Calculator Model / No.

Name ________________________ **Class:** ___________ **Reg Number:** ______

MERIDIAN JUNIOR COLLEGE

Preliminary Examination

Higher 2

Chemistry

9647

Paper 2 Structured Questions

10 September 2012
2 hours

Additional Materials: *Data Booklet*

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.
Write your calculator brand and model/number in the box provided above.

Answer **all** questions in the spaces provided on the question paper.
All working must be shown clearly.

INFORMATION FOR CANDIDATES

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

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

FOR EXAMINER'S USE	
Q1	**/ 12**
Q2	**/ 8**
Q3	**/ 12**
Q4	**/ 12**
Q5	**/ 9**
Q6	**/ 19**
Total	**/ 72**

This document consists of **21** printed pages and **1** blank page.

1 Planning (P)

(a) The **'solubility'** of a substance in aqueous solution is defined as the mass of anhydrous solid that will dissolve in and just saturate 100 g of water at a fixed temperature.

$$\textbf{'solubility'} = \frac{\text{mass of solid in a saturated solution}}{\text{mass of water in the saturated solution}} \times 100$$

- A solution that is saturated at a particular temperature is one in which no more solid may be dissolved.
- A saturated solution can be recognised by undissolved solid in equilibrium with aqueous solution.
- For example, a saturated solution of potassium chlorate(V) can be represented by the equilibrium:

$$KClO_3(s) \rightleftharpoons KClO_3(aq)$$

You are provided with solid potassium chlorate(V), $KClO_3$, and distilled water. In addition to the standard apparatus present in a laboratory you are provided with the following materials:

- evaporating basin
- measuring cylinders

(i) Use the information given above to plan an experiment to describe how you would prepare a saturated solution of potassium chlorate(V) at room temperature.

(ii) Hence, describe an experiment to determine the ‘**solubility**’ of the potassium chlorate(V) prepared in **(a)(i)**.

(iii) Create specimen results for your experiment and show how you would use these results to calculate the ‘**solubility**’ of potassium chlorate(V) at room temperature.

(iv) Identify a potential safety hazard in the experiment and state how you would minimise this risk.

[7]

(b) Sodium bromide crystallises as $NaBr.2H_2O$ at low temperatures and as NaBr at higher temperatures.

Temperature / ^{o}C	10	20	30	40	50	60	70	80	90	100
‘**Solubility**’ of sodium bromide /g per 100g H_2O	84.2	90.5	97.2	105.8	116.0	116.9	117.4	118.3	119.8	121.2

Plot the ‘**solubility**’ temperature data for sodium bromide and draw one line for the ‘**solubility**’ of $NaBr.2H_2O$ and another line for the ‘**solubility**’ of NaBr. Draw **two** separate lines and extrapolate them to a point of intersection. The line at higher temperatures represents the ‘**solubility**’ of NaBr. The line at lower temperatures represents the ‘**solubility**’ of $NaBr.2H_2O$.

[2]

(i) Read from the graph the temperature where the two lines intersect. This is the transition temperature.

Estimated transition temperature = ______________________

(ii) Describe the difference in the variation of '**solubility**' with temperature

- above the transition temperature,

- below the transition temperature.

The '**solubility**' curve represents equilibrium conditions between solid sodium bromide and dissolved sodium bromide.

The position of equilibrium can be influenced by temperature change and whether a change is exothermic or endothermic.

From the shape of your graph, comment on the likely enthalpy change for solid sodium bromide dissolving under equilibrium conditions. Explain your answer.

[3]
[Total: 12]

2 A ketene is an organic compound of the form RR'C=C=O.

Ketenes can be prepared from acyl chlorides.

$$RR'CHCOC\mathit{l} \xrightarrow{\text{base}} RR'C{=}C{=}O + HC\mathit{l}$$

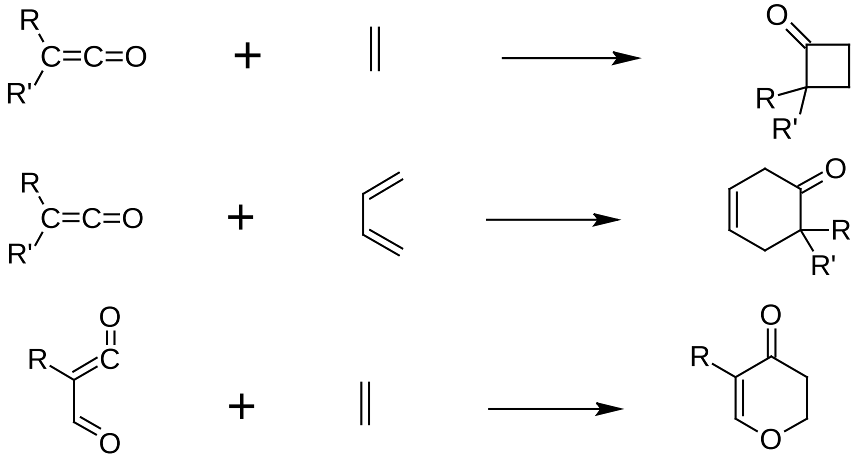
(a) Suggest the type of reaction that might occur during the preparation of ketenes from acyl chlorides.

[1]

Ketene is a reactive compound which readily undergoes addition reaction, for example

$$RR'C{=}C{=}O + H_2O \text{ ® } RR'CHCOOH$$

Ketenes also undergo cycloaddition reaction with unsaturated compounds to form four-membered or larger rings.



The simplest ketene is ethenone, $CH_2{=}C{=}O$, where R and R' are hydrogen atoms.

(b) **(i)** Describe the mechanism for the reaction between ethenone and water.

(ii) Ethenone reacts with ethanoic acid to give compound **R,** $C_4H_6O_3$, which reacts with phenylamine to give compound **S**, C_8H_9NO. Compound **S** yields phenylamine and sodium ethanoate with hot aqueous sodium hydroxide.

Suggest the structures of **R** and **S**.

R	**S**

(iii) Compound **T**, an ester, is formed when two molecules of ethenone react with one molecule of hydrogen cyanide.

$$2CH_2{=}C{=}O \;+\; HCN \;\text{®}\; \underset{\mathbf{T}}{C_5H_5NO_2}$$

Suggest a structure for the compound **T** using the given information on the addition and cycloaddition reactions of ketenes.

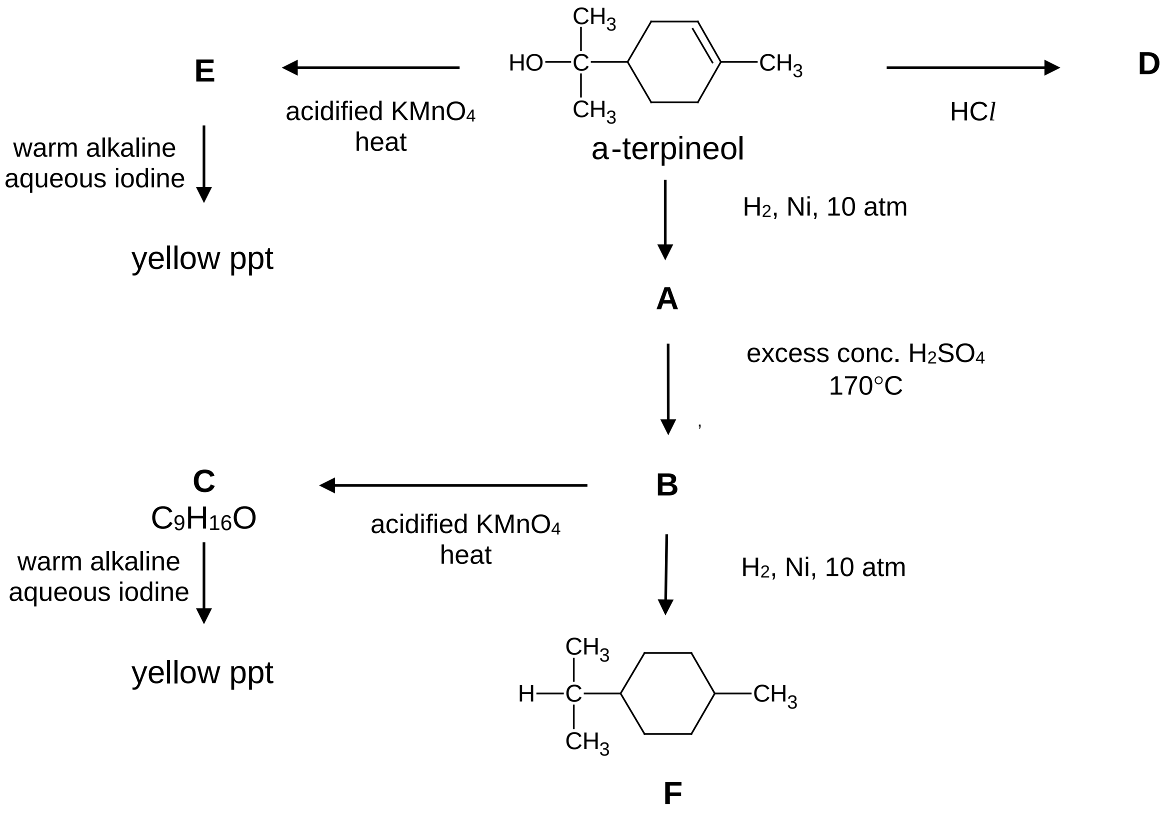
(iv) State the type of hybridisation and sketch the hybrid orbitals present at C-**1** in ethenone.

$$CH_2{=}\overset{\mathbf{1}}{C}{=}O$$

[7]
[Total: 8]

3 a-Terpineol, $C_{10}H_{18}O$, contains an alcoholic group which is not easily oxidised.

(a) Identify compounds **A** to **E** in the following reaction scheme.



A	**B**	**C**
D	**E**	

[3]

(b) The conversion of a-terpineol to compound **D** uses HC*l* as the reagent.

(i) Suggest how you prepare gaseous HC*l* in the laboratory using sodium chloride as one of the reactants.

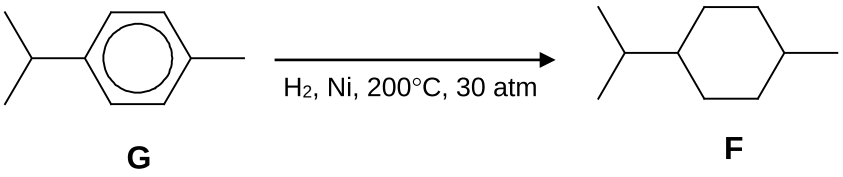
(ii) Explain, with aid of balanced equations, why small amounts of gaseous HI is produced when sodium iodide is used instead of sodium chloride in **(b)(i)**.

(iii) Gaseous HI can also be prepared by another two-step method. Firstly, iodine is directly combined with red phosphorous to form phosphorus triiodide. In the next step, water is added to phosphorus triiodide to form gaseous HI and H_3PO_3 as a by-product.

Write balanced equations for the reactions above.

[5]

(c) Compound **F** can also be formed by using compound **G**.



Suggest why compound **B** undergoes reduction with hydrogen over a nickel catalyst at room temperature and slight pressure, but compound **G** requires elevated temperature and pressure to form compound **F**.

[1]

(d) Compound **G** is oxidised by hot potassium manganate(VII) to form compound **H**, $C_8H_6O_4$.

(i) Draw the displayed formula of compound **H**.

(ii) Two isomers of compound **G** undergo oxidation with hot potassium manganate(VII) to give compound **H** in **(d)(i)**.

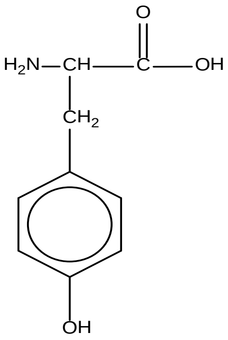
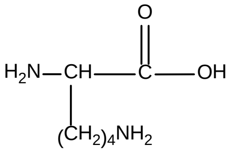
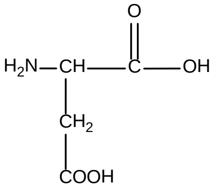
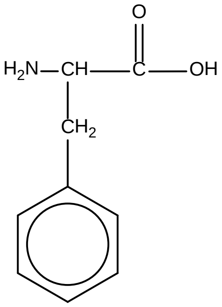
Suggest the structures of the two isomers.

[3]
[Total: 12]

4 (a) Electrophoresis can be used to separate amino acids produced by hydrolysing proteins. The amino acids are placed in a buffered solution in an electric field.

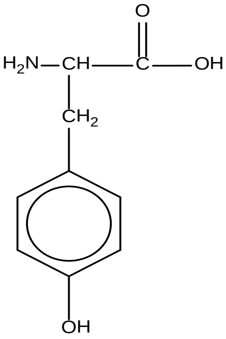
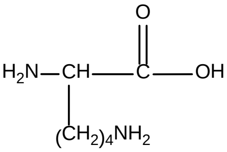
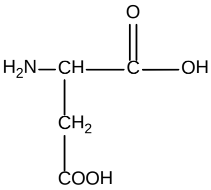
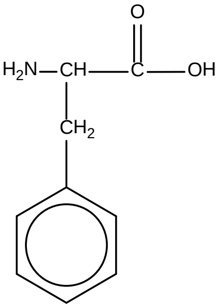
In an experiment, a spot of a solution containing a mixture of the 4 amino acids (tyr, lys, asp and phe) was placed in the middle of the plate in a buffered solution of pH 7. Following electrophoresis, the amino acids move to a new position under the influence of the electric charge.

Table 1: Amino acid data. This data is repeated on page 12.

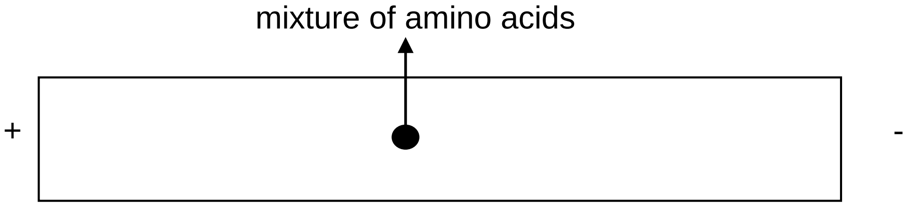
Amino acid	Tyrosine (tyr)	Lysine (lys)	Aspartic Acid (asp)	Phenylalanine (phe)
Isoelectric point	5.66	9.74	2.77	5.48
Structure				

(i) Draw the structure of tyrosine formed in the buffered solution of pH 7.

This data is repeated from page 11.

Amino acid	Tyrosine (tyr)	Lysine (lys)	Aspartic Acid (asp)	Phenylalanine (phe)
Isoelectric point	5.66	9.74	2.77	5.48
Structure		 $H_2N-CH((CH_2)_4NH_2)-C(=O)-OH$	 $H_2N-CH(CH_2COOH)-C(=O)-OH$	

Before electric current is applied



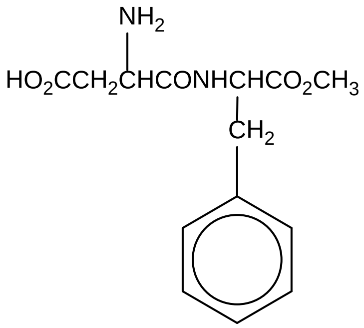
(ii) Using the information provided, indicate on the diagram below the new position of the 4 amino acids when an electric current is applied.

After electric current is applied

(iii) Explain the relative position of the tyrosine and aspartic acid after the electric current is applied.

[3]

(b) *Aspartame* is an artificial sweetener which is about 200 times sweeter than sucrose.



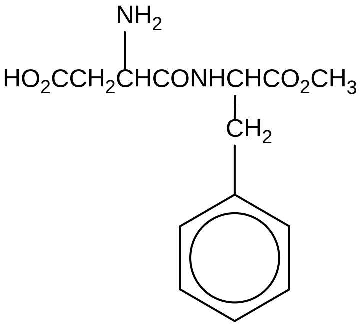
Aspartame

(i) *Aspartame* is a high melting point crystalline white solid.

Explain the bonding in this solid that accounts for the high melting point.

(ii) A disadvantage of using *aspartame* as a sweetener is that it undergoes a chemical reaction and breaks up at a fast rate in acidic soft drinks.

1 Suggest a possible reason for the breaking up of *aspartame* in soft drinks.



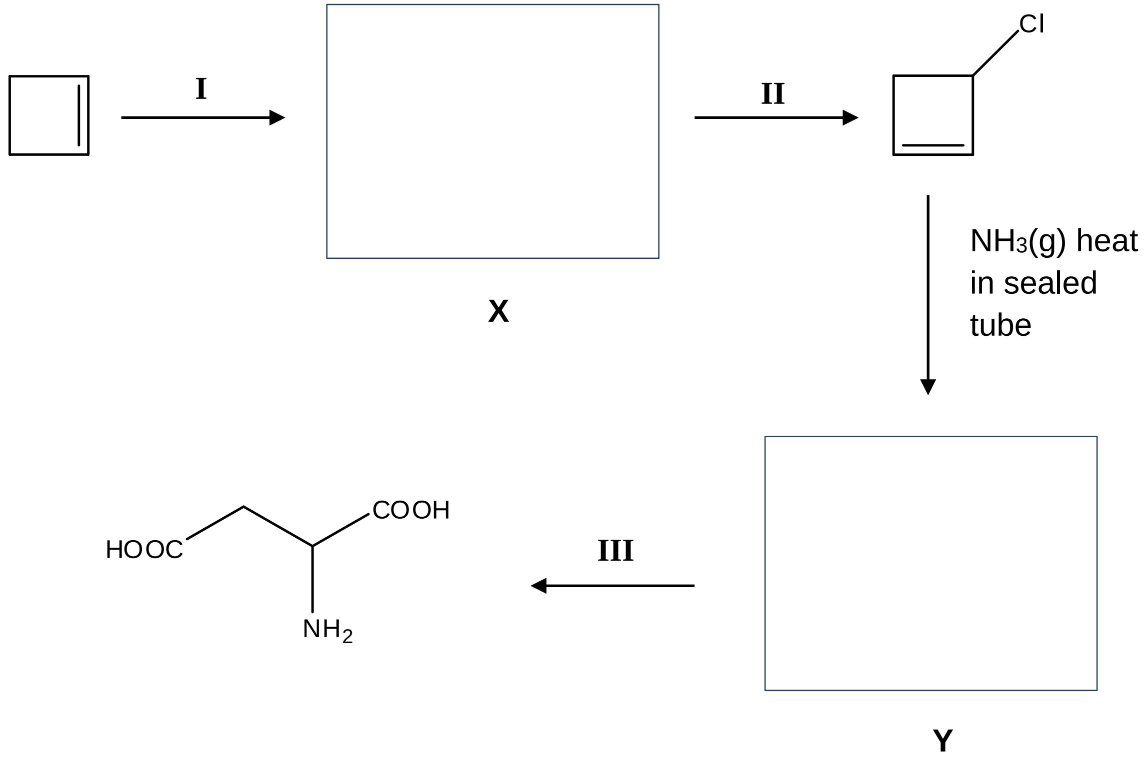
Aspartame

2 Hence, suggest the structure of all the organic products formed in the reaction.

[4]

(c) One possible synthesis route of aspartic acid is shown below.

Identify structures **X** and **Y,** and suggest the reagent(s) and conditions for steps **I**, **II** and **III**.



Step	Reagent(s) and conditions
I	
II	
III	

[5]
[Total: 12]

5 *Tris* is an abbreviation for tris(hydroxymethyl)aminomethane with the formula $(HOCH_2)_3CNH_2$. In biochemistry, *Tris* is widely used as a component of buffer solutions especially for solutions of nucleic acids.

(a) Describe and explain why the basicity of *Tris* differs from that of *tert*-butylamine, $(CH_3)_3CNH_2$.

[2]

(b) A solution containing *Tris* and *Tris-Hydrochloride*, $(HOCH_2)_3CNH_3^+Cl^-$ can resist pH changes on addition of small amounts of acid and base.

Write two relevant equations to illustrate how this occurs.

[2]

(c) Calculate the final pH, at 298 K, after a 5.00 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added separately to

(i) 100 cm^3 of 1.00×10^{-4} mol dm^{-3} sodium hydroxide solution.

(ii) 100 cm^3 of solution **X** that contains 0. 200 mol dm^{-3} *Tris*, $(HOCH_2)_3CNH_2$, and 0.200 mol dm^{-3} *Tris-Hydrochloride*, $(HOCH_2)_3CNH_3^+Cl^-$.
(Given that pK_b for *Tris* is 5.93 at 298 K)

[4]

(d) Solution **Y** contains 1.00 mol dm^{-3} *Tris*, $(HOCH_2)_3CNH_2$, and 1.00 mol dm^{-3} *Tris-Hydrochloride*, $(HOCH_2)_3CNH_3^+Cl^-$.

State which solution, **X** or **Y**, has a larger buffering capacity and explain why.

[1]
[Total: 9]

6 Iron is the most common element (by mass) on Earth. It exists in a wide range of oxidation states, although +2 and +3 are the most common states.

The chemical equation below shows the reaction of chlorine gas and iron(II) ion.

$$Cl_2(g) + 2Fe^{2+}(aq) \longrightarrow 2Cl^-(aq) + 2Fe^{3+}(aq)$$

(a) **(i)** Draw a diagram to show the apparatus needed to measure the $E^{\ominus}_{cell}$ for the above reaction. Label the chemicals and concentration of the chemicals used in the diagram. Indicate the direction of the electron flow.

(ii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this reaction.

[5]

(b) On the other hand, ruthenium is a rare transition metal with oxidation states ranging from 0 to +8. The most common oxidation states are also +2 and +3.

The standard electrode potentials for Ru(III)/Ru(II) and Fe(III)/Fe(II) are given below.

$$[Ru(H_2O)_6]^{3+} + e^- \rightleftharpoons [Ru(H_2O)_6]^{2+} \qquad E^\ominus = +0.23\text{ V}$$

$$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+} \qquad E^\ominus = +0.77\text{ V}$$

Comment on the relative stability of the +2 and +3 oxidation state of ruthenium compared to that of iron using the data above.

[1]

(c) When ruthenium(III) ions are treated with aqueous ammonia, an aqueous complex **A** is formed. Zinc is added to complex **A** and the resulting solution is treated with NaC*l*. Orange crystals of compound **B** are formed which contains 37% of ruthenium by mass.

(i) Suggest a formula for complex **A** and compound **B**.

Complex **A** ……………………….. Compound **B** ………………………..

(ii) Aqueous ammonia is added to iron(III) chloride solution. The resulting mixture is treated with Zn metal to form compound **C**. Using the *Data Booklet*, suggest with reasoning the identity of compound **C**.

[4]

The following table lists some iron complexes together with their colours and their equilibrium constants, K_c.

Complex	**Colour**	K_c
$[Fe(SCN)(H_2O)_5]^{2+}(aq)$	Deep red	1×10^{2}
$[FeF_6]^{3-}$ (aq)	Colourless	2×10^{15}
$[Fe(CN)_6]^{4-}$ (aq)	Pale yellow	1×10^{24}
$[Fe(CN)_6]^{3-}$ (aq)	Orange	1×10^{31}
$[Fe(edta)]^{2-}$ (aq)	Colourless	2×10^{14}
$[Fe(edta)]^{-}$ (aq)	Yellow	1×10^{25}

[edta = $(^{-}O_2CCH_2)_2NCH_2CH_2N(CH_2COO_2^{-})_2$]

(d) Write down the equation for the formation of the complex ion formed when Fe^{3+} is mixed with F^- ions.

[1]

(e) Write an expression for the equilibrium constant, K_c, of $[FeF_6]^{3-}$.

[1]

(f) Use the data in the table to predict and explain:

(i) the effect of adding edta **on the colour** of a solution containing $[Fe(SCN)(H_2O)_5]^{2+}$,

(ii) the effect of adding edta **on the $E^\ominus$ value** for the $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ system.

[4]

(g) Explain why $[Fe(CN)_6]^{3-}$ is orange in colour.

[3]
[Total: 19]

End of paper