

NANYANG JUNIOR COLLEGE JC 2 Preliminary Examinations Higher 1

CANDIDATE NAME

Mark Scheme

CLASS

TUTOR'S NAME

CHEMISTRY

Paper 2

8872/02

22 September 2014 2 hours

Candidates answer on the Question Paper

Answer Paper Data Booklet

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

Section **A** Answer **all** questions.

Section **B** Answer any **two** questions on separate answer paper.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

For Examiner's Use		
1	/ 20	
2	/ 8	
3	/ 12	
Total	/ 40	

This document consists of **14** printed pages and **0** blank page.

Section A

Answer all the questions in this section in the spaces provided.

1 A gas is said to exhibit ideal gas behavior if it obeys the ideal gas equation

$$pV = nRT$$

where
$$p = \text{pressure of gas in atm},$$

 $V = \text{volume of gas in dm}^3,$
 $n = \text{amount of gas (mol)},$
 $R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ (a constant),
and $T = \text{temperature in K}.$

- (a) A 2.00 dm³ flask contains oxygen at 1.20 atm and 314 K.
 - (i) Use the ideal gas equation to find the amount of oxygen in the flask.

$$n = \frac{pV}{RT} = \frac{1.20 \times 2.00}{0.0821 \times 314}$$
[1]

= 0.0931 mol [1]

(ii) Hence calculate the mass of oxygen in the flask.

0.0931 × 32.0 = 2.98 g [1]

5.6

[3]

 V/dm^3 *T /* K p / atm1.0 12.3 300 1.4 17.6 600 2.1 5.9 300 3.6 6.8 600 4.8 2.6 300

4.4

600

(b) The data below were derived using the ideal gas equation for 1 g of hydrogen.

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(i) How does *p* vary with *V* for 1 g of hydrogen at a constant temperature?

p is inversely proportional to V[1]

(ii) Sketch the graphs of *p* against *V* for 1 g of hydrogen at 300 K and at 600 K on the same axes below.
 Label each graph.



shape of both graphs [1] relative positions of graphs [1] For examiner's use only (iii) Sketch the graph of pV against p for 1 g of hydrogen at 450 K.



- (c) Oxygen gas behaves ideally because the intermolecular forces of attraction are very weak. On the other hand, the intermolecular forces in methanol vapour cause it to behave less ideally.
 - (i) What are the intermolecular forces of attraction in each substance?

Oxygen: van der Waals forces / dispersion forces [1]

Methanol vapour: hydrogen bonds [1]

(ii) Draw a labelled diagram to show the forces of attraction between two molecules of methanol in the vapour state.



dipoles on four atoms [1]

lone pair on O atom [1]

correctly labelled hydrogen bond [1]

For

(d) The ideal gas equation can be used to derive a relationship for the relative molecular mass of a gas.

 $M_{\rm r} = \frac{mRT}{pV}$

where *m* is the mass of the gas in grams.

A 0.458 g sample containing a gaseous mixture of $AICI_3$ and AI_2CI_6 takes up a volume of 54 cm³ at a temperature of 98 °C and a pressure of 1 atm.

(i) Draw a dot-and-cross diagram for the AICl₃ molecule.



only three dot-cross pairs on AI and no lone pair on AI [1]

lone pairs on Cl [1]

(ii) Draw the structural formula of the Al₂Cl₆ molecule.



(iii) Calculate the average M_r of the mixture. $M_r = \frac{0.458 \times 0.0821 \times (98 + 273)}{1 \times \frac{54}{1000}}$

= 258 [1]

Converts temperature 98+273 = 371 K [1]

Converts volume 54/1000 dm³ [1]

(iv) Hence calculate the percentage by mass of Al_2Cl_6 in the mixture.

$$\frac{267.0x + 133.5(100 - x)}{100} = 258.1$$
 [1]

x = 93.5% [1]

[8] [Total: 20] For

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 (a) Explain what is meant by the term order of reaction. For a general reaction aA + bB → products The rate equation is rate = k [A]^x[B]^y, order of reaction wrt A is x & order of reaction wrt B is y overall order of reaction is (x+y)

OR

The order of reaction with respect to a given reactant/catalyst is the power to which the concentration of that reactant/catalyst is raised in the experimentally determined rate equation.

[1]

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(b) Hydrogen peroxide reacts with iodide ions in acidic solution as shown below.

$$\mathrm{H_2O_2(aq)} + 2\mathrm{H^+(aq)} + 2\mathrm{I^-(aq)} \rightarrow 2\mathrm{H_2O(I)} + \mathrm{I_2(aq)}$$

The results of some investigations of the rate of this reaction are shown below.

Experiment	[H ₂ O ₂]	[H⁺]	[[-]	Relative initial rate
number	/ mol dm ⁻³	/ mol dm ⁻³	/ mol dm ⁻³	/ mol dm $^{-3}$ s $^{-1}$
1	0.030	0.050	0.060	1.80
2	0.020	0.060	0.050	1.00
3	0.0375	0.060	0.060	2.25
4	0.025	0.060	0.050	1.25

- (i) Use the above data to determine the order of reaction with respect to
 - H₂O₂
 - H⁺
 - |-

Comparing expt 2 and 4, when $[H_2O_2]$ increased by 1.25 times (0.025/0.020), rate increased by 1.25 times (1.25/1.00)

Order wrt H₂O₂ is 1 [1]

Comparing expt 1 and 3, when $[H_2O_2]$ increased by 1.25 times (0.0375/0.030), rate should increased by 1.25 times because order wrt H_2O_2 is 1. Hence rate increased from 1.80 in expt 1 to 2.25. When $[H^+]$ increased by 1.2 times, rate remains unchanged from the increased due to H_2O_2 . Rate is independent of the $[H^+]$. Order wrt H^+ is 0 [1]

Since order wrt H ⁺ is 0, we can ignore [H ⁺] as we deduce the order v Rate = $k[H_2O_2][I^-]^a$	wrt [I ⁻].
Comparing experiment 1 and 2,	
$1.80 = k (0.03)(0.06)^{a}$ (1)	
$1.00 = k(0.02)(0.05)^{a}$ (2)	
(1) $1.80 (0.06)^a (0.03)$	
$\frac{1}{(2)} \qquad \frac{1}{1.00} = \frac{1}{(0.05)^a (0.02)}$	
a = 1; order with respect to I^- is 1[1]	
(ii) Hence write a rate equation for the above reaction	
Rate = $k[H_2O_2][I^-][1]$	

[4]

For

(c) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature increases the rate of a chemical reaction.



An increase in temperature will lead to increase in the average kinetic energy of reactant molecules. More molecules will have energy larger than E_a resulting in more collisions with energy greater than E_a . Hence frequency of activated collisions will increase. Rate increases. [1]

[3] [Total: 8] **3** Esters are compounds which provide the flavour of many fruits and the perfumes of many flowers.

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- (a) The ester $CH_3(CH_2)_2CO_2CH_3$ contributes to the aroma of apples.
 - (i) State the reagents and conditions needed for the hydrolysis of this ester.

Aqueous HCI / H₂SO₄, heat under reflux

OR aqueous NaOH, heat under reflux.....[1]

(ii) Write the equation for the hydrolysis of this ester.

 $CH_3(CH_2)_2CO_2CH_3 + H_2O \rightleftharpoons CH_3(CH_2)_2CO_2H + CH_3OH$

OR $CH_3(CH_2)_2CO_2CH_3 + NaOH \Rightarrow CH_3(CH_2)_2CO_2^-Na^+ + CH_3OH \dots [1]$

(iii) Apart from their use as perfumes and food flavourings, state **one** major commercial use of esters.

The most common uses of esters are

- (1) in artificial scents or perfumes, and
- (2) as artificial flavorings for sweets, ice-creams and soft drinks

Industrial uses of esters include [1] any one

(3) as solvents in the manufacture of fats, cellulose, varnishes and paints;

- (4) as solvents within pharmaceutical industries, and
- (5) as softeners or plasticizers in plastic and molding industries.

[3]

(b) Leaf alcohol is a stereoisomer that can form when insects such as caterpillars eat green leaves.

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(i) Draw the other stereoisomer of leaf alcohol.



(ii) Draw the displayed formula of the ester formed when leaf alcohol reacts with ethanoic acid.



[3]

(c) (i) Deduce the relative molecular mass, M_r , for leaf alcohol.

The molecular formula is $C_6H_{12}O$.

$$M_{\rm r} = 6(12.0) + 12(1.0) + 16.0 = 100.0$$
 [1]

(ii) Leaf alcohol was reacted to form a product with an M_r value 18 units less. Suggest a structure for this product and deduce the type of reaction that took place.

 $CH_2=CH-CH=CHCH_2CH_3$ [1]

Type of reaction: elimination / dehydration [1]

[3]

(d) Describe a simple chemical test to distinguish between leaf alcohol and your product in (c)(ii). Draw the structures of the products of any reactions that occur.

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	Observations [1] both compounds			
	Observations [1] both compounds			
Reagent & cond. [1]	Leaf alcohol	Answer in (c)(ii)		
Sodium	Sodium dissolves. Gas evolved gives a 'pop' sound with a lighted splint. Products: [1] Na ⁺ O ⁻ CH ₂ CH ₂ CH=CHCH ₂ CH ₃ H ₂ (g)	No gas evolved.		
PCl ₅ / SOCl ₂	White fumes seen. Products: [1] CICH ₂ CH ₂ CH=CHCH ₂ CH ₃ HCI(g)	No white fumes seen.		
K ₂ Cr ₂ O ₇ , aq H ₂ SO ₄ heat	Orange solution turns green. Products: [1] OHCCH ₂ CH ₂ CH=CHCH ₂ CH ₃	Orange solution remains.		
KMnO ₄ , aq H ₂ SO ₄ heat Bubble gas evolved through limewater	Purple solution decolourises. Products: HOOCCH ₂ COOH CH ₃ CH ₂ COOH	Purple solution decolourises. Products: CO_2 , H_2O CH_3CH_2COOH Gas evolved forms a white ppt in limewater.		
		[3]		

[Total: 12]

Section B

Answer any **two** questions from this section on separate answer paper.

4(a) Sodium hydrogencarbonate decomposes on heating to form sodium carbonate. It is difficult to measure the enthalpy change of this reaction directly.

 $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$

One method of determining this enthalpy change is to react known amounts of sodium hydrogencarbonate and sodium carbonate, separately with excess dilute hydrochloric acid.

(i) 0.48 g of sodium hydrogencarbonate was added to 25 cm³ of 0.100 mol dm⁻³ of dilute hydrochloric acid. The temperature rise was found to be 6.8 K and the process was found to be only 85% efficient.

Calculate the enthalpy change for the reaction when one mole of sodium hydrogencarbonate reacts with dilute hydrochloric acid.

The standard enthalpy change for the reaction between sodium carbonate and dilute hydrochloric acid is found by a similar method to be -321.6 kJ mol⁻¹.



Enthalpy change = $\frac{1}{0.0025} \times 836 = -334 \text{ kJmol}^1$ [1] sign must be included

(ii) Using the energy cycle provided, calculate the value of ΔH_3 .

 $\Delta H_1 = \Delta H_2 + \Delta H_3$ [1] Applying Hess' Law 2 x -334.4 = -321.6 + ΔH_3 $\Delta H_3 = -347$ kJ mol⁻¹ [1] correct sign and units

(iii) Hence, sketch an energy profile diagram for the decomposition of sodium hydrogencarbonate.



(b) Sea water is a source of chemicals. The most abundant chemical dissolved in sea water is sodium chloride. Compounds of magnesium and bromine are also present. Magnesium occurs at 1300 parts per million (ppm) and bromine at 60 ppm by mass.

The solution left after crystallising sodium chloride from sea water is even richer in bromine, and contains around 2.2 g dm^{-3} of bromine. Bromine is extracted from this solution by passing in chlorine gas. The mixture is acidified to prevent the following hydrolysis of bromine.

$$Br_2(aq) + H_2O(I) \rightleftharpoons 2H^+(aq) + Br^-(aq) + BrO^-(aq) \qquad \Delta H > 0$$

The bromine can be separated by heating the solution to collect bromine vapour which is then condensed, or by blowing air through the solution.

(i) Show by calculation that a solution containing 2.2 g dm⁻³ of bromine is richer in bromine than one containing 60 ppm. [1 ppm = 1 mg / L]

60 ppm = 60 mg dm⁻³ = 0.06 g dm⁻³ < 2.2 g dm⁻³ (shown) [1]

(ii) Explain how a low pH level would affect the hydrolysis of bromine.

Low pH level will mean the concentration of H^+ is high [1], therefore by Le Chatelier's Principle, position of equilibrium shifts left [1] to decrease the concentration of H^+ , preventing the hydrolysis of bromine.

(iii) Explain how an increase in temperature would affect the equilibrium position for the hydrolysis of bromine.

An increase in temperature will favour the endothermic reaction to remove the excess heat. [1] By Le Chatelier's Principle, position of equilibrium will shift to the right [1], favouring the hydrolysis of bromine.

[5]

[8]

(c) Compound **A** has the molecular formula of $C_9H_{11}Br$, which has three positional isomers.

On reaction with hot ethanolic potassium hydroxide, \bf{A} gives only a single product, \bf{B} .

B reacts with cold acidified potassium manganate(VII) to give **C**.

C reacts with hot acidified potassium dichromate to give **D**, C₉H₈O₃.

D gives an orange precipitate with 2,4-dinitrophenylhydrazine, but does not react with Fehling's solution. One mole of **D** reacts with one mole of propanol with hot concentrated sulfuric acid to give **E**, $C_{12}H_{14}O_3$.

Deduce the structures of the compounds **A** to **E**. Explain your reasoning for the reactions involved.

- 1: 1 carbon to hydrogen ratio → A must contain a benzene ring. (•)
- Three positional isomers \rightarrow the benzene ring is disubstituted. (•)
- Reaction with hot ethanolic potassium hydroxide → Elimination of a halogenoalkane has taken place to form an alkene in B. One of the carbon side chain must contain at least 2 carbons. (•)





B reacts with cold acidified KMnO₄ to form C. → Mild oxidation of alkene to form a diol. (•)



- C reacts with hot acidified potassium dichromate to give D → oxidation of a 1° and 2° alcohol to form ketone and carboxylic acid respectively in D. (•) (Note: side chain oxidation will not take place as potassium dichromate is not a strong enough oxidising agent)
- D, gives an orange precipitate with 2,4-dinitrophenylhydrazine, but not Fehling's solution. → This further confirms that D contains a ketone functional group. (•)
- One mole of D reacts with one mole of propanol with hot concentrated sulfuric acid to give E, C₁₂H₁₄O₃. → Condensation of D and propanol to give an ester, E contains an ester. (•)





 $4(\bullet), 5(\bullet) - 2 m$ $6(\bullet), 7(\bullet) - 3 m$

Alternative structures for A, B, C, D and E



[Total: 20]

- **5(a)** Sodium chlorate(V), NaClO₃, is a colourless crystalline compound, which is used as a bleaching and oxidising agent. The main commercial use for sodium chlorate(V) is for making chlorine dioxide, ClO₂. The largest application of ClO₂, which accounts for about 95% of the use of chlorate, is in bleaching of pulp. Industrially, sodium chlorate(V) is produced by the electrolysis of a hot sodium chloride solution.
 - (i) Draw a dot-and-cross diagram to illustrate the bonding in NaClO₃.



(ii) State the bond angle of the CIO_3^- ion and use the VSEPR (Valence Shell Electron Pair Repulsion) theory to predict its shape.

Shape is trigonal pyramidal.

Bond angle: 107° Both – [1]

According to VSEPR Theory, <u>electron pairs stay as far apart as possible</u> to minimise electrostatic repulsion and to maximize stability. Around each of the central CI atom, there are 3 bond pairs and 0 lone pairs of electrons. [1]

An alternative method to form sodium chlorate(V) involves a reaction between chlorine and warm aqueous NaOH in a 1:2 mole ratio. In this reaction, water, sodium chloride and sodium chlorate are formed.

- (iii) Write a balanced equation for the above reaction. $3CI_2 + 6 NaOH \rightarrow 5NaCI + NaCIO_3 + 3 H_2O$ [1]
- (iv) Use oxidation numbers to explain what type of reaction has occurred in this alternative method.

Disproportionation	[1]
Oxidation state of CI decreases from 0 in CI_2 to -1 in NaCI.	
Oxidation state of CI increases from 0 in CI_2 to +5 in NaClO ₃ .	[1]

[7]

(b) An organic compound **S** ($M_r = 112$) contains by mass 64.3% carbon, 7.1% hydrogen, and 28.6% oxygen. **S** undergoes an addition reaction with bromine in a 1:1 mole ratio. It also reacts with alkaline aqueous iodine to give a yellow precipitate and reacts with hot KMnO₄ to give **T**, C₄H₆O₃, as the only organic product.

Element	С	Н	0
% by mass	64.3	7.1	28.6
No. of moles	63.2 / 12.0 = 5.36	7.1 / 1.0 = 7.1	28.6 / 16.0 = 1.79
Mole ratio	3	4	1

(i) Determine the molecular formula of **S**.

Empirical formula of **S** is C_3H_4O . [1] with working Let the molecular formula of **S** be $(C_3H_4O)_n$. $(3 \times 12.0 + 5 \times 1.0 + 16.0)n = 112$ n = 2

Molecular formula of **S** is **C**₆**H**₈**O**₂. [1]

(ii) Deduce with reasoning, a possible structure for compound **S** and **T**.

S contains <u>a methyl ketone or a methyl alcohol</u> functional group since it gives a yellow precipitate. [1]

S undergoes addition reaction with Bromine and hence contains <u>one C=C</u> **double bond** as it reacts with bromine in a 1:1 mole ratio. [1]

Since **S** undergoes oxidation with hot $KMnO_4$ to give **T**, $C_4H_6O_3$, as the only organic product, the by product should be CO_2 which should come from <u>ethanedioic acid</u>. [1]

Therefore S is CH₃COCH₂CH=CHCHO [1] and T is CH₃COCH₂CO₂H [1]

[7]

(c) A solution containing sodium glutamate functions as a buffer solution. The structure of the salt is shown below:



sodium glutamate

Assume the R group in the above compound is inert

(i) What is meant by a buffer solution?

A buffer solution is a solution that is able to maintain a fairly constant pH when a small amount of acid or base is added. [1]

(ii) With the aid of ionic equations, explain how the above solution reacts with H^+ and OH^- ions.

When a small amount of H^+ ions is added, it is removed by reacting with the large reservoir of glutamate ions present.



When a small amount of OH⁻ ions is added, it is removed by reacting with the large reservoir of the acid present.



Explanation – [1]

(iii) Predict the solubility of sodium glutamate in water, explaining the types of bonding involved.

Sodium glutamate is <u>soluble in water</u> [1] as they can form both <u>hydrogen bonds</u> and <u>ion-dipole interactions</u> with water molecules. [1]

[6]

[Total: 20]

- **6(a)** Octet rule is a chemical rule of thumb that states that atoms of main-group elements tend to combine in such a way that each atom has eight electrons in its valence shell, giving it the same electronic configuration as a noble gas.
 - (i) There are exceptions to the octet rule. Suggest examples of species with
 - odd number of valence electrons e.g. NO, NO₂ [1]
 - less than 8 valence electrons
 e.g. BeCl₂, BH₃, AlCl₃ [1]
 - (ii) The compound SF_2 readily reacts with fluorine to give SF_4 . Suggest reasons why MgF_2 does not react with more fluorine to give MgF_4 .

```
Mg is a period 2 element. [1] positions of Mg and S in Periodic Table

_{12}Mg: 1s^2 2s^2 2p^6 3s^2

To produce the ionic compound MgF<sub>4</sub>, Mg atom will need to form Mg<sup>4+</sup>.

The 3<sup>rd</sup> and 4<sup>th</sup> electrons are removed from the inner shell. [1]

A lot of energy is required hence the formation of Mg<sup>4+</sup> is unfavourable.

Sum of first 4 ionisation energy = 736 + 1450 + 7740 +10500 = 20426 kJ mol<sup>-1</sup>

Hence MgF<sub>4</sub> does not exist.
```

S is a period 3 element. $_{16}$ S: $1s^2 2s^2 2p^6 3s^2 3p^4$ Sulfur can expand its octet [1] and form two more S–F bonds. Hence SF₄ exists. (b) An element in the second period (lithium to neon) in the Periodic Table often shows a diagonal similarity to the element a group higher in the third period (sodium to argon). Discuss this statement with special reference to beryllium and aluminium.

	Group 1	Group 2	Group 3	Group 4
Period 2	Li	Be	В	
Period 3		Mg	AI	Si

Electronegativity increases across a period but decreases down a group. Hence beryllium and aluminium have similar electronegativity. [1]

The nature of the compound formed depends on the electronegativity difference between the 2 atoms in the compound. The compounds of beryllium and aluminium exhibit similar physical and chemical properties.

[6]

The diagonal relationship between beryllium and aluminium can be illustrated in the following ways:

(1) The amphoteric nature of the oxides [1] $AI_2O_3(s) + 6HCI(aq) \rightarrow 2AICI_3(aq) + 3H_2O(I)$ $AI_2O_3(s) + 2NaOH(aq) + 3H_2O(I) \rightarrow 2NaAI(OH)_4(aq)$ $BeO(s) + 2HCI(aq) \rightarrow BeCI_2(aq) + H_2O(I)$ $BeO(s) + 2NaOH(aq) + H_2O(I) \rightarrow Na_2Be(OH)_4(aq)$ [1] both equations for BeO

(2) The covalent nature of the bonding in the chlorides [1] BeCl₂ and AlCl₃ are covalent chlorides. The chlorides dissolve and undergo hydrolysis to form acidic solution. [1] AlCl₃(s) + 6H₂O(l) \rightarrow [Al(H₂O)₆]³⁺(aq) + 3Cl⁻(aq) [Al(H₂O)₆]³⁺(aq) + H₂O(l) \rightleftharpoons [Al(H₂O)₅(OH)]²⁺(aq) + H₃O⁺(aq) BeCl₂(s) + 4H₂O(l) \rightarrow [Be(H₂O)₄]²⁺(aq) + 2Cl⁻(aq) [Be(H₂O)₄]²⁺(aq) + H₂O(l) \rightleftharpoons [Be(H₂O)₃(OH)]⁺(aq) + H₃O⁺(aq)

[1] both equations for BeCl₂

- (c) The molecular formula of an organic compound is $C_3H_6O_3$. 1 mol of this compound reacts with sodium to give 1 mol of hydrogen. Draw the structure for the compound using
 - (i) displayed formula,



[1] correct structure + displayed formula

(ii) skeletal formula, and



(iii) stereochemical formula to show spatial arrangement of bonds, atoms and groups with respect to central carbon atom



[3]

(d) State examples of an oxidising agent and a reducing agent used in organic reactions. For each reaction, give the conditions used, write the structural formulae of the organic reactants and products. You must suggest different organic compounds for the oxidation and reduction reactions.

Oxidising agent: Organic reactant: Organic product:	aq KMnO ₄ , aq H ₂ SO ₄ , heat CH ₃ CH ₂ OH CH ₃ CO ₂ H	[1] [1] [1]		[6]
Reducing agent: LiA/H ₄ in dry ether / Organic reactant: Organic product:	Na in ethanol / H_2 gas with Pd c CH ₃ CH ₂ CN CH ₃ CH ₂ CH ₂ NH ₂	atalyst [1] [1]	[1]	

[Total: 20]