Name:

Index Number:

Class:



DUNMAN HIGH SCHOOL Preliminary Examination Year 6

H2 CHEMISTRY

Paper 3 Free Response

9647/03

18 September 2012 2 hours

Additional Materials: Data Booklet Graph Paper

INSTRUCTIONS TO CANDIDATES

Write your name, register number and class on this question paper and on the Cover Sheet provided.

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 any four questions.

Start each question on a fresh sheet 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 work securely together with the Cover Sheet on top.
- Hand in the question paper separately.

The total marks for this paper is 80 marks.

Answer any four questions.

- 1 The study of organic compounds includes the collection of kinetic data and thermodynamic data of the compounds.
- (a) The kinetics of the hydrolysis of the ester, CH₃CH₂CO₂CH₃, may be investigated by the following method.

 $CH_3CH_2CO_2CH_3 + H_2O \otimes CH_3CH_2CO_2H + CH_3OH$

In a 1 dm³ mixture, 0.350 mol of the ester was hydrolysed by heating with water and using hydrochloric acid as catalyst. The following results were obtained.

Time/s	Concentration of CH ₃ CH ₂ CO ₂ H/mol dm ⁻³
0	0
340	0.105
680	0.185
1080	0.243
1440	0.278

- (i) Suggest how the progress of this reaction may be followed in order to obtain the results as stated.
- (ii) By drawing a suitable graph using the data given above, show that the reaction is first order with respect to the ester. It has been found that the hydrolysis reaction is first order with respect to the hydrochloric acid.
- (iii) Deduce the units of the rate constant.
- (iv) State and explain the effect of a catalyst on the rate constant.
- (v) Using suitable bond energy values from the *Data Booklet*, calculate the ΔH for the hydrolysis of the ester.
- (vi) Given that the standard enthalpy change of reaction for the hydrolysis is +7.6 kJ mol⁻¹, suggest a reason for the difference between this given value and the value that you have calculated in (a)(v).

[11]

- (b) Hydrolysis of ester can be achieved in the biological system by enzymes known as esterase. Enzymes are proteins that catalysed a specific chemical transformation in the biological system. Such enzymes are generally quaternary proteins.
 - (i) Sketch and explain the graph showing how the rate of hydrolysis changes with increasing concentration of the ester.
 - (ii) Explain the meaning of quaternary structure of proteins.
 - (iii) List 2 other major functions of proteins in the body.
 - (iv) Suggest and explain a chemical method for distinguishing the following pair of esters. You should state the expected observations.

HCO₂CH₂CH₃ and CH₃CH₂CO₂CH₃

[9]

[Total: 20]

2

- 2 This question is about the chemistry of the transition metal, nickel and its compound.
- (a) Explain why the colour of $[Ni(NH_3)_6]^{2+}(aq)$ is blue.
- (b) Ni(CO)₄ is a compound formed by the reaction between nickel and carbon monoxide. The Mond process was developed by Ludwig Mond to extract and purify nickel from its ores. One of the stages of this process involves the decomposition of Ni(CO)₄ at 227 °C to give nickel as shown in this equation below:

 $Ni(CO)_4(g) \implies Ni(s) + 4CO(g)$

The equilibrium constant, K_p , for the equilibrium at 227 °C is 1.01 atm³. A sample of gaseous Ni(CO)₄ was placed in a 2 dm³ evacuated container at 227 °C. At equilibrium, the partial pressure of CO was 2.00 atm. [1 atm = 1.01 x 10⁵ Pa]

- (i) Sketch the shapes of the hybrid orbitals around the C atom in carbon monoxide.
- (ii) Write an expression for K_{p} .
- (iii) Calculate the total pressure of the system at equilibrium.
- (iv) Calculate the mass of Ni(CO)₄ placed in the container initially.

[8]

[3]

(c) Ni is commonly used in catalytic hydrogenation reactions. One such example is given below.

Compound **A**, $C_{10}H_{12}NOCl$, has a chiral centre and dissolves in dilute sulfuric acid. It reacts with 2,4–dinitrophenylhydrazine to form an orange precipitate, but does not react with Tollens' reagent. **A** reacts with H₂ in the presence of Ni catalyst followed by addition of aqueous bromine to form **B**, $C_{10}H_{11}NOClBr_3$. When 1 mol of compound **B** is heated under reflux with aqueous iodine and excess alkali, followed by careful acidification, compound **C**, $C_8H_4NO_4Br_3$ is formed together with 2 mol of yellow solid CHI₃.

Deduce the structures of compounds **A**, **B** and **C**, giving reasons for your answer. [9]

- 3 This question is about the varied chemical uses of HC*l*.
- (a) (i) In the electrolysis of a solution of hydrochloric acid with inert platinum electrodes, an ammeter showed a reading of 0.450 A in the external circuit of the cell. 110 cm³ of gas was evolved at the cathode after 30 minutes under room temperature and pressure. Determine the actual current used in the electrolysis process. Hence, determine the percentage error (if any) of the ammeter reading.
 - (ii) A student carried out a reaction involving acidified potassium dichromate(VI), together with an unknown half-cell which consists of transition metal ions. The Gibbs Free Energy of the reaction was known to be -324 kJ mol⁻¹ and the procedure involved transferring 6 mol of electrons from the unknown solution to potassium dichromate(VI).

Using the expression of $DG^q = -nFE^q_{cell}$, where n is the number of moles of electrons transferred, F is the Faraday constant and E^q_{cell} is the overall cell potential, determine the E^q_{cell} value and hence deduce the identity of the unknown half cell.

[4]

- (b) A sample of sodium hypochlorite, NaOC*l*, was dissolved in 100 cm³ of 0.123 mol dm⁻³ HOC*l* (p K_a = 7.50) solution forming a buffer of pH 6.20. The buffer is then used to absorb HC*l* gas. Calculate the concentration of gaseous HC*l* (in mol dm⁻³) that is required to be added to the buffer solution until it reaches pH 6. [5]
- (c) The decomposition temperature of hydrogen chloride is close to 3000 K. Predict, with reasoning, if the decomposition temperature of hydrogen astatide would be higher or lower than 3000 K.

[3]

- (d) Concentrated hydrochloric acid is commonly used in the reduction of trinitrobenzene (2,4,6-trinitrobenzene).
 - (i) Suggest the complete set of reagents, together with concentrated HC*l*, to be used in this reduction process.
 - (ii) Suggest the structural formula of the product formed.
 - (iii) Explain the relative basicity between the product formed in (d)(ii) and the melamine molecule as shown below in terms of their structures. The melamine molecule contains a triazine ring with 3 nitrogen atoms present in the ring.

 NH_2 H₂N NH_2

Melamine

[5]

(e) 2,4,6-trinitrobenzene can also undergo Friedel-Crafts alkylation with CH₃Cl to form 2,4,6-trinitromethylbezene. The alkyl side chain can then be further reacted to form useful halogen derivatives. However, some side products like hydrogen chloride gas and compound D can also be formed in the process.



Compound **D**

Using 2,4,6-trinitromethylbezene as the starting material, describe an appropriate mechanism that would result in the production of compound **D**. [3]

- 4 Chlorine and its compounds are used to manufacture many products such as pesticides, medicines, plastics, bleaches and solvents.
- (a) 1 mol of the following compounds is added to 1 dm³ of water.

CH₃COC*l*, C*l*CH₂COOH and SiC*l*₄

Arrange the compounds in order of increasing pH of the resultant mixture formed. Briefly explain your answers, giving equations where appropriate. [4]

- (b) Both chloric(I) acid, HOC*l* and hydrogen chloride react with propene. In the reaction between chloric(I) acid and propene, chlorine is added to carbon-1 of propene in the major product. However, in the reaction between hydrogen chloride and propene, chlorine is added to carbon-2 of propene in the major product.
 - (i) Draw the displayed formula of the major product formed between propene and chloric(I) acid.
 - (ii) Explain briefly why chlorine from chloric(I) acid and from hydrogen chloride add to different carbon atoms in their reactions with propene.

[4]

(c) Despite health and environmental concerns, the chlorinated compound **MCPA**, is widely used as a weed killer.



MCPA

Using **not** more than 3 steps, draw a reaction scheme to show how **MCPA** can be synthesised from 2–methylphenol. [3]

(d) Compound **E** is a derivative of **MCPA** which may be a potential insecticide. The synthesis of Compound **E** is given below.



Compound E

Describe the mechanism for the synthesis of Compound E.

[3]

- (e) Describe the variation in melting points of the chlorides of the elements from sodium to phosphorus and explain the variation in terms of structure and bonding. [4]
- (f) Describe a reaction, without the use of bromide solution, which shows that chlorine is a stronger oxidising agent than iodine. [2]

- **5** Phosphorus is an element in Period 3 of the Periodic Table with wide ranging application in inorganic and organic synthesis.
- (a) Explain why the first ionisation energy of phosphorus is higher than that of sulfur, S, and arsenic, As, respectively. [2]
- (b) Define the second ionisation energy of phosphorus with an appropriate equation. [2]
- (c) When heated in air, phosphorus and sodium forms oxides which can react with acids, bases or water.
 - (i) Write balanced equations for the reaction between oxides for the two elements and an appropriate acid or base.
 - (ii) Describe the reactions, if any, of the two oxides with water containing universal indicator. Chemical equations are not required.

[5]

- (d) Phosphoric acid is used as a catalyst in the industrial preparation of $CH_3CH_2CH(OH)CH_3$ from compound **F**, $CH_3CH_2CH=CH_2$.
 - (i) State the reagent and any other conditions required in this industrial preparation.
 - (ii) Compound G, which is an isomer of F, exists as a pair of geometric isomers. Deduce the structure of G.
 - (iii) Predict the carbon–containing products obtained when **F** and **G** are separately heated with acidified potassium manganate(VII).

[3]

(e) PCl_5 is used for substitution reactions in organic chemistry.

An optically active compound **P**, with molecular formula $C_3H_7O_2N$, reacts with PC l_5 to give white fumes. When a solution containing **P** is warmed with aqueous sodium hydroxide, a pungent gas is evolved. Upon acidification of the resulting mixture, compound **Q**, $C_3H_6O_3$, can be isolated. When **Q** is warmed with concentrated sulphuric acid, a cyclic compound **R**, $C_6H_8O_4$, is formed. Compound **S** is a structural isomer of **Q** and is not optically active. When **S** is warmed with concentrated sulphuric acid, a non–cyclic compound **T**, $C_3H_4O_2$, is produced.

Deduce the structures of compounds P, Q, R, S and T. Explain the chemistry of the reactions described. [8]