

NANYANG JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION Higher 1

CANDIDATE NAME

ANSWERS

CLASS

TUTOR'S NAME

CHEMISTRY

Paper 2

8872/02 16 September 2015 2 hours

Candidates answer Section A on the Question Paper.

Additional Materials:

Answer Paper Data Booklet Graph Paper

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 HB pencil for any diagrams or graphs. Do not use staples, paper clips, glue or correction fluid. The use of an approved scientific calculator is expected, where appropriate.

Section A

Answer all the questions.

Section B

Answer two questions on separate answer paper.

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	
Section A	
B5	
B6	
B7	
Total	

This document consists of **15** printed pages.

Section A

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

1 (a) Predict and explain which of the following isomers has a higher solubility in water.



Isomer B is more soluble in water.

Isomers A and B both have simple molecular structures with <u>hydrogen</u> bonding between molecules.

There is <u>intramolecular</u> hydrogen bonding in isomer A as the –OH and –NH₂ groups are <u>close to each other</u> (and hence, less intermolecular hydrogen bonding). <u>More energy</u> is required to overcome the more <u>extensive</u> intermolecular hydrogen bonding between isomer B.

(b) (i) Draw the 'dot-and-cross' diagram of NH_2OH .



(ii) Using VSEPR theory, explain why the bond angle about the N atom is greater than the bond angle about the O atom.

About N atom – 3 bond pairs, 1 lone pair About O atom – 2 bond pairs, 2 lone pairs Lone pair-lone pair repulsion is greater than lone pair-bond pair / bond pair-bond pair repulsion.

[3]

[3]

[Total: 6]

2 (a) Describe the bonding in ethene in terms of orbital overlap. You may draw a diagram to illustrate your answer.

Each <u>C atom forms 2 sigma bonds with 2 neighbouring H atoms</u> and <u>1 sigma</u> bond with the other <u>C</u> atom when their <u>orbitals overlap head-on</u>. The <u>two <u>C</u></u> atoms forms a pi bond when their <u>p orbitals overlap side-on above and below</u> the plane of the molecule.



(b) (i) Ethene can be converted into ethane-1,2-diol. State the reagents, conditions and type of reaction for this reaction.

reagents: dilute KMnO₄, H₂SO₄(aq) or dilute KMnO₄, NaOH(aq) conditions: cold type of reaction: mild oxidation

(ii) Ethene and ethane both react with chlorine. Suggest with particular reference to bonding, why ethane needs the presence of UV light but ethene does not.

Ans:

Ethene has <u>pi electron cloud</u> along the C=C double bond that is <u>electron rich</u> enough to <u>polarise Cl_2 </u>, thus <u>increasing the reactivity of Cl_2 </u> as an electrophile to react with ethene without the presence of UV light.

Ethane contains C-C and C-H bonds which are strong and non-polar. Hence, ethane is <u>unreactive</u>. UV light is required to cause homolytic fission of Cl_2 to generate a more reactive CI• radical to react with ethane.

[6]

[Total: 9]

3 When compound **C** is placed in a 2 dm³ closed container, the following equilibrium is established. The backward reaction is exothermic.





i) Write an expression for K_c for this equilibrium.

$$K_{c} = \frac{[D]}{[C]^{2}}$$

(ii) Calculate the value of the equilibrium constant for the reaction at the 1st minute, stating its units.

At the 1st min:
$$K_c = \frac{\left[\frac{0.8}{2}\right]}{\left[\frac{0.4}{2}\right]^2} = 10 \text{ mol}^{-1} \text{ dm}^3$$

(iii) A change was made to the system at the 2nd and 4th minute respectively. State the change and explain your reasoning.

Change at 2nd minute:

Temperature is increased.

Reason:

Since backward reaction is exothermic, forward reaction is endothermic.

By Le Chatelier's Principle, the system will react to remove the heat. The endothermic forward reaction is favoured and position of equilibrium shifts to the right. Therefore, the amount of C decreases and D increases. Change at 4th minute:

Compound C was added.

Reason:

By Le Chatelier's Principle, when C is added, the system will react to reduce some of the added C. The forward reaction is favoured and position of equilibrium shifts to the right. Therefore, the amount of C decreases and C increases.

[7]

(b) 10.0 cm³ of 0.100 mol dm⁻³ of ethanoic acid is titrated against 0.0300 mol dm⁻³ of Ba(OH)₂. The graph of pH against volume of Ba(OH)₂ added is shown:

5



[Total: 11]

- 4 (a) Define order of reaction. [1] The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised in the experimentally determined rate equation.
 - (b) The reaction kinetics of a reaction using CH₃CH₂Br and excess NH₃ to synthesise an amine is determined by monitoring the change in the concentration of CH₃CH₂Br with time. The results are shown below.



- (i) Write a balanced equation for the above reaction. $CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$
- (ii) Use the graphs to deduce the rate equation.

Since $t_{1/2}$ is constant at 30 min (using [NH₃] = 3.0 mol dm⁻³) graph, reaction is 1st order with respect to CH₃CH₂Br.

OR $t_{1/2}$ is constant at 60 min (using [NH₃] = 1.5 mol dm⁻³) graph, reaction is 1st order with respect to CH₃CH₂Br.

Using initial rate method, Initial rate for graph where $[NH_3] = 1.5 \text{ mol dm}^{-3}$ = 0.2/95 = 0.00211 mol dm⁻³ min⁻¹

Initial rate for graph where $[NH_3] = 3.0 \text{ mol dm}^{-3}$ = 0.2/50 = 0.00400 mol dm⁻³ min⁻¹ As $[NH_3]$ increases 2 times, initial rate also increases 2 times($\frac{0.004}{0.00211} = 1.90 \approx 2$)

Hence, order of reaction with respect to NH₃ is 1.

Rate = $k [CH_3CH_2Br] [NH_3]$

(iii) Using the graph where $[NH_3] = 1.5 \text{ mol dm}^{-3}$, calculate a value for the rate constant and state its units. Rate = k [CH₃CH₂Br] [NH₃] 0.00211 = k [0.20] [1.5] k = 7.03 × 10⁻³ mol⁻¹ dm³ min⁻¹

[6]

(c) Halogenoalkanes are known to undergo different types of substitution reaction – unimolecular nucleophilic substitution $(S_N 1)$ and bimolecular nucleophilic substitution $(S_N 2)$, depending on the type of alkyl halide.

Compound	Type of reaction
CH ₃ CH ₂ CH ₂ Br	S _N 2
CH₃Br	S _N 2
(CH ₃) ₃ CBr	S _N 1
(CH ₂ CH ₃)CBr(CH ₃) ₂	S _N 1

Identify the type of alkyl halide and suggest if CH_3CH_2Br undergoes S_N1 or S_N2 .

 CH_3CH_2Br is a primary alkyl halide and it undergoes S_N2 .

[2]

2-bromo-2-methylpropane reacts with NaOH via an S_N1 mechanism. The S_N1 mechanism proceeds via the formation of a carbocation intermediate.



(d) (i) Write the rate equation for the above S_N1 reaction. Rate = k [(CH₃)₃CBr] (ii) On the axis below, sketch the graph of rate against concentration of $(CH_3)_3CBr$.



(e) Depending on the solvents used for S_N1 reaction, the rate of reaction is found to change.

Solvents	Dielectric polarisation	Relative rates for S_N1 reaction
Ethanol	24.3	1
Methanol	33.6	10
Formic acid	58.0	1000
Water	80.4	100000

Table 1: The dielectric polarisations of some common solvents and relative rates for S_N 1 reaction

Dielectric polarisation measures the ability of a solvent to act as an insulator of electric charges. Solvents of low dielectric polarisation, such as hydrocarbons, are non-polar, whereas solvents of high dielectric polarisation, such as water, are polar.

- (i) State how dielectric polarization affect the rate for S_N1 reactions. As the value of dielectric polarisations increases, the rate for S_N1 reactions increases.
- (ii) Suggest with a suitable diagram, how water stabilise the carbocation intermediate in the S_N 1 mechanism.



(iii) Suggest a solvent that will result in a slower rate than using ethanol. Any hydrocarbons.

> [3] [Total: 14]

Section B

Answer two questions from this section on separate answer paper.

5 (a) 60.0 cm³ of 0.30 mol dm⁻³ ethanedioic acid, $H_2C_2O_4$ (aq), was mixed with 30.0 cm³ of 1.00 mol dm⁻³ calcium chloride solution, CaCl₂ (aq). The precipitate, CaC₂O₄, obtained was filtered off, leaving behind the filtrate containing excess Ca²⁺ and C₂O₄²⁻ ions.

The CaC₂O₄ precipitate was subsequently dissolved in dilute sulfuric acid. The resultant solution was then diluted to 1.0 dm³ and labelled **F**. 25.0 cm³ of this solution **F** required 11.80 cm³ of 0.015 mol dm⁻³ potassium manganate(VII) solution for complete reaction according to the following equation:

 $2MnO_4^{-} + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} 10CO_2 + 8H_2O$

- (i) What is the purpose of dissolving the precipitate in dilute sulfuric acid? To acidify the reaction mixture (OR) H^+ is needed to form Mn^{2+} .
- (ii) Calculate the concentration of the ethanedioate in solution **F**. $n(MnO_4^-)$ reacted = 0.015 x (11.80/1000) = 0.000177 mol $n(C_2O_4^{2^-})$ reacted = (11.8/1000 x 0.015) x 5/2 = <u>4.443 x 10^{-4} mol</u> $[C_2O_4^{2^-}] = 4.443 x 10^{-4}/0.025 = 0.0177 mol dm^{-3}$
- (iii) What mass of CaC_2O_4 precipitated out when $CaCl_2$ (aq) was mixed with $H_2C_2O_4$ (aq)? $n(C_2O_4^{2^-})$ in 1 dm³ = 0.0177 mol $n(CaC_2O_4 \text{ ppt})= 0.0177 \text{ mol}$ mass of $CaC_2O_4 = 0.0177 \times 128.0 = 2.266 \text{ g} = 2.27 \text{ g}$
- (iv) Hence, determine the concentration of $Ca^{2+}(aq)$ and $C_2O_4^{2-}(aq)$ remaining in the filtrate.

 $n(CaC_2O_4 ppt) = 0.0177 mol$

 $n(C_2O_4^{2-})$ in excess (in filtrate) = $(0.30 \times \frac{60.0}{1000}) - 0.0177 = 0.0003 \text{ mol}$

n(Ca²⁺) in excess (in filtrate) = $(1.00 \text{ x} \frac{30.0}{1000}) - 0.0177 = 0.0123 \text{ mol}$

$$[C_2O_4^{2^-}] = \frac{0.0003}{0.09} = \frac{0.00333 \text{ mol dm}^{-3}}{0.09}$$
$$[Ca^{2^+}] = \frac{0.0123}{0.09} = \frac{0.137 \text{ mol dm}^{-3}}{0.09}$$

[7]

- (b) (i) Define with an equation, the first ionisation energy of calcium. $Ca(g) \rightarrow Ca^+(g) + e$
 - (ii) Write the electronic configuration of the resulting calcium species. $1s^22s^22p^63s^23p^64s^1$

(iii) Sketch the trend of the successive ionisation energies of the first 10 electrons of a calcium atom. Suggest explanation for the trend you have shown.



After the removal of the 1st electron, the <u>remaining electrons are more</u> <u>strongly attracted</u> to the <u>constant positive nuclear charge</u>. Hence, successive I.E.s always shows an increasing trend.

The largest difference is between the 2^{nd} and 3^{rd} ionisation energies as calcium has <u>2 valence electrons</u> and the <u> 3^{rd} electron being removed from</u> the inner shell.

The second difference occurs between the 8th and 9th ionization energies. Less energy is required to remove the 3p electron in calcium as it experiences increased shielding provided by the <u>filled 3s subshell</u>.

[5]

(c) Phenylpropanone, C₆H₅CH₂COCH₃, is used in the manufacture of amphetamine, a stimulant commonly used to treat Attention Deficit Hyperactivity Disorder (ADHD). Due to the illicit use in clandestine chemistry, it was made a controlled substance in 1979 in the United States.

A reaction scheme beginning with phenylpropanone is shown below.



(i) Compound **W** shown in the reaction scheme, exists as a pair of stereoisomers. Draw the structures of the isomers and state the type of isomerism shown.

Type of isomerism: geometric isomerism / cis-trans isomerism



(ii) Draw the structures of compounds X, Y and Z.

X: NO₂ O_2N HN CH₃



(iii) Suggest reagents and conditions for steps I to III.

Steps	Reagents and conditions
Ι	LiAlH ₄ in dry ether / NaBH ₄ / H ₂ (g), Ni catalyst, heat
П	Excess conc. H ₂ SO ₄ , 170 °C / Al ₂ O ₃ , 350 °C
III	Conc. KMnO ₄ , H ₂ SO ₄ (aq), heat under reflux

[8]

[Total: 20]

6 (a)



13

benzoic acid

(i) Explain in terms of structure, why benzoic acid is acidic.
In benzoic acid, the hydrogen atom is bonded to <u>highly electronegative</u> <u>oxygen</u> atom in the –O-H group. The highly electronegative oxygen atom <u>causes the –O-H bond to be weakened</u> and the compound <u>loses H⁺ more</u> <u>readily to form a stable carboxylate ion</u>, hence it is acidic.

OR

The p orbital of the oxygen atom overlaps with the π electron cloud of the –C=O. The negative charge is effectively dispersed over the carbon atom and the two electronegative oxygen atoms. This stabilises the benzoate ion. Benzoic acid acts as a proton donor, hence it is acidic.

It is found that an aqueous solution of benzoic acid of concentration 0.10 mol dm⁻³ has a pH of 2.6 while an aqueous solution of ethanoic acid of concentration 0.50 mol dm⁻³ has a pH of 2.5.

(ii) Calculate the hydrogen ion concentration, [H⁺], of benzoic acid solution and ethanoic acid solution respectively.

 $[H^+]$ of benzoic acid = $10^{-2.6} = 2.51 \times 10^{-3} \text{ moldm}^{-3}$ $[H^+]$ of ethanoic acid = $10^{-2.5} = 3.16 \times 10^{-3} \text{ moldm}^{-3}$

(iii) By comparing the respective ratio of hydrogen ion concentration to acid concentration, explain which is the stronger acid.

Ratio of $[H^+]$ from benzoic acid / [benzoic acid] = 0.0251 Ratio of $[H^+]$ from ethanoic acid / [ethanoic acid] = 0.00632

Since benzoic acid dissociates to a greater extent to form H^+ , it is the stronger acid.

[4]

(b) Explain why chloroethanoic acid is more acidic than ethanoic acid.

 $CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$

In chloroethanoate ion (CH_2CICO_2) , the electron-withdrawing -CI group disperse the negative charge on the oxygen atom, stabilising the carboxylate ion. Hence the Position of Equilibrium of dissociation lies more to the right and chloroethanoic acid is more acidic than ethanoic acid.

[2]

(c) Ethyl benzoate is isomeric with phenyl ethanoate and undergoes hydrolysis in the same way.



ethyl benzoate

phenyl ethanoate

(i) Write equation to show how ethyl benzoate undergoes hydrolysis using HC*l*.



(ii) Hence suggest a simple chemical test to distinguish between ethyl benzoate and phenyl ethanoate.

Reagent & Condition: <u>KMnO₄ /K₂Cr₂O₇ (aq), HCl/H₂SO₄ (aq), heat.</u>

(Ester is hydrolyzed into acid and corresponding ethanol/phenol. Ethanol can be oxidised to acids)

Observation for product of ethyl benzoate: <u>purple KMnO₄</u> <u>decolourised/Orange $K_2Cr_2O_7$ turned green</u>

Observation for product of phenyl ethanoate: <u>purple KMnO₄</u> remains/Orange $K_2Cr_2O_7$ remains.

[4]

- (d) In a titration reaction, 25.0 cm³ of the benzoic acid was found to react completely with 23.00 cm³ of 0.15 mol dm⁻³ NaOH (aq).
 - (i) Suggest, with a reason, a suitable indicator for the titration.

This is a <u>strong base-weak acid titration</u>. Phenolphthalein is a suitable indicator as the <u>pH range of the indicator (8-10) falls within the pH change</u> at equivalence point (7-11)

The aqueous solution of benzoic acid and sodium benzoate constitutes a buffer system. With the aid of suitable equations, explain how such a system works when

- (ii) small amounts of acid are added.
- (iii) small amounts of alkali are added.

(ii) When acid is added, the small amount of H⁺ ions added is removed by reacting with the large reservoir of benzoate ions present, hence keeping pH relatively constant.



(iii) When base is added, the small amount of OH⁻ ions added is removed by reacting with the large reservoir of benzoic acid molecules present, hence keeping pH relatively constant.



[6]

- (e) Aluminium chloride is a yellowish-white solid that reacts with water in two separate ways.
 - When a few drops of water are added to the solid, steamy white fumes are evolved and a white solid remains, which is insoluble in water.
 - When a large amount of water is added to the solid, a clear, weakly acidic solution results.

Write equations, including state symbols, for these two reactions and explain the observations.

In limited water, AICl₃ produces white solid of AI(OH)₃ and steamy fumes of HCl.

 $AICI_3$ (s) + $3H_2O$ (l) $\rightarrow 2AI(OH)_3$ (s) + 3HCI (g)

In excess water, the Al^{3+} ion is <u>hydrated</u> by water to form $[Al(H_2O)_6]^{3+}$ ion which will undergo <u>hydrolysis</u> to give weakly acidic solution.

AICI₃ (s) + 6H₂O (l) → $[AI(H_2O)_6]^{3+}$ (aq) + 3Cl⁻ (aq) $[AI(H_2O)_6]^{3+}$ (aq) + H₂O (l) $\square \square \square$ $[AI(H_2O)_5OH]^{2+}$ (aq) + H₃O⁺ (aq)

[4]

[Total: 20]

7 (a) In an experiment to measure the enthalpy change of neutralisation, 20 cm³ of 2.0 mol dm⁻³ sulfuric acid was placed in a polystyrene cup. A 30 cm³ of 1.0 mol dm⁻³ sodium hydroxide, at the same initial temperature, is added. The temperature rose by 8.2 K. Calculate the enthalpy change of neutralization, given the heat capacity of water is 4.2 J K⁻¹ cm⁻³.

 $\begin{array}{c} H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O \\ 0.04 \qquad 0.03 \end{array}$

NaOH is the limiting reagent

Amount of water formed = 0.0300 mol

Heat gained by solution = m x c x Δ T = 50 x 4.2 x 8.2 = 1722 J

Enthalpy change of neutralisation = $-1722/0.0300 = -57400 \text{ J mol}^{-1} = -57.4 \text{ kJ mol}^{-1}$

(b) Across period 3, the elements changes from metallic to non-metallic nature. Correspondingly, the difference in electronegativity between the elements and the oxide decreases, giving rise to different type of oxides.

Choose and describe **three** oxides which are **different** in terms of structure and bonding. For each type of oxide, write equations for the reactions with water where appropriate and give the approximate pH of any solutions formed.

Na₂O or MgO or Al₂O₃ have giant ionic lattice with oppositely charged ions held by strong electrostatic forces of attractions. Na₂O (s) + H₂O (I) \rightarrow 2NaOH (aq) pH=13 MgO (s) + H₂O (I) \rightleftharpoons Mg(OH)₂ (aq) pH=9 Al₂O₃ is insoluble in water and hence pH=7.

 SiO_2 is a giant molecular structure with strong covalent bonds between the Si and O atoms.

 SiO_2 is insoluble in water and hence pH=7.

 P_4O_6 or P_4O_{10} or SO_2 or SO_3 have simple molecular structure with weak dispersion forces between molecules. P_4O_6 (s) + 6H₂O (l) → 4H₃PO₃ (aq) pH = 1-2 P_4O_{10} (s) + 6H₂O (l) → 4H₃PO₄ (aq) pH = 1-2 SO_2 (g) + H₂O (l) → H₂SO₃ (aq) pH = 1-2 SO_3 (g) + H₂O (l) → H₂SO₄ (aq) pH = 1-2

[6]

(c) Compound **P** has the molecular formula $C_9H_{12}O$. **P** gives a yellow precipitate in the presence of alkaline aqueous iodine. When **P** is heated with a mixture of NaBr and concentrated H_2SO_4 under reflux, **Q** is formed.

When a solution of silver nitrate in ethanol is added to **Q** a pale cream precipitate appears after a few minutes. When **P** is heated under reflux with acidified KMnO₄ the colour of the solution turns from purple to colourless. The resulting organic compound **R** reacts with sodium carbonate in a 1:1 mole ratio and produced effervescence. Reaction of **R** with methanol in the presence of concentrated sulfuric acid with heating gives a sweet smelling compound **S**, $C_{10}H_{10}O_{4}$.

Identify and suggest structures for **P**, **Q**, **R** and **S**. Show how you deduced these structures, write equations for all of the reactions described above and suggest the types of reactions that are occurring.



Methyl alcohol in **P** undergoes oxidative cleavage/oxidation with alkaline aqueous iodine to form yellow precipitate of CHI_3



 2° alcohol in **P** undergoes substitution with HBr (formed from NaBr and concentrated H₂SO₄)to form a 2° alkyl halide in **Q**.



 2° alkyl halide in **Q** undergoes hydrolysis/substitution with ethanolic silver nitrate to form 2° alcohol and cream precipitate of AgBr.



 2° alcohol in **P** and alkyl side chain of benzene undergoes oxidation to form carboxylic acid in **R**. Purple KMnO₄ is reduced to form colourless/pale pink of Mn²⁺.

$$H_3C \longrightarrow H_3C \longrightarrow HOOC \longrightarrow HOOC \longrightarrow COOH + 3H_2O + CO_2$$

Carboxylic acid in **R** undergoes acid-base/neutralisation with sodium carbonate to produce carboxylate salt and effervescence of carbon dioxide.



Carboxylic acid in R undergoes condensation with methanol to form ester in S.

$$HOOC \longrightarrow COOH + 2CH_3OH \implies H_3CO_2C \longrightarrow CO_2CH_3 + 2H_2O$$

[10]

[Total: 20]