

INNOVA JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION 2 in preparation for General Certificate of Education Advanced Level **Higher 2**

CANDIDATE NAME			
CLASS		INDEX NUMBER	
CHEMISTRY			9647/03
Paper 3 Free R	esponse		12 September 2011
			2 hours

Candidates answer on separate paper.

Writing Papers
Data booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in. Write in dark blue or black pen on both sides of the paper. You may use a soft pencil for any diagrams, graphs or rough working. Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer 4 out of 5 questions.

Begin each answer on a fresh sheet of paper.

You are advised to show all working in calculations. You are reminded of the need for good English and clear presentation in your answers. You are reminded of the need for good handwriting. Your final answers should be in 3 significant figures.

At the end of the examination, fasten all your work securely together. The number of marks is given in the brackets [] at the end of each question or part question.



Answer 4 out of 5 questions.

1 (a) (i) Manganese(IV) oxide, MnO_2 is the most common starting material for the production of compounds of manganese of other oxidation states.

With reference to the *Data Booklet*, state which of the following ions would convert manganese(IV) oxide to manganese(II) sulfate in an acidic solution.

Pb ⁴⁺ (aq) / Pb ²⁺ (aq)	<i>E</i> ^θ = +1.69V
Co ³⁺ (aq) / Co ²⁺ (aq)	<i>E</i> ^θ = +1.82V
Fe ³⁺ (aq) / Fe ²⁺ (aq)	$E^{0} = +0.77V$

- (ii) Calculate the E_{cell}^{θ} value to prove that the reaction between MnO₂ and the ion that you have chosen in **a(i)** is feasible and write a balanced equation for the reaction.
- (iii) What would be the colour of the final solution observed?

[5]

- (b) (i) Write the full electronic configuration of Zn^{2+} and Mn^{2+} .
 - (ii) Explain why manganese forms compounds that are often coloured whereas compounds of zinc are usually white.

[5]

(c) MnO₂ undergoes the following reaction as shown in the schematic diagram below:

 $MnO_2 \xrightarrow[step I]{O_2/KOH} Green solution, A \xrightarrow[step II]{dilute acid} MnO_2 + Purple solution, B$

- Step I: Oxidation of MnO_2 in molten KOH with oxygen from the air produces a green compound, **A**.
- Step II: Reaction of **A** with dilute acid produced 0.174 g of MnO₂ and a purple solution of compound **B** was observed. A solution of compound **B** is just decolourised by 40.0 cm³ of 0.500 mol dm⁻³ iron(II) sulphate.
- (i) **B** contains potassium, manganese and oxygen only. Suggest the chemical formula of compound **B** that causes the solution to appear purple.
- (ii) Calculate the number of moles of MnO₂ produced in step II.
- (iii) Calculate the number of moles of compound **B** produced in step II, given that compound **B** and iron(II) sulphate reacted in a 1:5 mole ratio.
- (iv) With reference to step II of the above reaction scheme, let the oxidation number of manganese in A be n, i.e. Mnⁿ⁺. Using your answer to c(ii) and c(iii), write an expression in n to show
 - (I) the no. of moles of electrons gained by Mn^{n+} when Mn^{n+} is reduced to MnO_2 (II) the no. of moles of electrons lost by Mn^{n+} when Mn^{n+} is oxidised to **B**
- (v) Hence, using your answer to **c(iv)**, calculate the oxidation number of manganese in compound **A**.

[5]

- (d) (i) Cl_2 reacts with benzene in the presence of a suitable catalyst. Describe the mechanism and suggest the product obtained.
 - (ii) The reaction in **d(i)** can only take place under anhydrous conditions. Suggest a reason to explain why it is so.

[5]

2 (a) This question is related to the chemistry of carbonyl compounds to form nitrogencontaining compounds.

Bupropion is an anti-depressant that was subsequently found to be useful as a smoking cessation aid. It reduces the severity of nicotine cravings and withdrawal symptoms. It can be synthesised from compound **C**, from which many derivatives of bupropion can also be synthesised.



- (i) Suggest the type of reaction occurring in step I.
- (ii) Name the type of reaction in step III and state the reagent(s) and condition(s) involved.
- (iii) Given that bupropion is basic, without using fractional distillation, suggest a reagent and a suitable separation technique that you will use to isolate the product bupropion from the reaction mixture. Describe what you will observe in the process.
- (iv) Suggest the reagents and conditions required in step IV and state and describe the mechanism of this step.
- (v) Based on your answer in **a(iv)**, suggest and explain whether the product of step IV is optically active or optically inactive.

[12]

(b) When two colourless gases dinitrogen tetraoxide and nitrogen monoxide are mixed at room temperature, the two gases react slowly to form the blue compound dinitrogen trioxide according to the following equilibrium.

 $N_2O_4(g) + 2NO(g) \rightleftharpoons 2N_2O_3(g) \qquad \Delta H \text{ negative}$ blue

A gas syringe is filled with the colourless gases and sealed. When the gases are compressed, the blue colour becomes more intense. When the system is warmed, the blue colour fades.

- (i) Use Le Chatelier's Principle to explain the above observations.
- (ii) At low temperatures, N_2O_3 exists as a deep blue liquid. Using your knowledge of the chemistry of P_4O_6 , state the acid-base nature of N_2O_3 and write an equation with state symbols to illustrate your answer.

[5]

(c) (i) A large portion of the copper produced in the world is obtained by the smelting of chalcopyrite. It is an iron-containing mineral with the molecular formula of CuFeS₂. Smelting of chalcopyrite can be represented by the following equation:

$$3CuFeS_2 + 8O_2 \longrightarrow 3Cu + FeO + Fe_2O_3 + 6SO_2$$

Calculate the volume of sulfur dioxide gas released into the atmosphere at r.t.p. if 1 tonne of the rock sample is smelted. It is estimated that the rock contains 1.5% by mass of chalcopyrite. [1 tonne = 1000 kg]

(ii) Why is it important to remove SO₂ from the products of smelting before release into the atmosphere?

[3]

3 (a) Atenolol is a drug used mainly to prevent hypertension and coronary heart disease.



Atenolol

[Assume that the ether functional group is inert and does not undergo any reaction.]

Draw the structural formula of the organic product formed when Atenolol is treated with the following reagents:

- (i) Hot aqueous hydrochloric acid
- (ii) Ethanoyl chloride

[4]

(b) Part of the reaction scheme for the formation of Atenolol involves the synthesis of the ether functional group via two possible routes:



- (i) Which route will give a greater yield of the product? Explain your reasoning.
- (ii) Another drug, Ketoprofen, commonly used in painkillers, has the structure as shown below. Describe a simple chemical test which would enable you to distinguish between Atenolol and Ketoprofen.



Ketoprofen

[4]

(c) (i) Group II carbonates decompose in a similar manner as Group II nitrates. The following table shows the temperature at which Group II carbonates decompose.

Carbonate	Decomposition temperature / K
MgCO ₃	523
CaCO ₃	1098
SrCO ₃	1373
BaCO ₃	1573

Based on the above data, state and explain the trend of thermal stabilities of Group II carbonates down the group.

(ii) One of the products in the thermal decomposition of magnesium carbonate is magnesium oxide. It is used as a refractory material as it is able to withstand high temperatures.

Relate this use of magnesium oxide to its structure and bonding.

(iii) A mixture of magnesium oxide, MgO, alumina, Al_2O_3 and silica, SiO₂ is usually used in the manufacture of such refractory material.

Suggest, using suitable equations with state symbols, how magnesium oxide can be separated from a mixture containing these three oxides.

[9]

(d) (i) One of the important uses of transition metals or their compounds is their role as catalysts in industrial processes.

Tartrate ions, $(CHOHCO_2^{-})_2$ are oxidised by hydrogen peroxide to carbon dioxide and water. The reaction is catalysed by $Co^{2^+}(aq)$. The solution is pink at the beginning and end of the reaction, but green during it.

The redox reaction between tartrate ions and hydrogen peroxide is represented by the following half-equations:

 $(CHOHCO_2^-)_2(aq) + 2H_2O(l) \implies 4CO_2(g) + 8H^+(aq) + 10e$ $2H^+(aq) + H_2O_2(aq) + 2e \implies 2H_2O(l)$

Suggest a **two-step** mechanism by which $Co^{2+}(aq)$ ions catalyse this reaction.

(ii) Besides the example in d(i), give another example of a reaction that uses a transition metal or its compound as a homogenous catalyst and state the identity of this catalyst.

[3]

4 (a) Since its invention in 1950 by John Hopps, the heart pacemaker has saved the lives of many cardiac patients by regulating their heartbeat.

In this device, electrical energy is generated by implanting zinc and platinum electrode in body tissues. These electrodes in the oxygen-containing body fluid will form a bioelectric battery in which zinc is oxidized and oxygen is reduced to water.

- (i) Write balanced half equations, with state symbols, for the reactions that occur at the anode and cathode of the bioelectrical battery.
- (ii) Calculate the time taken for a 6.5 g of zinc electrode to be used up, given that a current of 4×10^{-5} A is generated.

[4]

(b) Acetylsalicyclic acid is known for its ability to ease pains and reduce fevers since ancient times. It is an active component found in aspirin, an anti-inflammatory drug. Acetylsalicyclic acid is a monobasic acid with $K_a = 1.56 \times 10^{-5}$ mol dm⁻³.



Acetylsalicyclic acid

A 25.0 cm³ sample of acetylsalicyclic acid with a pH of 2.8 was titrated with 0.20 mol dm⁻³ of aqueous sodium hydroxide. 20.00 cm³ of aqueous sodium hydroxide was needed for complete reaction.

- (i) Calculate the pH at maximum buffering capacity.
- (ii) Sketch and label the titration curve obtained, clearly indicating the following:
 - the initial pH
 - equivalence point
 - maximum buffering capacity

[3]

(c) A mixture of acetylsalicyclic acid, C₈H₇O₂COOH and its salt, sodium acetylsalicyclate, C₈H₇O₂COO⁻Na⁺ is used as a buffer solution in biochemical studies. Write equations to illustrate how the above mixture acts as a buffer when small amounts of ac id or alkali are added to it.

[2]

(d) The following reaction scheme involves Compound **D**, benzene 1,2-dicarboxylic acid which is a derivative of acetylsalicyclic acid.



- (i) State the type of reactions for reaction I and III.
- (ii) Suggest reagent(s) and condition(s) for reaction II and III.

[4]

(e) Compound E, C₁₀H₇NO can exhibit geometric isomerism. E can react with silver diamine but not Fehling's solution. On reacting E with lithium aluminium hydride, F, C₁₀H₁₃NO is formed. F is readily soluble in acid. 1 mole of F reacts with 2 moles of ethanoyl chloride to give the compound below:



When **E** is heated with dilute sodium hydroxide, the dried product is a white crystalline solid, **G**, $C_{10}H_7O_3Na$.

Deduce the structural formula of **E**, **F** and **G**, explaining your reasoning.

[7]

5 Ethanol fuel cells are a more practical and viable source of energy as compared to hydrogen fuel cells.



- (a) (i) Write balanced half-equations, with state symbols, for the reactions taking place at the anode and cathode when the fuel cell is in operation.
 - (ii) Use appropriate data from the *Data Booklet* to explain why an acidic electrolyte is often preferred over an alkaline or neutral electrolyte.

[4]

(b) A metallic salt containing the anion $I_xCl_y^-$ decomposed when heated to form iodine vapour and the metallic chloride. When 0.270g of this compound was heated, the iodine evolved was bubbled into excess potassium iodide solution.

The dissolved iodine required 21.30 cm³ of 0.0600 moldm⁻³ of aqueous sodium thiosulfate for complete reaction. When the residue was dissolved in water, the resultant solution required 6.40 cm³ of 0.100 mol dm⁻³ aqueous silver nitrate for complete reaction.

- (i) Determine the value of x and y in $I_x C l_y^-$.
- (ii) Hence, determine the identity of the metallic element.

[6]

(c) Predict the observations when aqueous silver nitrate is added to a solution containing both $C\Gamma$ and Γ , followed by an addition of excess aqueous ammonia to the resultant mixture.

[2]

(d) α-Terpineol, C₁₀H₁₈O, has a pleasant smell similar to lilac and is a common ingredient in perfumes, cosmetics, and flavours.

 α -Terpineol contains a *cyclohexene ring* and an alcohol group which is not readily oxidised.

Heating α -Terpineol with concentrated acidified KMnO₄ gives **H**, C₁₀H₁₈O₄, which gives a yellow precipitate on warming with alkaline aqueous iodine. On hydrogenation in the presence of palladium catalyst, α -Terpineol gives **J**, C₁₀H₂₀O.

J reacts readily in the presence of a few drops of concentrated sulfuric acid to give **K**, $C_{10}H_{18}$. **K** is oxidised by warm acidified KMnO₄ to give **M**, $C_9H_{16}O$ along with the evolution of CO₂ gas.



Deduce the structural formulae for H, J, K and α -Terpineol. Explain your reasoning. [8]

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12