

RAFFLES JUNIOR COLLEGE PRELIMINARY EXAMINATION 2008



HIGHER 2

| CANDIDATE |
|-----------|
| NAME |
| |

CLASS

INDEX NUMBER

CHEMISTRY

9746/02

Paper 2 Structured

15 September 2008 1 hour 30 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

DO NOT open this question booklet until you are told to do so.

Write your name, class and index number in the spaces provided on the top of this page.

Write in dark blue or black pen in the space provided.

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 **all** questions.

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.

For Examiner's Use

| Question | 1 | 2 | 3 | 4 | 5 | 6 | Total |
|----------|-----|-----|-----|-----|-----|-----|-------|
| Marks | /10 | /10 | /10 | /10 | /10 | /10 | /60 |

This question booklet consists of **16** printed pages.

2

Answer **all** the questions in the spaces provided.

1 (a) Household bleach contains sodium chlorate(I), NaC*I*O. When bleach solution is acidified with dilute hydrochloric acid, chlorine is produced by the following reaction:

$$ClO^{-}(aq) + 2H^{+}(aq) + Cl^{-}(aq) \rightarrow Cl_{2}(aq) + H_{2}O(l)$$

Chlorine oxidises iodide to iodine, and the amount of iodine produced can be estimated using a standard sodium thiosulphate solution.

A 25.0 cm³ sample of a household bleach is diluted to 250 cm³. To a 25.0 cm³ portion of this diluted solution, dilute hydrochloric acid is added. This is followed by the addition of excess potassium iodide solution. The resultant mixture is then titrated against 0.200 mol dm⁻³ sodium thiosulphate solution. The volume required is 18.50 cm³. What is the concentration of sodium chlorate(I) in the household bleach?

- (b) The rate of reaction between peroxodisulphate ions, $S_2O_8^{2-}$, and iodide ions, I^- , can be increased by the addition of Fe³⁺(aq).
 - (i) With the aid of the *Data Booklet*, explain how Fe^{3+} catalyses the reaction between $S_2O_8^{2-}$ and I^- .

(ii) With the aid of a suitable diagram, explain why the rate of the reaction can also be increased by heating.

(c) Certain gas-phase or liquid-phase reactions which are catalysed by solid catalysts often exhibit zero order kinetics with respect to the reactants at high concentrations of reactants. Suggest a reason why this might be so.

[1] [Total: 10] 2. The first and second ionisation energies (IE), standard enthalpy changes of atomisation and hydration for some Group II elements and their ions are shown in the table below.

| Element | 1 st IE | 2 nd IE | ΔH^{Θ}_{atom} | ΔH_{hvd}^{Θ} of $M^{2+}(g)$ |
|---------|------------------------|------------------------|----------------------------|--|
| | / kJ mol ^{–1} | / kJ mol ^{–1} | / kJ mol ^{–1} | / kJ mol ⁻¹ |
| Mg | +737 | +1450 | +148 | -2003 |
| Ca | +590 | +1146 | +178 | -1557 |

(a) The standard enthalpy change of hydration of Mg^{2+} is more exothermic than that of Ca^{2+} . Explain why.

(b) (i) Define standard enthalpy change of formation, ΔH^{Θ}_{f} , of Mg²⁺(aq).

(ii) Making use of the data in the table above, construct an energy cycle and calculate ΔH_{f}^{Θ} of Mg²⁺(aq).

[1]

(iii) Group II elements with more exothermic ΔH_{f}^{Θ} of its aqueous ions also have more negative E^{Θ} values. Explain why.

(iv) Given that the standard enthalpy change of solution, ΔH_{soln}^{Θ} , of MgC l_2 is -150 kJ mol⁻¹, explain why MgC l_2 is soluble in water at all temperatures.

[7]

(c) On heating, Group II peroxides decompose to their respective oxides and oxygen. Explain why strontium peroxide (SrO₂) decomposes at a lower temperature than barium peroxide (BaO₂).

[2] [Total: 10]





(i) Give an equation that represents the second ionisation energy of chromium.

(ii) Why is the second ionisation energy of chromium and copper higher than that of manganese and zinc respectively?

(iii) Explain briefly why the fourth ionisation energy of cobalt is lower than that of iron and nickel.

[5]

(b) The colours and standard reduction potential of two complex ions of iron(III) are shown below:

| lon | Colour | Equation and E ⁹ |
|--|--------|---|
| [Fe(H ₂ O) ₆] ³⁺ | Violet | $[Fe(H_2O)_6]^{3+} + e^- \Longrightarrow [Fe(H_2O)_6]^{2+}, E^{\Theta} = +0.77 V$ |
| [Fe(CN) ₆] ³⁻ | Yellow | $[Fe(CN)_6]^{3-} + e^- \Longrightarrow [Fe(CN)_6]^{4-}, E^{\Theta} = +0.36 V$ |

(i) Why do transition metal ions form complexes readily?

(ii) Explain why standard reduction potential of $[Fe(CN)_6]^{3-}$ is lower than that of $[Fe(H_2O)_6]^{3+}$.

(iii) Outline one simple experiment that could be performed to demonstrate that $[Fe(CN)_6]^{3-}$ is a weaker oxidising agent than $[Fe(H_2O)_6]^{3+}$.

(iv) Explain briefly why the colours of the two complexes of iron(III) are different.

[5] [Total: 10]

- **4 (a)** To combat pollution and soaring fuel cost, luxury sports car maker Ferrari is experimenting with ethanol to help produce cars with lower carbon dioxide emissions and improve fuel economy. Titled "Drunk with Power", this project using ethanol as fuel also claims to bring about an increase in the horsepower of the automobile too!
 - (i) Write an equation for the complete combustion of ethanol.
 - (ii) Draw a dot–and–cross diagram of ethanol and hence suggest a value for the C–O–H bond angle.

[3]

- (b) Ethanol is often used in the synthesis of many organic compounds, such as ethanal, ethanoic acid and sodium methanoate.
 - (i) Write an equation for the synthesis of sodium methanoate from ethanol.
 - (ii) Draw a dot–and–cross diagram of sodium methanoate.

[2]

(c) (i) Explain the following observations.

| Compound | Structure | Observations after adding Pb(NO ₃) ₂ (aq) |
|----------|-------------------|---|
| A | O U C Br | white precipitate forms immediately |
| В | Br | slight white precipitate forms after 3 minutes |
| С | Br | no precipitate forms |

(ii) 0.01 mol of compound **A** is completely dissolved in 1 dm³ of water. Given that 0.01 mol dm⁻³ of benzoic acid has a pH of 3.09, suggest the pH of the resultant solution. Explain your answer briefly.

[5] [Total: 10]

- **5 (a)** The haemoglobin molecule in humans is an assembly of four globular protein subunits. Two of the subunits have beta-pleated sheet structures while the other two subunits have alpha-helical structures.
 - (i) With the aid of a sketch, describe the structure of the beta-pleated sheet.

(ii) Human haemoglobin undergoes denaturation in the presence of strong alkali. With respect to the globular protein subunit, explain why the denaturation takes place.

(iii) A pentapeptide segment of the haemoglobin subunit was subjected to partial hydrolysis and the following dipeptides were obtained:

ala-asp leu-ser pro-ala ser-pro

Determine the primary structure of this pentapeptide segment using the abbreviations provided above.

(iv) The five amino acids have the following structural formulae:

| abbreviation | ala asp | | leu | pro | ser |
|-----------------------|---|--|---|-----|--|
| structural formula | $\begin{array}{c} CH_3\\ H_2N{-}C{-}COOH\\ H\\ H \end{array}$ | $ \begin{array}{c} $ | $\begin{array}{c} CH_2CH(CH_3)_2\\ H_2N-C-COOH\\ H \end{array}$ | | СН ₂ ОН |

Draw the displayed formulae of residues of asp and ser formed when this pentapeptide segment is heated with NaOH(aq).

(b) Arrange the following compounds in order of **increasing** basicity, giving reasons for your answer.



[3] [Total: 10]

6 (a) With the crude oil prices hitting over US\$200 a barrel, many motorists are opting for lower octane rating petrol to make ends meet. The octane rating of a fuel is the knock resistance (anti-knock rating) compared to a mixture of an isomer of octane and heptane. As octane has a total of 18 isomers, It is useful to study how these isomers may be used to derive cheaper but yet acceptable knock resistance fuel.

Isomers of octane may be distinguished by their *optical activity* (or lack of it) when they are passed through a polarimeter.

- (i) Explain what is meant by *optical activity*.
- (ii) Two isomers of octane have the same properties except in their interactions with plane polarised light. Draw the structures of these isomers.

(iii) Draw an isomer of octane which contains chiral carbons but is optically inactive.

- (b) Isomers of octane may be distinguished by the number of mono-brominated products formed upon reaction with bromine dissolved in tetrachloromethane under ultraviolet light.
 - (i) Draw an isomer of octane which reacts with limiting bromine to give

| (1) only <u>one</u> mono-brominated product | (2) | <u>three</u> (ignor | mono-brominated e stereoisomers) | products |
|---|-----|------------------------|-------------------------------------|----------|
| | | | | |

(ii) Describe the mechanism of the reaction between octane and bromine to form 3-bromooctane under ultraviolet light.

[5]

(c) The reaction of octene with bromine can take place in the absence of ultraviolet light. Explain by comparing the structures of octane and octene.

End of Paper

[2] [Total: 10] 1. (a) $I_2(aq) + 2S_2O_3^{2^-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2^-}(aq)$ Amount of $S_2O_3^{2^-}$ used = 18.50/1000 x 0.200 = 3.7 x 10⁻³ mol Amount of I_2 produced = 3.7 x 10⁻³ / 2 = 1.85 x 10⁻³ mol Amount of C/O^- ions in 25.0 cm³ of diluted solution = $n_{iodine} = n_{chlorine} = 1.85 \times 10^{-3} mol$ Concentration of sodium chlorate(I) in household bleach = (1.85 x 10⁻³ x 250/25.0) ÷ 25.0/1000 = 0.740 mol dm⁻³

(b) (i)
$$I_2 + 2e^- \rightleftharpoons 2I^-$$

 $S_2O_8^{2^-} + 2e^- \rightleftharpoons 2SO_4^{2^-}$
 $Fe^{3^+} + e^- \rightleftharpoons Fe^{2^+}$
 $E^{\Theta} = +0.54V$
 $E^{\Theta} = +2.01V$
 $E^{\Theta} = +0.77V$
 $2Fe^{3^+} + 2I^- \rightarrow 2Fe^{2^+} + I_2$
 $2Fe^{2^+} + S_2O_8^{2^-} \rightarrow 2Fe^{3^+} + 2SO_4^{2^-}E^{\Theta}_{cell} = +1.24V$

Repulsion between negatively charged I⁻ and S₂O₈²⁻ ions causes the reaction to proceed slowly due to high activation energy. Since Fe^{3+} and $S_2O_8^{2-}$ are oppositely charged, the activation energy (via an alternative pathway) is lower and thus the rate of reaction is increased.

(ii)





Heating causes an increase in kinetic energy of the reactant molecules. In addition, there is an increase in the proportion of molecules with energy \geq activation energy which results in an increase in the frequency of effective collisions of the reactant molecules. The rate of the reaction increases.

(c) At high concentrations, active sites on the heterogeneous catalyst are saturated. Thus, any increase in concentration/pressure of reactants will not cause an increase in rate.

2

- (a) Charge density of Mg^{2+} is greater as its radius is smaller than that of Ca^{2+} . Thus, stronger ion-dipole interactions with water are formed during hydration of Mg^{2+} resulting in a more exothermic enthalpy change of hydration.
- (b) (i) The enthalpy change when <u>1 mole</u> of Mg²⁺(aq) is formed from <u>Mg(s)</u>, at <u>298 K and 1 atmospheric pressure</u>. Mg(s) \longrightarrow Mg²⁺(aq) + 2e⁻

$$\Delta H_{f}^{\Theta}[Mg^{2+}(aq)] = \Delta H_{atom}^{\Theta}[Mg(s)] + 1^{st} IE + 2^{nd} IE + \Delta H_{hyd}^{\Theta}[Mg^{2+}(g)]$$

= +332 kJ mol⁻¹

A more favourable backward reaction results in a more negative E^{Θ} value.

 $M(s) \longrightarrow M^{2+}(aq) + 2e^{-}$

Since ΔH_{f}^{Θ} [M²⁺(aq)] involves the backward reaction, a more exothermic ΔH_{f}^{Θ} would have a more negative E^{Θ} value.

- (iv) Change in entropy of solution is positive as there is a change from a more ordered solid state to less ordered aqueous state for MgCl₂ [½]. $\Delta G = \Delta H T\Delta S$ and since ΔH is negative while ΔS is positive, ΔG is negative for all temperatures and the reaction is spontaneous [½].
- (c) Sr^{2+} has a smaller ionic radius than Ba^{2+} . Thus, it has a higher charge density and is able to distort the electron cloud on O_2^{2-} to a greater extent than Ba^{2+} , resulting in greater ease in decomposition of the compound.

Thus, strontium peroxide decomposes more easily at lower temperatures.

- 3 (a) (i) $\operatorname{Cr}^{+}(g) \longrightarrow \operatorname{Cr}^{2+}(g) + e^{-}$
 - (ii) The second electron removed from manganese and zinc is a 4s-electron while the second electron removed from chromium and copper is a 3d-electron.

Since a 3d-electron is closer to the nucleus and has lower energy, a greater energy is required to remove it, causing second ionisation energy of Cr and Cu to be higher than that of Mn and Zn respectively.

[Note: Electronic configurations: $Cr = [Ar]3d^54s^1$, $Mn = [Ar]3d^54s^2$, $Cu = [Ar]3d^{10}4s^1$, $Zn = [Ar]3d^{10}4s^2$]

(iii) Electronic configuration of Fe³⁺, Co³⁺ and Ni³⁺ are [Ar]3d⁵, [Ar]3d⁶ and [Ar]3d⁷ respectively.

Ni has higher 4th ionisation energy than Co since it has a greater nuclear charge but shielding is approximately the same so that Ni has a higher effective nuclear charge than Co resulting in Ni having greater 4th ionisation energy than Co.

The 4th electron from Co is removed from an orbital containing a pair of electrons while the 4th electron from Fe is removed from a singly occupied orbital. Despite the higher effective nuclear charge of Co compared to Fe, the removal of the 4th electron from Co is aided by electron–electron repulsion and hence the 4th ionisation energy of Co is higher than that of Fe.

- (b) (i) Transition metal ions have low-lying empty orbitals (eg 3d and/or 4s) which can accept lone-pair of electrons from ligands via coordinate/dative bond to form complexes.
 - (ii) Reduction involves addition of electrons. It is energetically easier to add an electron to the positively charged $Fe(H_2O)_6^{3^+}$ than the negatively charged $Fe(CN)_6^{3^-}$ complex so that the standard reduction potential of $Fe(H_2O)_6^{3^+}$ is higher.
 - (iii) Add aqueous potassium iodide followed by starch to two test-tubes, one containing Fe(H₂O)₆³⁺ and the other containing Fe(CN)₆³⁻.
 A blue-black colouration due to iodine-starch complex is observed

A blue–black colouration due to iodine–starch complex is observed for $Fe(H_2O)_6^{3^+}$ but not for $Fe(CN)_6^{3^-}$.

This is because $Fe(H_2O)_6^{3+}$ is strong enough an oxidising agent to oxidise iodide ions to iodine but $Fe(CN)_6^{3-}$ is too weak an oxidising agent to oxidise iodide ions to iodine.

(iv) Ligands coordinated to transition metal ions split the d-orbitals of transition metal ions into two sets of energy level.
 The energy gap between the two sets of energy level is dependent on the ligand. Different ligands eg H₂O and CN⁻ give rise to

different energy gaps so that absorbed light (which has wavelength corresponding to the energy gap) is different, resulting in complexes with different colour.

4 (a) (i)
$$CH_3CH_2OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$



- 4 (c) (i) The white ppt formed is $PbBr_2(s)$. Water acts as the nucleophile in this reaction. The acyl halide undergoes hydrolysis readily as the carbonyl group gives a <u>partial positive charge on the carbonyl carbon</u>, making it <u>more susceptible to nucleophilic attack</u>. In the alkyl halide, the partial positive charge on the halide containing carbon is weaker, and water is also a weak nucleophile, resulting in a slower rate of hydrolysis. C₆H₅Br does not undergo hydrolysis due to the <u>partial double bond character of the C-Br bond</u>, a result of p-orbital overlap with π electron cloud of benzene ring.
 - (ii) HBr formed is a strong acid. $pH = -lg10^{-2} = 2$ (acceptable range: pH = 1.97 - 2, if H^+ from benzoic acid is considered)
- 5 (a) (i) Students can draw parallel or anti-parallel sheets.



Sketch showing

- Mirror image of pleated sheets, with C=O mirroring N-H
- Show and label hydrogen bonds

State

- R groups (side chains) project above or below the sheet and are 90° to the plane of the pleated sheet.
- Can be anti-parallel or parallel
- (ii) In alkali medium, the some of the R groups are deprotonated which affect the electrostatic interactions between them, causing <u>unfolding</u> of the protein chain

(OR for mentioning the disruption of tertiary structure of protein)

(iii) leu-ser-pro-ala-asp

(iv)



(b) Order of basicity: Phenylamide < phenylamine < aminocyclohexane

Order of basicity is determined by the availability of the lone pair. The more available it is, the more basic the compound. For the amide, the lone pair on N is delocalized over the O-C-N moiety and is therefore not available for bonding to a proton. Comparing the 2 amines, phenylamine is less basic as the lone pair on N is delocalized into the benzene ring and is thus less available for donation to a proton as compared to the N in aminocyclohexane.

- 6 (a) (i) Optical activity is the ability to rotate the plane of plane-polarised light.
 - (ii) Pair of enantiomers of any of the isomers below. Draw 3-D structure of isomer and mirror image



Termination

(c) Octene contains an electron rich π bond which polarises Br-Br bond in bromine. This causes electrophilic addition to take place in the absence of UV light. However in the reaction of bromine with octane, UV light is required for homolytic fission in the generation of radicals.