Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

9647/03

Paper 3 Free–Response

12 September 2011

2 hours

Additional Materials: Cover Sheet
Writing Papers
Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **register number** and **class** on this question paper and on the Cover Sheet provided.
2 Write in dark blue or black pen on both sides of the paper.
3 You may use a soft pencil for any diagrams, graphs or rough working.
4 Do not use staples, paper clips, highlighters, glue or correction fluid.
5 Answer any **four** questions.
6 Start each question on a fresh sheet of paper.
7 A Data Booklet is provided.
8 You are reminded of the need for good English and clear presentation in your answers.
9 The number of marks is given in brackets [ ] at the end of each question or part question.
10 At the end of the examination:
11 Fasten all work securely together with the Cover Sheet on top.
12 Hand in the question paper separately.
13 The total marks for this paper is 80 marks.

[Turn over

Answer *any* **four** questions.

1 Iron is the cheapest and one of the most abundant of all metals, comprising nearly 5.6% of the earth's crust and nearly the earth's entire core. It exists in a wide range of oxidation states, from −2 to +6, although ferrous (Fe^{2+}) and ferric (Fe^{3+}) compounds are more common.

(a) Acidic solutions containing ferrous ions are oxidised to ferric ions in air, with no precipitation seen. On the other hand, ferrous ions give a precipitate in alkaline solutions and the precipitate turns reddish–brown in air.

With reference to the *Data Booklet*, explain the two reactions using relevant E^{θ} values, writing equations where appropriate.

[4]

(b) Ferric ions can catalyse the reaction between I^-(aq) and $S_2O_8^{2-}$(aq).
By considering relevant E^{θ} values, describe and explain the role of the ferric ions in this reaction, writing equations where appropriate.

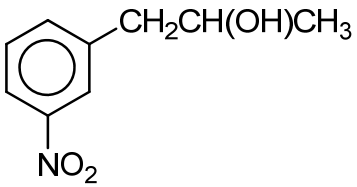
[3]

(c) Ferric chloride is an industrial scale commodity inorganic compound which is often used as catalyst in organic synthesis. One example is its use as a Lewis acid for catalysing the alkylation reaction of benzene by chloroethane to form ethylbenzene. This reaction is similar to the reaction between benzene and chlorine.

(i) Write a balanced equation for the overall reaction of chloroethane and benzene.

(ii) State and outline the mechanism, with equations only, for the above reaction using ferric chloride as a catalyst.

(iii) Hence, or otherwise, suggest how you would synthesise the following alcohol, 1–(3–nitrophenyl)propan–2–ol, starting from a chloroalkene and benzene as your only organic reagents. Your synthesis route should be no more than three steps.



1–(3–nitrophenyl)propan–2–ol

(iv) Explain why 1–(3–nitrophenyl)propan–2–ol exists as enantiomers, and describe how pure samples of the enantiomers can be distinguished by a physical method.

[8]

(d) Consider this iron compound, $NH_4[Fe(SCN)_x(NH_3)_y]$, with the following composition by mass:

Fe	16.4%
S	37.7%
N	28.8%

(i) Define the term *ligand*, and identify the ligands in this complex.
(ii) Calculate the values of x and y in the formula.
(iii) Determine the oxidation number of iron in the compound. [5]

[Total: 20]

2(a) The Van Slyke's method, named after an Amercian biochemist Van Slyke Donald Dexter, refers to a method to test for primary amino groups. Amino acids can be determined by measuring the volume of nitrogen released from their reaction with nitrous acid. For example, alanine can be reacted as shown in the equation below.

$$CH_3CH(NH_2)COOH + HNO_2 \rightarrow CH_3CH(OH)COOH + N_2 + H_2O$$

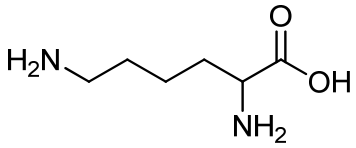
Another method to test for primary amino groups consists of reacting amino acids with a volumetric solution of perchloric acid, for example:

$$CH_3CH(NH_2)COOH + HClO_4 \rightarrow CH_3CH(N^+H_3)COOH + ClO_4^-$$

The reaction above is a weak base and strong acid neutralisation reaction. The excess perchloric acid is then determined by titration with aqueous sodium hydroxide.

(i) Explain, with the aid of an equation, why alanine is a weaker base than propylamine.

The above method is used to test for primary amino groups in lysine. 50.0 cm^3 of 0.100 mol dm^{-3} perchloric acid is added to a sample of lysine.



lysine

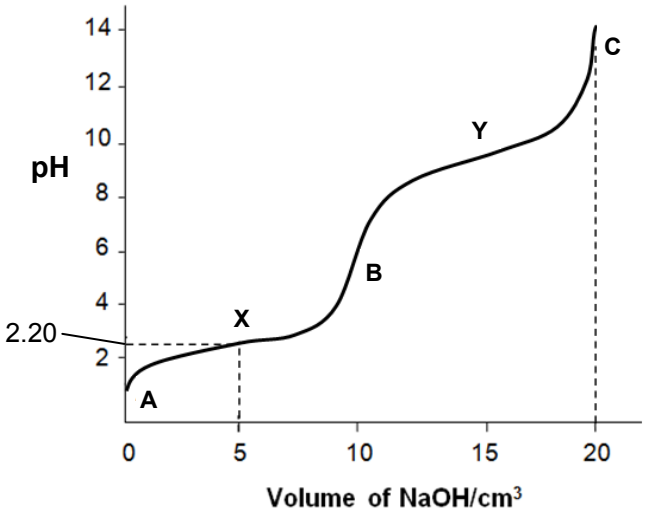
The amount of excess perchloric acid is determined by titration with 0.150 mol dm^{-3} of sodium hydroxide solution. 16.0 cm^3 of sodium hydroxide is needed to complete the titration.

(ii) Write an equation for each of the following reaction between:
(I) nitrous acid and lysine
(II) perchloric acid and lysine

(iii) Calculate the volume of the nitrogen released at a pressure of 103 kPa and a temperature of 20 °C by the same lysine sample.

[6]

(b) Amino acids like lysine show both acidic and basic properties. In acidic solution, lysine is completely protonated and exists as the conjugate acid. 10.0 cm^3 of completely protonated lysine is titrated with 0.10 mol dm^{-3} sodium hydroxide solution. Its titration curve is shown below.



(i) Calculate the first dissociation constant K_{a1} of lysine.

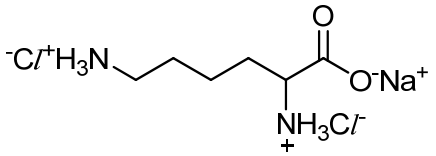
(ii) Identify the species present at point **X**.

(iii) Calculate the concentration and initial pH of lysine at **A**.

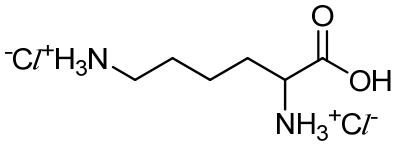
(iv) Explain why the predominant species at point **C** has a high melting point.

[6]

(c) Equimolar amount of **R** and **S** are mixed and dissolved in a 1 dm^3 of distilled water. The pH of this mixture is then adjusted by adding a suitable amount of solid NaOH.



R



S

By means of a balanced equation, show how the mixture above can act as a buffer when a few drops of aqueous sodium hydroxide are added to it.

[1]

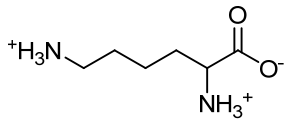
(d) When 30 cm^3 of 1.0 mol dm^{-3} **S** in its neutral form, is added to 25 cm^3 of 1.0 mol dm^{-3} sulfuric acid in a plastic container, the temperature rose by 6.3 °C. The process efficiency is expected to be 90%.

(i) Calculate the standard enthalpy change of the reaction assuming that it takes 4.18 J to increase the temperature of 1 cm^3 of the solution by 1.0 °C.

(ii) Predict if the enthalpy change of the reaction will be higher, the same or lower than that calculated in **(i)** if sulfuric acid is replaced by a weak acid. Explain.

[4]

(e) One mole of solid **R** in **(c)** dissolves in water to release 930 kJ of energy. Given the lattice energy of **R** is –234 kJ mol^{-1} and the following enthalpy changes of hydration, draw an energy cycle to determine the enthalpy change of hydration of the $^{-}O_2CCH(NH_3^{+})(CH_2)_4NH_3^{+}$ ion.

ions	ΔH^{θ}_{hyd} /kJ mol^{-1}
Na^+	–499
	?
Cl^-	–381

[3]

[Total:20]

3(a) An optically active ester, **L**, (11.6 g) with the molecular formula of $C_6H_{12}O_2$, is hydrolysed by heating with an excess of aqueous sodium hydroxide solution. After terminating the hydrolysis, the alkaline reaction mixture is extracted several times with an organic solvent.

The aqueous and organic layers are then collected separately. The aqueous solution is found to be optically inactive.

Anhydrous magnesium sulfate is added to the organic layer. The mixture is filtered and the filtrate distilled. 7.4 g of a liquid **J** is obtained (assume 100 % purity and yield).

(i) Suggest the role of anhydrous magnesium sulfate in the procedure above.

(ii) Calculate the number of moles of ester used and hence calculate the M_r of liquid **J.**

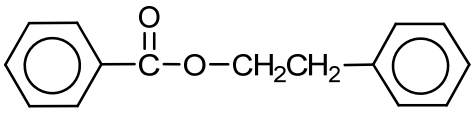
(iii) Propose a possible structural formula of the ester.

(iv) What would be the structure of an isomeric ester that would produce an optically active aqueous layer after hydrolysis?

(v) Write an equation for the alkaline hydrolysis of **L** with sodium hydroxide.

[6]

(b) A food chemist decides to synthesise the ester as shown below, for possible use as a flavouring agent.



The **only** organic compound available is phenylethanal ($C_6H_5CH_2CHO$).

Outline how the food chemist is able to synthesise this ester using only phenylethanal and other appropriate inorganic reagents.

[2]

(c) **L** can be reduced to alcohol via an intermediate, ethanal, with the use of lithium aluminium hydride. The attacking species is the AlH_4^- ion which, in effect, is a carrier of hydride ions, H^-. Ethanal is then further reduced in the following two steps.

Step 1 Attack of the hydride ion, H^-, at the carbonyl carbon of ethanal gives a tetrahedral intermediate.

Step 2 The anion reacts with aqueous acid to give the alcohol product.

Describe the mechanism in steps **1** and **2** using only equations. Include relevant charges and curly arrows to show the movement of electrons.

[3]

(d) The anhydrous magnesium sulfate from **(a)** exists as a hydrated salt when dissolved in aqueous sodium hydroxide. Equal volumes of 1.0 mol dm^{-3} hydrated magnesium sulfate and 2.0 mol dm^{-3} aqueous sodium hydroxide are mixed. The resulting mixture produces a white precipitate and has a pH of 10.2.

(i) Suggest the identity of the white precipitate.

(ii) Write the expression for the solubility product of this sparingly soluble salt.

(iii) Calculate the solubility product of the precipitate formed, including its units.

(iv) Explain, with the aid of equations, the effect on the solubility upon adding aqueous sodium hydroxide in excess to the resulting mixture containing the white precipitate.

(v) Magnesium sulfate dissolves in water to give a solution of pH ≈ 6.5.
Explain, with equations only, why this solution is slightly acidic.

[9]

[Total: 20]

4 This question is about the chemistry of Group II elements and carbonyl compounds.

(a) The thermal decomposition of beryllium ethanoate produces its metal carbonate and a carbonyl compound.

$$(CH_3CO_2)_2Be \xrightarrow{\Delta} BeCO_3 + (CH_3)_2CO$$

An acidic gas and a mixture of three carbonyl compounds, namely **D**, **E** and **F**, can possibly be obtained when the reaction mixture of beryllium ethanoate and beryllium methanoate is heated.

(i) Suggest the identity of the acidic gas.

(ii) Both **D** and **E** but **not F** decolourise potassium manganate(VII) solution. Both **D** and **F** but **not E** gives a yellow precipitate with alkaline aqueous iodine.

Suggest the structural formulae of **D**, **E** and **F**.

(iii) There is no organic product obtained when **E** is reacted with hot acidified potassium manganate(VII). Account for this observation.

[5]

(b) When **D** is warmed with Tollens' reagent, an organic product, **K**, is formed. **K** is then reacted with 2–chloro–2–methylpropane, $(CH_3)_3CCl$, forming a sweet–smelling liquid.

(i) Suggest the structural formula of **K**.

(ii) In the formation of the sweet–smelling liquid, **K** reacts with $(CH_3)_3CCl$. Suggest the type of reaction.

(iii) Propose, with the aid of appropriate equations, the reaction mechanism for the organic synthesis in part **(ii)**.

(iv) Given that the half–life of 2–chloro–2–methylpropane is 1500 s and the rate constant, k has a numerical magnitude of 4.62×10^{-4}, prove that the order of reaction with respect to $[(CH_3)_3CCl]$ is first order.

(v) State and explain the effect of a catalyst on the rate constant.

(vi) Predict, with reasoning, the solubility of 2–chloro–2–methylpropane, $(CH_3)_3CCl$ in water.

[11]

(c) Calcium ethanoate, one of the Group II salts of carboxylic acids, is also commonly used in the production of propanone.

Predict, with reasoning, if the decomposition temperature of calcium ethanoate will be higher or lower than that of beryllium ethanoate.

[2]

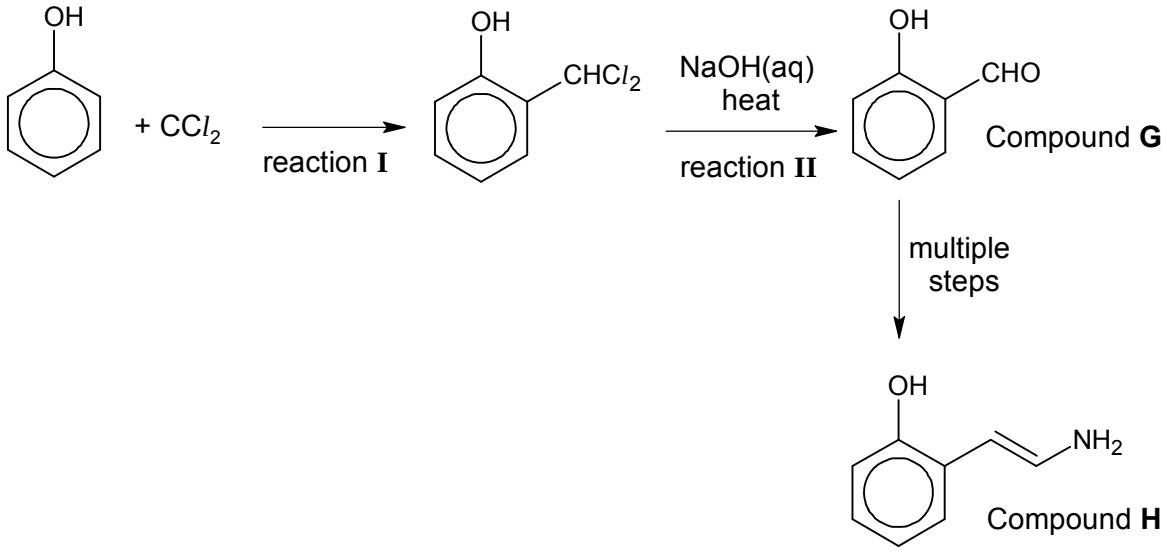
(d) Beryllium is very similar to aluminium in several ways.
State and explain whether beryllium oxide is acidic, basic or amphoteric.

[2]

[Total: 20]

5 Aqueous sodium hydroxide is an important reagent used in many chemical reactions whereby the hydroxide ion can either act as a base, or a nucleophile in organic synthesis.

(a) In the production of 2–hydroxybenzaldehyde (Compound **G**), phenol is heated with a reactive intermediate, CCl_2. $CHCl_3$ reacts with the hydroxide ions via neutralisation to produce the reactive intermediate. A typical synthetic route is shown below.

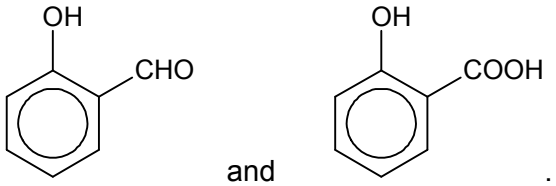


(i) Write the balanced equation for the formation of the reactive intermediate.

(ii) Explain why CCl_2 attacks phenol readily in reaction **I**.

(iii) Suggest an effective synthetic route (within 3 steps), with the reagents, conditions and intermediates clearly stated for each step, for the conversion of **G** to **H**.

(iv) State and explain the relative acid strength between



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[8]

(b) Besides being used as a favourable nucleophile in many organic syntheses, aqueous sodium hydroxide also reacts with halogens, for example chlorine, under different conditions to yield different products, typically NaC*l*O and $NaClO_3$.

(i) Write the balanced equation when chlorine is reacted with aqueous sodium hydroxide at 10 – 20 °C.

(ii) State the type of reaction that chlorine undergoes in **(i)**.

(iii) Draw the Lewis structure of ClO_3^- ion, giving its shape and bond angle.

(iv) Predict, with reasoning, the relative volatility of Cl_2 and I_2.

[6]

(c) Construct an energy cycle for the formation of solid NaC*l*O from its elements, using relevant data from the table below as well as from the *Data Booklet*. Hence calculate the lattice energy of NaC*l*O.

enthalpy term	**ΔH / kJ mol^{-1}**
standard enthalpy change of formation of NaC*l*O	–619
standard enthalpy change of atomisation of Na	+108
C*l*(g) + O(g) + $e^- \rightarrow$ C*l*O$^-$(g)	–181

[6]

[Total: 20]

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