitrogen and hydrogen.

$$3H_2(g) + N_2(g) \implies 2NH_3(g)$$
 DH = -92.4 kJ mol<sup>-1</sup>

In an experiment starting with a 3:1 ratio of  $H_2$  and  $N_2$  mixture at 400 °C and a constant total pressure of 200 atm in the presence of iron catalyst, the equilibrium mixture was found to contain 36.3 % by volume of ammonia.

- (i) Justify the conditions of temperature and pressure used.
- (ii) Write an expression for  $K_p$  of this reaction.
- (iii) Calculate the partial pressures of each of these three gases at equilibrium, and hence calculate K<sub>p</sub> at this temperature, stating its units.

[6]

(c) Hydrazine, NH<sub>2</sub>NH<sub>2</sub>, is a flammable liquid with ammonia-like odour. It has basic chemical properties like ammonia.

Compound	$NH_2NH_2$	$NH_3$	
K <sub>b</sub> / mol dm <sup>-3</sup>	1.3 x 10 <sup>−6</sup>	1.8 x 10 <sup>−5</sup>	

Explain the difference in the  $K_b$  values of these two compounds.

[2]

- **1 (d)** Hydrazine is miscible with water but immiscible with trichloromethane.
  - (i) Explain, in terms of bonding, and with appropriate diagrams to illustrate, the difference in the miscibilities of hydrazine with the two stated solvents.
  - (ii) Hydrazine hydrate, made from hydrazine, takes part in the following reaction:

$$NH_2NH_2.H_2O + IO_3^- + 2H^+ + Cl^- \otimes N_2 + ICl + 4H_2O$$

Calculate the change in the oxidation states of the species oxidised.

[4]

(e) Hydrazines are part of many organic syntheses and undergo condensation reactions with carbonyl compounds. Below is a scheme showing some reactions of phenylethanone, which includes the reaction mentioned.



- (i) Draw the structural formulae of Compounds E, F and G.
- (ii) State what Reagent X is, and give the conditions under which the reaction will take place.

[4]

(f) Hydrazine reacts in a similar way with an isomer of phenylethanone, H. H is also a monosubstituted benzene like phenylethanone. Suggest the identity of H.

[1]

[Total: 20]

2 The Group II element, barium, was first isolated by Sir Humphry Davy, a British chemist and inventor in the nineteenth century. Besides being used widely in pyrotechnics, barium is also used in the production of hydrogen peroxide, a colourless liquid with a boiling point of 150 °C.

Hydrogen peroxide was originally produced commercially in a two-stage process. In the first stage, barium was heated in air to form barium peroxide. In the second stage, barium peroxide was added to aqueous nitric acid. The equations for the reactions are shown below.

Stage 1:  $Ba(s) + O_2(g) \otimes BaO_2(s)$ Stage 2:  $BaO_2(s) + 2HNO_3(aq) \otimes H_2O_2(aq) + Ba(NO_3)_2(aq)$ 

- (a) (i) Suggest **one** method of separating hydrogen peroxide from the reaction mixture in Stage **2**.
  - (ii) Suggest **one** reason why nitric acid was eventually replaced by sulfuric acid in Stage **2** to lower the cost of this commercial production.
  - (iii) Draw the dot-and-cross diagram for barium peroxide.

[3]

- (b) (i) Write an equation for the reaction of barium with water.
  - (ii) Would the reaction in (i) occur more or less vigorously than that for magnesium? Justify your answer by quoting relevant data from the *Data Booklet*.

[3]

- (c) Although Group II elements can form many compounds, the standard enthalpy of formation of solid barium chloride cannot be obtained directly.
  - (i) Define the term standard enthalpy of formation of barium chloride.
  - (ii) Given the standard enthalpy change of solution of barium chloride is 13.2 kJ mol<sup>-1</sup>, write a thermochemical equation to represent the standard enthalpy change of solution of barium chloride.

Reaction	DH <sup>θ</sup> / kJ mol <sup>-1</sup>
$Ba(OH)_2(aq) + 2HCl(aq) \otimes BaCl_2(aq) + 2H_2O(I)$	- 114.4
$H_2(g) + \frac{1}{2}O_2(g) \otimes H_2O(I)$	- 285.9
$1/_{2}$ H <sub>2</sub> (g) + $1/_{2}$ Cl <sub>2</sub> (g) ® HCl(g)	- 92.3
$HCl(g) + aq \otimes HCl(aq)$	- 71.9
$Ba(s) + O_2(g) + H_2(g) + aq \ \ Ba(OH)_2(aq)$	- 1002

2 (c) (iii) Using the information from (ii) and the following data:

draw an appropriate energy cycle and use it to calculate the enthalpy change of formation of solid barium chloride.

(iv) Use the following entropy data and your answer to (iii),

	$BaCl_2$ (s)	Ba(s)	C <i>l</i> <sub>2</sub> (g)
S <sup>e</sup> /J K <sup>-1</sup> mol <sup>-1</sup>	124	63	223

calculate the lowest temperature at which the following reaction becomes feasible.

$$BaCl_2(s) \otimes Ba(s) + Cl_2(g)$$

[9]

(d) Catalytic poisoning is normally undesirable as it results in a loss of the usefulness of expensive metals like platinum and palladium. However, poisoning of a catalyst can be used to enhance selectivities of some reactions.

An example of such practice is seen in the Rosenmund reduction where carbonyl compounds are produced. The palladium catalyst required for this reduction reaction is poisoned with barium sulfate.

The scheme below shows a 4-step synthesis of compound **G** which has the molecular formula  $C_3H_9ON$ . One of the steps involves the Rosenmund reduction.

 $CH_{3}COOH \xrightarrow{SOCl_{2}} \mathbf{D} \xrightarrow{H_{2}/Pd} \mathbf{E} \xrightarrow{HCN} \mathbf{F} \xrightarrow{Step (i)} \overset{\mathbf{G}}{C_{3}H_{9}ON}$ 

Give the structural formulae of compounds D - G and the reagent(s) and conditions required for **Step (i)**.

[5]

[Total: 20]

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**3 (a)** In the Clemmensen reaction, zinc is used, along with hydrochloric acid, for the reduction of a carbonyl compound into an alkane.



Clemmensen reaction

**W** and **X** are carbonyl compounds which undergo Clemmensen reaction to form the same alkane, **Y**. **W** is an optically active compound but **X** and **Y** are not. Only **W** forms a silver mirror with Tollen's reagent. 0.3 mol of **Y** burns in excess oxygen to produce 33.6 dm<sup>3</sup> of  $CO_2$  at standard temperature and pressure.

Calculate the number of moles of  $CO_2$  produced, and hence deduce the possible structures of **W**, **X** and **Y**.

[4]

- (b) Compound J has molecular formula of  $C_4H_7Cl$  and exhibits the following properties:
  - J reacts with acidified potassium manganate(VII), giving effervescence of a colourless gas.
  - J reacts with ethanolic potassium cyanide to produce compound K with molecular formula C<sub>5</sub>H<sub>7</sub>N.
  - **J** rotates plane-polarised light.

Draw the displayed formula for **J**. Explain how the identity you suggest for **J** fits in with the reactions described above.

[3]

(c) A number of experiments were carried out at constant pressure and temperature in which compound J was reacted with ethanolic potassium cyanide. The concentrations of compound J and ethanolic potassium cyanide were varied and the results are as shown below:

Experiment	[ <b>J</b> ] / mol.dm <sup>- 3</sup>	[KCN] / mol.dm <sup>- 3</sup>	Initial rate of formation of product
Number	7 1101 011	7 1101 0111	
1	0.10	0.10	0.015
2	0.30	0.10	0.045
3	0.20	0.20	0.030

- **3 (c) (i)** Deduce the rate equation for the reaction between **J** and potassium cyanide. Hence, describe the mechanism for this reaction, showing any relevant charges, lone pairs of electrons and movement of electrons.
  - (ii) It is common to plot a graph of concentration against time to determine the rate law for a reaction. This approach works well for simple systems with numerically exact data. However, in practice, experimental data suffers from random errors, making it difficult to determine the gradient or slope accurately.

A better approach is to make characteristic kinetics plots based on the integrated rate law:

Reaction order	Integrated rate law
zero	$[A] = [A]_{o} - kt$
first	ln [A] = ln [A] <sub>o</sub> -  k <i>t</i>
second	$\frac{1}{[A]} = \frac{1}{[A]_{o}} + kt$

Note:

[A] = conc of a reactant at any moment of time

 $[A]_{o}$  = initial concentration of that reactant

t = time since reaction started

Based on the information given and your answer to c(i), sketch a graph for the reaction of J with potassium cyanide and show how the rate constant for the reaction could be determined from it.

[7]

- (d) In the above reaction between J and potassium cyanide, ethanol was used as the solvent. Another similar reaction was carried out using propanone as the solvent and the rate constant, k, for this experiment was found to be 1.50 mol<sup>-1</sup> dm<sup>3</sup> min<sup>-1</sup>.
  - (i) State the overall order of reaction when propanone is used as the solvent.
  - (ii) Explain why the mechanism described in **c(i)** was favoured when ethanol was used as the solvent instead of propanone.

[3]

(e) With the aid of a suitable diagram, state and explain how the rate of a reaction will change when temperature is decreased.

[3]

[Total: 20]

- 4 This question describes two methods for the syntheses of organic compounds which have one carbon atom fewer than the starting material.
- (a) One method is the Hoffmann degradation whereby treating a primary amide with aqueous alkaline bromine produces a primary amine.

 $R-CONH_2 \xrightarrow{Br_2+OH^-} R-NH_2$ 

The Hoffmann degradation can be used as the last step in the following synthesis of phenylamine from benzoyl chloride.



- (i) Suggest reagents and conditions for Step I and the structure of compound P.
- (ii) Suggest a route to prepare phenylamine from benzene.
- (iii) Give a test (stating reagents and observations) that would enable you to distinguish phenol from phenylamine.

[6]

(b) Another method is *decarboxylation* whereby a carboxylic acid loses CO<sub>2</sub>.

In 1849, the German chemist Kolbe first published a method describing the preparation of an alkane from the electrolysis of the sodium or potassium salt of a carboxylic acid. The reaction occurs via the formation of radicals.

The following steps summarise the preparation of ethane using an aqueous solution of potassium ethanoate:

Step 1	$CH_3COO^- \rightarrow CH_3COO + e$	 Anode reaction
Step 2	$CH_3COO \rightarrow \ CH_3 + CO_2$	 Decarboxylation
Step 3	$2 \text{ CH}_3 \rightarrow \text{CH}_3\text{CH}_3$	 Dimerization

- (i) What do you understand by the term 'radical'?
- (ii) Draw the dot-and-cross diagram of the radical in **Step 1**, and predict the OCO bond angle.
- (iii) Write the half equation for the cathode reaction.

- (b) (iv) In the electrolysis of an aqueous solution containing 2.43 g of potassium ethanoate at 1 atm pressure and 28 °C, 200 cm<sup>3</sup> of ethane gas was collected. Calculate
  - (I) the percentage yield of ethane in this electrolysis.
  - (II) the time for this electrolysis if a current of 0.5 A was used.

[9]

- (c) In the electrolysis of potassium butanoate solution, hexane (b.p. 63 °C) was formed together with its isomer P (b.p. 58 °C). Account for
  - (i) the identity of **P** and its formation.
  - (ii) the difference in the boiling points of the isomers.

[4]

(d) Another electrolysis was carried out using a mixture of potassium ethanoate and potassium methanoate solution.

Draw the structure(s) of the organic product(s) formed.

[1]

### [Total: 20]

**5 (a)** The typical oxides of tin and lead are SnO, SnO<sub>2</sub>, PbO and PbO<sub>2</sub>.

The following two generalisations can be made about the oxides of the elements in Group IV of the Periodic Table.

- As the metallic character of the elements increases down the Group, the oxides become more basic.
- The oxides of the elements in their higher oxidation states are more acidic than the oxides of the elements in their lower oxidation states.
- (i) Use these generalisations to suggest which of the above oxides of tin or lead is the most
  - · acidic
  - basic
- (ii) PbO is found to be amphoteric. Write a balanced equation, with state symbols, for its reaction with aqueous NaOH.

[3]

- (b) 0.00425g of lead(II) sulfate can dissolve in 100 cm<sup>3</sup> of deionised water at 25 °C.
  - (i) What is the solubility, in mol  $dm^{-3}$ , of lead(II) sulfate in deionised water at 25 °C?
  - (ii) Determine the solubility product of lead(II) sulfate at 25 °C.
  - (iii) How would you expect the solubility of lead(II) sulfate to differ from the calculated value in (i) when it is dissolved in potassium sulfate solution? Explain your answer.

[5]

(c) The table below gives the melting points of  $CO_2$ ,  $SiO_2$  and PbO.

	Melting point/ °C
CO <sub>2</sub>	-78
SiO <sub>2</sub>	1610
PbO	888

In terms of structure and bonding, explain the difference in the melting points of

- (i) CO<sub>2</sub> and SiO<sub>2</sub>
- (ii) SiO<sub>2</sub> and PbO

(d) Styrene is used for making polystyrene, a common plastic material.



The pathway below shows the production of styrene from compound **R**.



Compound U

- (i) Suggest reagents and conditions for steps I and II and the structures of compounds **S** and **T**.
- (ii) Give the structural formula for **U**. Explain clearly why you placed the new functional group in its particular position.
- (iii) Suggest how styrene will react with cold alkaline KMnO<sub>4</sub>, giving the observations and the organic product(s) formed.
- (iv) What is the major product formed when styrene reacts with iodine monochloride, ICl?