

SERANGOON JUNIOR COLLEGE General Certificate of Education Advanced Level Higher 2

CANDIDATE NAME		
CLASS]	

CHEMISTRY

Preliminary Examination Paper 3 Free Response Questions

27 Aug 2013 2 hours

9647/03

Additional Materials: Data Booklet, Cover Page Writing Papers

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 work. Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

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 the brackets [] at the end of each question or part question.

Start each question on a fresh piece of paper.

At the end of the examination, fasten all your work securely together with the cover page provided and ensure your script is arranged in an orderly manner.

- (a) One example of a highly reactive phosphorus-containing ion is phosphonium, PH_4^+ .
 - (i) Write a balanced chemical equation for the reaction between phosphonium iodide and potassium hydroxide to form phosphine, PH_3 .
 - (ii) Hence, suggest a suitable method of measuring the rate of reaction.
 - (iii) Draw a 'dot-and-cross' diagram showing the electrons (outer shells only) in the phosphonium ion, and use the VSEPR (valence shell electron pair repulsion) theory to predict its shape.

You may find both a written description and a 3-dimensional sketch useful in your answer.

(iv) The bond angle in ammonia is 107.8° .

Predict the H - P - H bond angle in phosphine and justify your answer.

[7]

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(b) Although phosphorus is present in numerous harmful chemicals, it is a useful feature in organophosphorus compounds. Ylides are a class of organophosphorus compounds that are well-known for their role in the Wittig reaction. The synthesis of methylpropene via the Wittig reaction is shown below.



- (i) Name the type of reaction that occurs in step ${\bf I}$ and outline the mechanism for the reaction.
- (ii) Suggest why 2-bromo-2-methylpropane is not preferred in step I.
- (iii) State the role of butyl lithium, C_4H_9Li , in step II.

[5]

(c) Two resonance structures exist to stabilise the ylide used in step III above.



In this step, tetrahydrofuran, THF, is used as an aprotic solvent – one that lacks an acidic hydrogen.

- (i) Explain why, unlike phosphorus, nitrogen cannot form organic compounds similar to ylides.
- (ii) Explain why THF is a suitable solvent to employ in step III whereas water is not.

[4]

(d) β-carotene is a food colouring that can be extracted from the pigmentation found in red-orange plants and fruits such as carrots. It can be synthesised using excess of an aldehyde and a diylide, a compound with two equivalents of phosphorus in its structure.



 β -carotene

Suggest the structures of the **aldehyde** and a symmetrical **diylide** with 6 stereoisomers that can be used to produce β -carotene. [2]

(e) Compounds X and Y are isomers that can undergo the Wittig reaction with the following ylide.



The products formed have the same molecular formula, C_7H_{14} , but only the product formed from **X** displays stereoisomerism. **X** and **Y** both do not react with ammonical silver nitrate.

Draw the structures of **X** and **Y**.

[2] [Total : 20] 2 (a) **Deuterium** (symbol **D** or $_{1}^{2}$ H) was discovered in 1931. Deuterium accounts for approximately 0.0156% of all the naturally occurring hydrogen in the oceans, while the most common isotope (hydrogen-1) accounts for more than 99.98%.

Chemically, deuterium behaves similarly to ordinary hydrogen.

(i) On the same diagram, sketch how a beam of singly positively-charged deuterium ions and a beam of hydrogen ions will behave in an electric field.

In your diagram, indicate clearly the angle of deflection for each beam.

- (ii) Suggest the difference in the melting point and thermal stability of DC*l*, DBr and DI.
- (iii) Chloride and iodide ions are known to react differently with concentrated deuterium sulfate, D₂SO₄.

For the reaction involving iodide, it was observed that the yield of DI was significantly lower as compared to the yield of DC*l* for the reaction using chloride. It was also noted that a foul rotten egg smell was detected for the reaction involving the iodide.

With reference to the *Data Booklet* and with the aid of equations, explain the above mentioned observations.

[10]

(b) Deuterium can replace the normal hydrogen in water molecules to form heavy water, D₂O. This difference increases the strength of water's hydrogen-oxygen bonds which makes it more difficult to undergo electrolysis.

Property	D ₂ O	H₂O
	(Heavy water)	(Light water)
Freezing point (°C)	3.82	0.00
Boiling point (°C)	101.4	100.0
Density at standard	1.1056	0.9982
condition (g/mL)		

Some data between light water and heavy water are given below.

Heavy water and light water can be tested using their freezing points and boiling points.

Suggest with reasoning, how a scientist can deploy another **physical** method to differentiate the two types of water without the use of a temperature measuring device.

[2]

- (c) During World War II, German scientists were known to conduct experiments using heavy water.
 - (i) With reference to the data given below, determine why it is more difficult for heavy water, D₂O, to undergo electrolysis.

Bond type	Bond length (m)
C <i>l</i> –C <i>l</i>	1.76 x 10 ⁻¹⁰
D–Cl	1.27 x 10 ^{−10}
H–Cl	1.29 x 10 ⁻¹⁰

(ii) Heavy water is processed via electrolysis using a **concentrated** potassium hydroxide-light water mixture.

During the process, oxygen gas is produced at the anode and hydrogen gas is produced at the cathode.

Write ion-electron half equations at the respective electrodes and suggest how heavy water can be obtained from the mixture.

(iii) Suggest why distillation is not effective as the initial stage in separating heavy water from the potassium hydroxide-light water mixture.

[8]

[Total : 20]

3 Chlorine is often used as a disinfectant in swimming pools to remove organic molecules and pathogens. The disinfecting action is due to the presence of hypochlorous acid, HC/O, and chlorate(I) ion, OC*l*⁻ formed by the reaction of chlorine with water.

6

 $Cl_2(aq) + H_2O(l) \rightleftharpoons HClO(aq) + H^+(aq) + Cl^-(aq) --- (1)$

Hypochlorous acid ionises as a weak acid with dissociation constant of 3 x 10⁻⁸ moldm⁻³.

$$HC/O(aq) \rightleftharpoons H^+(aq) + OC\Gamma(aq) --- (2)$$

The hypochlorous acid and chlorate(I) ions make up 'free available chlorine' (FAC). When chlorine is added, FAC combines with the contaminants in the pool, called combined available chlorine (CAC). The total available chlorine (TAC) is the sum of free available chlorine (FAC) and combined available chlorine (CAC).

It is undesirable when CAC exceeds 0.2 ppm as chloroamines are produced. The removal of chloroamines, known as breakpoint chlorination, is achieved by adding appropriate amount of sodium hypochlorite, NaOC*l*, as follows:

Gallons of sodium hypochlorite needed to reach breakpoint chlorination = $\frac{\text{pool volume (in gallons) x 8.3 x combined available chlorine(ppm) x 1.0 x 10}{1\ 000\ 000}$

- (a) Sodium hypochlorite (NaOC*l*) is a compound that can be effectively used for water purification. It can be readily made with the use of caustic soda, NaOH and chlorine, at cold temperatures.
 - (i) With the aid of a chemical equation, suggest what complication can be avoided when this process is carried out in cold temperatures.
 - (ii) Using the data above, calculate the number of gallons of sodium hypochlorite needed to reach breakpoint chlorination for a 120, 000 gallon pool given that TAC = 1.5 ppm and FAC = 0.7 ppm respectively.

Leave your answer in two significant figures.

[4]

- (b) pH control is essential in the maintenance of the pool water and it was found that it should be maintained at an optimum pH of 7.4. When sodium hypochlorite is added to swimming pool, it increases the pH and often, acid is added to regulate it to the optimum pH.
 - (i) Using the equations and any relevant information from the question, comment on why pool waters have to be maintained at a pH of 7.4.

[You may consider the use of Le Chatelier's Principle in your explanation.]

- (ii) Calculate that the ratio of the concentration of OC*l*[−] to HC*l*O when the pH of the pool is 8.0.
- (iii) Using your ratio found in (c)(ii) and taking the concentration of HOC*l* to be x mol dm⁻³, what is the mass of HC*l* that should be added to 1 dm³ of swimming pool water so that the pH can be brought back down to the optimum pH of 7.4. Leave your answer in terms of x. [7]

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- (c) Disinfection by chlorination can be detrimental to health as chlorine can react with naturally occurring organic compounds found in the pool to produce disinfection byproducts (DBPs). The most common DBPs are trihalomethanes (THMs).
 - (i) State the type of reaction and the condition that optimises the formation of THMs.
 - (ii) Outline **only** the propagation step in the formation of trichloromethane, a type of THM.
 - (iii) The selectivity of the radical reactions can be predicted mathematically based on a combination of an experimentally determined reactivity factor, R_{i} , and a statistical factor, nH_{i} .

In order to use the equation shown below, we need to look at our original alkane and look at each H in turn to see what product it would give if it were to be substituted.

The following formula and data can be used effectively to determine the percentage yield of substituted halogenoalkanes for methane.

$\%P_i = \frac{100 \times nH_i \times R_i}{20}$		Reactivit	y factors,
		Br	Cl
where %P _i = % yield of product 'i' nH_i = number of H of type 'i' R_i = reactivity factor for type 'i'	Methyl / 1°	1	1
	2°	82	3.9
	3°	1640	5.2

Using the information provided, deduce which is the predominant species when methane undergoes free radical substitution with excess chlorine gas.

(iv) Suggest a property of chlorine that allows it to act as a disinfectant in swimming pools.

[6]

(d) Chlorine stabilisers such as cyanuric acid are typically added to pools in hot climates where the sun oxidises most of the chlorine in the pool, rendering it useless.

Cyanuric acid (relative molecular mass of 129) is found to have the following composition by mass:

- (i) Determine the molecular formula of cyanuric acid.
- (ii) Suggest a possible displayed structure of cyanuric acid.

[3]

[Total : 20]

4 Chromium is a transition element and is used widely industrially as it can exist in variable oxidation states. In particular, oxides of chromium are useful precursors in many chemical reactions.



- (a) Define the term *transition element* and suggest why chromium can exist in *variable oxidation states*.
- (b) 'X is amphoteric yet insoluble in water'

With balanced chemical equations, including state symbols, explain the *italicised* term and suggest why **X** is insoluble in water. [4]

(c) In reaction I, an exothermic reaction is initiated when ammonium dichromate(VI) is heated. Two colourless and odourless gases are evolved leaving only solid residue X, a grey-green powder

By using oxidation numbers, and showing all your working, identify the two gases evolved and construct a balanced equation for the decomposition.

[3]

- (d) In reaction II, sulfur is added to the reaction. X and a sulfur-containing product with the oxidation state +6 is formed.
 - (i) Suggest the role of sulfur.
 - (ii) Write a balanced ionic equation, including state symbols, to illustrate reaction II.

[2]

8

[2]

- (e) In reaction III, the extraction of chromium involves a thermite reaction of X with aluminium, which is a displacement reaction.
 - (i) Write a thermochemical equation for the Thermite reaction.
 - (ii) By quoting and using relevant E[⊕] values from the *Data Booklet*, explain why the extracted chromium metal dissolves in dilute sulfuric acid to give a blue solution but turns green **slowly** even in the absence of air.

[5]

(f) In reaction IV, describe and explain what happens when warm aqueous sodium hydroxide is added to aqueous ammonium dichromate(VI) solution.

You should include suitable observations and balanced equations for any reaction that occur.

[4]

[Total : 20]

- 5 Haemoglobin in the blood carries oxygen from the respiratory organs to the rest of the body (i.e. the tissues) where it releases the oxygen to burn nutrients to provide energy to power the functions of the organism, and collects the resultant carbon dioxide to bring it back to the respiratory organs to be dispensed from the organism.
 - (a) With reference to the haemoglobin (Hb) molecule, describe what is meant by the term *quaternary structure of proteins*.

[2]

(b) One molecule of haemoglobin can bind up to four molecules of oxygen, according to the following equation.

Hb (aq) + $4O_2$ (aq) \square Hb(O_2)₄ (aq) -----(1)

Carbon monoxide reacts with haemoglobin in the same way as oxygen.

Hb (aq) + CO (aq) \square HbCO (aq) -----(2)

- (i) Briefly explain how a haemoglobin molecule carries oxygen and why carbon monoxide is toxic to the human body.
- (ii) Write an expression for K_c for reaction 1, stating its units.
- (iii) Experiments have shown that when the concentration of O_2 (aq) is 7.6 x 10⁻⁶ mol dm⁻³, the concentrations of Hb and Hb(O_2)₄ are equal.

Use this information to calculate a value of K_c .

- (iv) Use your value of K_c in (b)(iii) to calculate the percentage of Hb converted to Hb(O₂)₄ when the concentration of O₂ (aq) is increased to 2.40 x 10⁻⁵ mol dm⁻³.
- (v) Briefly explain how a haemoglobin molecule carries oxygen and why carbon monoxide is toxic to the human body as shown in equation 2.

[8]

(c) In the formation of haemoglobin, the primary structures of the polypeptide chains of haemoglobin are first formed from their constituent amino acids, eg lysine, serine and alanine.

 $\begin{array}{ccccccc} H_2N-CH-COOH & H_2N-CH-COOH & H_2N-CH-COOH \\ & & & & & \\ CH_3 & & CH_2OH & (CH_2)_4NH_2 \end{array}$

	Alanine (ala)	Serine (ser)	Lysine (lys)
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In the presence of haem groups, these polypeptide chains spontaneously coalesce into a haemoglobin molecule. By considering the chemical interactions involved at each step, suggest what the signs of ΔG , ΔH and ΔS would be for the overall process. Explain your reasoning.

[3]

(d) Proteins can be denatured using heavy metals ions such as Fe³⁺ (aq). Explain how this denaturation occurs.

[1]

(e) The stability constant, K_{stab} , is an equilibrium constant for equilibrium that exists between a transition metal ion surrounded by water molecule ligands and the same transition metal ion surrounded by the ligands of another kind in a ligand displacement reaction.

Complex formed	$K_{\rm stab}$ of complex	Colour
[Fe(H ₂ O) ₅ (SCN)] ²⁺	9.17 x 10 ²	Deep Red
[Fe(H ₂ O) ₅ (F)] ²⁺	2.40 x 10 ⁵	Colourless
[FeC <i>I</i> ₄] ⁻	8.00 x 10 ⁻¹	Yellow
[Fe(CN) ₆] ^{3–}	4.08 x 10 ⁵²	Orange

Some of the K_{stab} for iron-based complexes are listed in the table below.

- (i) From the data above, suggest why the K_{stab} value for $[Fe(CN)_6]^{3-}$ is extremely large.
- (ii) Use the data in the table to predict what will be observed when a solution of $[Fe(H_2O)_5(SCN)]^{2+}$ is treated with sodium fluoride.
- (iii) Explain why $[Fe(H_2O)_5(F)]^{2+}$ forms a colourless complex.
- (iv) In the presence of thiocyanate ions, $[Fe(H_2O)_6]^{3+}$ is able to undergo ligand exchange reaction as shown below:

 $[Fe(H_2O)_6]^{3+} (aq) + SCN^{-} (aq) \longrightarrow [Fe(H_2O)_5(SCN)]^{2+} (aq) + H_2O$ (aq)
Yellow
Blood-red

Silver ions also react with thiocyanate ions to form a white precipitate, AgSCN.

State your observation when aqueous silver ions are added to the above equilibrium and explain your answer.

[6]

[Total : 20]

END