RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME									
CLASS	6								
CENTRE NUMBER	S					INDEX NUMBER				

H2 CHEMISTRY 9647/03

Paper 3 Free Response

16 September 2013

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of 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.
Begin each question on a fresh sheet of paper.
A Data Booklet is provided. Do not write anything on it.
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 together, with the cover page on top.

This document consists of **11** printed pages and **1** blank page.

Answer any **four** questions.

1 **(a)** **Orthocaine**, $C_8H_9O_3N$, is a local anaesthetic that causes temporary loss of pain.

Orthocaine:

- rapidly decolourises aqueous bromine to give **A**, $C_8H_6O_3NBr_3$.
- gives a violet colouration on addition of neutral $FeCl_3$ (aq).
- dissolves in NaOH(aq) to give **B**, $NaC_8H_8O_3N$.
- reacts with HCl(aq) to give a positively-charged ion **C**, $C_8H_{10}O_3N$.
- reacts in the presence of hot acidified $KMnO_4$(aq) to release a colourless gas that gives a white precipitate with limewater.

Suggest the structures of **orthocaine** and **A** – **C**, explaining your reasoning. [9]

(b) N_2O, commonly known as laughing gas, is used in surgery and dentistry for its anaesthetic effect. Other than N_2O, other oxides of nitrogen include NO_2 and NO.

NO_2 can be formed from NO as shown below:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Three experiments were carried out to find the relationships between the initial concentrations of NO and of O_2 and the initial rate of formation of NO_2.

Experiment	Initial [NO] / mol dm^{-3}	Initial [O_2] / mol dm^{-3}	Initial rate of formation of NO_2 / mol dm^{-3} s^{-1}
1	0.001	0.002	1.40×10^{-5}
2	0.002	0.003	8.40×10^{-5}
3	0.003	0.003	1.89×10^{-4}

(i) Determine with reasoning, the order of reaction with respect to each of the reactants and the rate constant, *k*, stating its units.

(ii) Calculate the initial rate of depletion of O_2 when [NO] = 0.002 mol dm^{-3} and [O_2] = 0.002 mol dm^{-3}. [5]

(c) NO_2 can react with water to form nitric acid, HNO_3. Given that all the silver salts as shown below are sparingly soluble in water, explain the following statement, using Le Chatelier's principle. Include equation(s) when possible.

AgC*l* & AgBr does not dissolve when nitric acid is added whereas CH_3COOAg dissolves readily when nitric acid is added.

[3]

(d) AgC*l* is a sparingly soluble salt and has a solubility value of 1.30×10^{-5} mol dm^{-3}. To a 2.0 dm^3 of saturated solution of AgC*l*, 0.025 g of $AgNO_3$(s) was added. Calculate the mass of precipitate formed. [3]

[Total: 20]

2 **(a)** Instant cold packs are a common direct replacement for crushed ice used as first aid on sports injuries. An instant cold pack consists of two bags; one containing water, placed inside another bag containing ammonium nitrate crystals, NH_4NO_3(s). When the package is squeezed, the inner bag of water is broken and allowed to dissolve the ammonium nitrate.

(i) Define the term *enthalpy change of solution*.

(ii) Given that the enthalpy change of hydration of ammonium ions and nitrate ions are –132 kJ mol^{-1} and –207 kJ mol^{-1} respectively and the lattice energy of ammonium nitrate is –365 kJ mol^{-1}, construct an energy cycle and find the ΔH_{soln} of the reaction.

(iii) In terms of structure and bonding, explain why ammonium nitrate gets cold spontaneously when dissolved in water.

(iv) The entropies of NH_4NO_3(s), ammonium and nitrate ions are given as such:

Species	S / J mol^{-1} K^{-1}
Ammonium nitrate	151
Ammonium ions	186
Nitrate ions	256

Calculate the range of temperatures that the instant cold pack will work. [7]

(b) Solid ammonium nitrate is commonly used to prepare nitrous oxide, N_2O with water as a by-product via decomposition when heated.

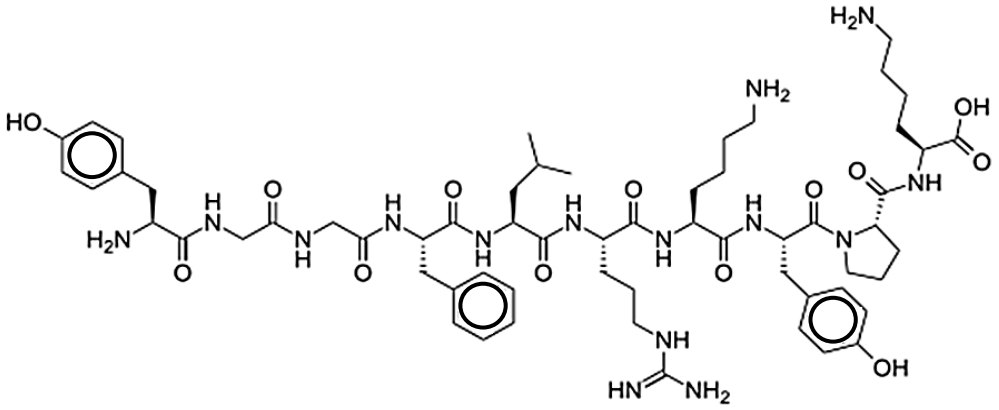
(i) Using the data provided below as well as your answer to **a(ii)**, find the enthalpy change of reaction for the production of nitrous oxide from ammonium nitrate.

	ΔH_f / kJ mol^{-1}
H_2O (*l*)	–285.8
HNO_3 (aq)	–174.1
N_2O (g)	+81.6
NH_3 (aq)	–80.8

NH_3 (aq) + HNO_3 (aq) → NH_4NO_3 (aq) ΔH_r = –57.0 kJ mol^{-1}

(ii) Draw the dot-and-cross diagram for nitrous oxide. [4]

(c) Nitrous oxide is used commercially as a mixture with oxygen gas and marketed as Entonox, which is a medical anesthesia gas used in normal childbirth. Endorphins are released upon inhalation of Entonox, producing a feeling of wellbeing. The structure of an endorphin, which is a peptide, is shown below. Under certain conditions, denaturation of a peptide can occur.



(i) What is meant by the term *denaturation*?

(ii) Suggest how pH changes can denature endorphins.

(iii) How many different amino acid residues are present in an endorphin peptide structure? [4]

(d) Another use of nitrous oxide is in the commercial preparation of sodium azide, NaN_3. Sodium azide is in turn used in air-bags put into automobiles. Upon severe impact, a detonator cap is ignited and causes sodium azide to decompose explosively according to the equation below and filling the air-bag:

$$2NaN_3(s) \rightarrow Na(s) + 3N_2(g)$$

(i) Draw and name the shape of the azide ion, N_3^-.

(ii) If 2.0 moles of NaN_3 is detonated, what volume of gas is produced under standard conditions?

(ii) A person driving a car with an air-bag system installed met with an accident at the top of the mountain where the atmospheric pressure is 0.8 atm and the temperature is -10 °C.

Will the air-bag containing 2.0 moles of NaN_3 inflate to the same volume as compared to the bag inflated under standard conditions? State any assumptions used in your evaluation. [5]

[Total: 20]

3 Poly(tetrafluoroethene) is a polymer used as a coating in non-stick kitchen utensils and for replacement bone joints. One of the stages in the manufacture of the polymer is

$$\text{Equilibrium 1:} \quad 2CHClF_2(g) = C_2F_4(g) + 2HCl(g)$$

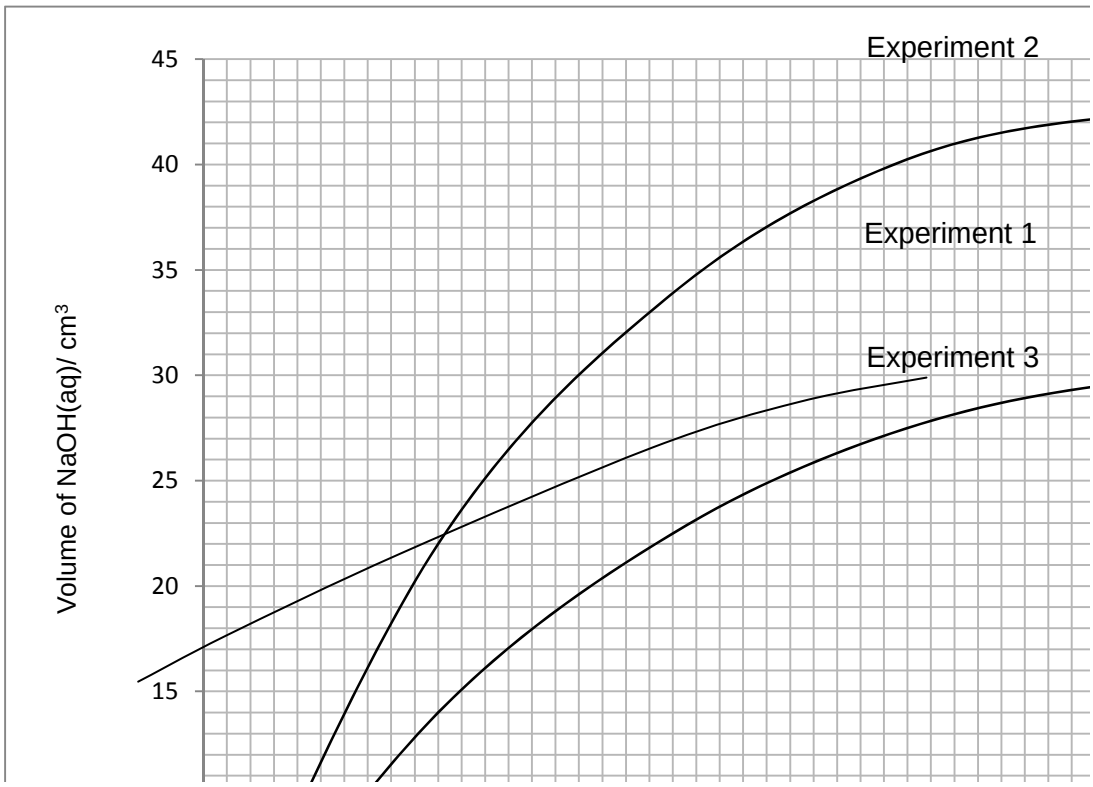
The progress of this reaction was monitored by sampling method as described below.

After a fixed concentration of $CHClF_2(g)$ is left to react in a sealed reactor at fixed temperature and pressure, 5.00 cm^3 of the resultant mixture is drawn at regular time interval. Each gas sample is quickly bubbled in 25.0 cm^3 of water and the solution formed is titrated with 0.100 mol dm^{-3} NaOH solution.

Three similar experiments were conducted in different conditions:

Experiment	$[CHClF_2(g)]$ / mol dm^{-3}	Temperature / K
1	1.00	373
2	1.00	423
3	0.500	423

The results of the three experiments are shown graphically.



Use these data where applicable in (a) and (b).

(a) **(i)** Calculate the equilibrium concentration of HC*l*, C_2F_4 and CHC*l*F_2 at 373K.

(ii) Write an expression for the equilibrium constant, K_c, and calculate its value at 373K.

(iii) Deduce whether the forward reaction is endothermic or exothermic. Explain your deduction. [6]

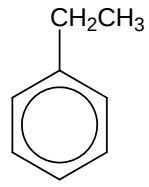
(b) **(i)** Suggest and justify how the rate of forward reaction can be determined from the graphs provided.

(ii) Using the data from relevant experiments, deduce the order of forward reaction with respect to CHC*l*F_2(g).

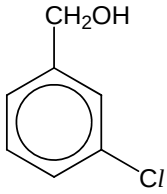
(iii) A study using Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry reveals that difluorocarbene (CF_2) is the only reactive intermediate formed in the forward reaction.

Propose a two steps mechanism and state which is the slower step. [6]

(c) Ethylbenzene is used to synthesize (3-chlorophenyl)methanol which is used as a general solvent for inks, pants, lacquers, epoxy resin coatings and as a degreasing agent.



ethylbenzene



(3-chlorophenyl)methanol

(i) Describe the reagents and conditions required to convert ethylbenzene into (3-chlorophenyl)methanol in three steps. Give the structure of all the intermediates.

(ii) Name and describe the mechanism for the reaction that introduces the chlorine atom into the benzene ring in **(c)(i)**. [8]

[Total: 20]

4 **(a)** *Use of the Data Booklet is relevant in this question*

When nickel metal is added to a solution of iron(II)chloride, there is no visible change.

When excess aqueous ammonia is added to the above mixture, a green ppt of $Fe(OH)_2(s)$ is initially formed. This green ppt dissolves slowly, and a grey ppt in a pale blue solution is formed.

(i) Write an equation to illustrate how this green precipitate is sparingly soluble in water.

(ii) By selecting appropriate E' values from the *Data Booklet*, explain

I. why there is no observable change when nickel is added to iron(II)chloride.

II. the chemical changes that occur when excess aqueous ammonia is added to the mixture.

(iii) Suggest the identities of the grey precipitate and the pale blue solution. [8]

(b) Stability constant, K_s, is a type of equilibrium constant which describes the ligand displacement in a solution. For the following complex formation:

$[Fe(H_2O)_6]^{2+}(aq) + 3(en)\ (aq) \rightarrow [Fe(en)_3]^{2+}(aq) + 6H_2O(l)$

$$K_s = \frac{[Fe(en)_3^{2+}]}{[Fe(H_2O)_6^{2+}][en]^3}$$

This K_s have a numerical value of 5.00×10^9.

(i) Explain in terms of entropy and free energy, why this ligand displacement reaction is considered favourable.

(ii) Given that the numerical value of K_{sp} of $Fe(OH)_2$ is 1.80×10^{-15}, calculate the maximum $[Fe^{2+}]$ when $Fe(OH)_2(s)$ is dissolved in water.

(iii) Solution **A** is produced by dissolving **y** grams of $Fe(OH)_2(s)$ into a $1dm^3$ of 0.500 mol dm^{-3} of ethane-1,2-diamine solution.

At equilibrium, solution **A** contained the following:

Compound	Concentration/ mol dm^{-3}
$[Fe(en)_3]^{2+}$	0.117
(en)	0.149
$[Fe(H_2O)_6]^{2+}$	**x**

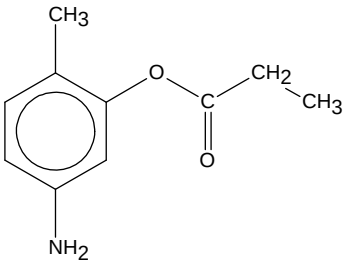
Calculate the value of **x** and **y**.

(iv) Using your answers from **(ii)** and **(iii)**, explain why all of **y** grams of $Fe(OH)_2(s)$ is able to dissolve in the solution. [8]

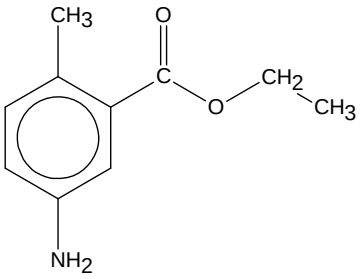
(c) Suggest simple chemical test to distinguish the following pairs of compounds.

Include reagents and conditions, as well as any expected observations.

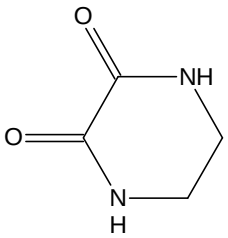
(i) **P**:



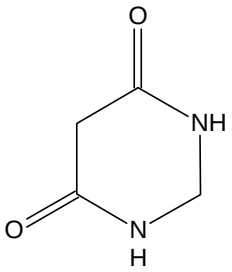
Q:



(ii) **R**:



S:

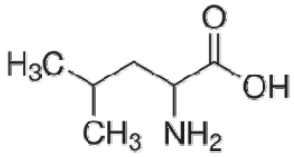


[4]

[Total: 20]

5 **(a)** Proteins are essential for life in all living things and have many biological functions in our bodies. The building blocks of proteins are amino acids, such as leucine and glutamine.

Leucine, $C_6H_{13}NO_2$, an essential amino acid, is found in legumes such as peas, soybeans and animal products such as beef and fish.



leucine

(i) The two pK_a values associated with leucine are given in the following table.

	pK_a
α-carboxyl	2.33
α-amino	9.74

Draw the structural formula of the predominant ionic species present at pH 2 and pH 10.

(ii) With the aid of equations, explain how the zwitterionic form of leucine behaves as a buffer when a small amount of base is added.

(iii) Sketch the pH against volume curve when 30.0 cm^3 of KOH is added to 10.0 cm^3 of the *protonated* form of leucine of the same concentration.

Show clearly on your curve where the two pK_a values and equivalence volumes occur.

(iv) Calculate the change in pH when 5.00 cm^3 of 0.0300 mol dm^{-3} HC*l* is added to 10.0 cm^3 of 0.150 mol dm^{-3} leucine at pH 2.33.

You may use HA and A^- to represent the acid and conjugate base respectively. [9]

(b) Many proteins contain significant amounts of secondary structures as α-helix structures or β-pleated sheets.

(i) What is meant by the *secondary structure of a protein*?

(ii) Draw a diagram with displayed formula, showing two strands of a β-pleated sheet structure and indicating any type of interactions present between the two strands. Use the general [4]

formula of a primary structure as shown below.

–NHCHRCONHCHRCO–

(c) The Group VII elements are also known as the halogens.

(i) When bromine is added to aqueous sodium thiosulfate, $Na_2S_2O_3$, followed by the addition of aqueous barium chloride, a white precipitate is formed. Identify the white precipitate.

(ii) Using your answer in **(c)(i)**, write an ionic equation to represent the reaction between bromine and thiosulfate ions.

(iii) No white precipitate is formed when the same experiment in **(c)(i)** is repeated with aqueous iodine instead of bromine. Write an ionic equation for the reaction between iodine and thiosulfate ions.

(iv) Quoting suitable data from the *Data Booklet* and your answers in **(c)(ii)** and **(c)(iii)**, explain the difference in the reactions of the two halogens with thiosulfate ions.

(v) When limited cold aqueous sodium hydroxide is added to a yellow solution of chlorine in tetrachloromethane and shaken together, two immiscible layers are observed.

Draw a diagram to show the relative positions of the two immiscible layers. Clearly identify the species present in each layer.

(Density of tetrachloromethane = 1.59 g cm^{-3}; density of water = 1.00 g cm^{-3}) [7]

[Total: 20]

- END OF PAPER -