

NANYANG JUNIOR COLLEGE JC 2 PRELIMINARY EXAM Higher 1

CANDIDATE
NAME

CLASS

TUTOR'S NAME

CHEMISTRY

Paper 2

Candidates answer Section A on the Question Paper.

Additional Materials:

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 **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	
A1	
A2	
A3	
A4	
B1	
B2	
В3	
Total	

This document consists of 15 printed pages.

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Section A

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

1 The rate of hydrolysis of a chloroalkane, RCl with aqueous sodium hydroxide depends on the concentration of the reactants at a fixed temperature T_1 . The values for the initial rates of hydrolysis at various initial concentrations have been determined. These are shown in the table below.

Expt	Initial conc. of	Initial conc. of	Initial rate /
	NaOH / mol dm ⁻³	RCl / mol dm ⁻³	mol dm⁻³ s⁻¹
1	0.0200	0.0150	4.0 x 10 ⁻⁴
2	0.0200	0.0225	6.0 x 10 ⁻⁴
3	0.0300	0.0225	9.0 x 10 ⁻⁴
4	0.0600	0.0300	X

(a) Deduce the orders of reaction with respect to each of the reactants. Hence, write the rate equation for the hydrolysis of the chloroalkane. [3]

Orders wrt NaOH = 1 Orders wrt RCI = 1 Rate = k [NaOH][RCI]

(b) Based on your answer above, calculate the magnitude of x. $x = (3 \times 2 \times 4.0 \times 10^{-4})$ $= 2.4 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ [1]

(c) Describe and explain, with an appropriate diagram, how the rate of this reaction examiner's is affected when the experiment is repeated at a higher temperature, T_2 . [3] use only



Correct Boltzmann distribution with legend.

As T increases, proportion of molecules with E > Ea increase. Frequency of activated collision increases. Rate increases.

[Total: 7 marks]

2 Nitrogen and phosphorous are in the same group in the Periodic Table. The information in the following table is provided for compounds of nitrogen and phosphorous.

Compound	Mr	Boiling point / K
NH_3	17.0	240
PH₃	34.0	185

Briefly explain the difference in boiling points of NH₃ and PH₃. (a)

[2]

For

More energy is needed to break the relatively strong hydrogen bonds between the NH₃ molecules than the weak van der Waals' forces of attraction between PH₃ molecules.

(b) Name and sketch the type of hybrid orbital used by nitrogen in forming the N - Hbond in NH₃. [2]

sp³ orbital



(c) (i) Identify the ion formed by NH_3 when it dissolves in HCl(aq).

 NH_4^+

(ii) The bond angle in NH₃ differs from the ion it formed in part (c)(i). By considering the change in the number and type of electron pairs around the central atom, explain why.

 NH_3 has 3 bond pair and 1 lone pair while NH_4^+ has 4 bond pairs. Thus the bond angle of NH_3 is smaller than that of NH_4^+ .

[Total: 6 marks]

3 Nitric acid, HNO₃, known to early chemists as aqua fortis (meaning "strong water"), is a major commercial acid. It is available as the concentrated acid which is a 70% aqueous solution. Although colourless when pure, the acid turns yellow when exposed to light as a result of decomposition.

$$4HNO_3(aq) \longrightarrow 4NO_2(g) + 2H_2O(l) + O_2(g)$$
 ------ (1)

Pure nitric acid can be prepared by distillation from a mixture of potassium nitrate and concentrated sulphuric acid as shown

 $KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$ ------ (2)

This method was at one time used in the commercial preparation of nitric acid, but it has now been replaced by the Oswald process, discovered in 1902 by the German chemist Wilhelm Ostwald, who received the Nobel Prize in chemistry in 1909 for his work on catalysts. In the Ostwald process, ammonia gas is burned in oxygen over a platinum catalyst. The product is nitric oxide, NO, which reacts with oxygen to give nitrogen dioxide. When dissolved in water, NO₂ produces nitric acid. The equations are

$$4NH_{3}(g) + 5O_{2}(g) \longrightarrow 4NO(g) + 6H_{2}O(g) \quad ; \quad \Delta H_{1} = -906 \text{ kJ mol}^{-1}$$

$$2NO(g) + O_{2}(g) \longrightarrow 2NO_{2}(g) \quad ; \quad \Delta H_{2} = -114 \text{ kJ mol}^{-1}$$

$$3NO_{2}(g) + H_{2}O(l) \longrightarrow 2HNO_{3}(aq) + NO(g) \quad ; \quad \Delta H_{3} = -137 \text{ kJ mol}^{-1}$$

The largest single use of nitric acid is in the production of ammonium nitrate, NH_4NO_3 , which is largely used as an agricultural fertiliser. It is also used to manufacture chemicals for nylon and to make explosives like nitroglycerine, $C_3H_5(NO_3)_3$. In making the explosive nitroglycerine, glycerol, $C_3H_5(OH)_3$, which is obtained from fats is used as the starting material. The manufacturing process is shown in two stages as shown below:

[1]

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Stage 2



Nitroglycerine is hazardous to handle in the pure state. It is very sensitive to shock, exploding by the following reaction:

 $\begin{array}{c} 4C_{3}H_{5}(ONO_{2})_{3}(l) \longrightarrow 6N_{2}(g) + 10H_{2}O(g) + 12CO_{2}(g) + O_{2}(g) \quad ; \\ \Delta H_{4} = -5.720 \times 10^{3} \text{ kJ mol}^{-1} \end{array}$

The reaction is highly exothermic and produces large volumes of gas. Alfred Nobel (1833 -1896) discovered that when nitroglycerine was mixed with clay and similar materials, it was much less shock-sensitive. The mixture is called dynamite. One stick of dynamite weighs 500 g and contains 80% of nitroglycerine by mass.

- (a) Explain why nitric acid in a bottle often turns yellow after some time. [1] Because when exposed to light nitric acid produces NO₂ gas which is light yellow at a lower concentration. (Or which is a brown gas).
- (b) State the type of reaction involved in the making of pure nitric acid as exemplified in reaction (2). Explain your answer. [2]

Acid-base reaction. Sulphuric acid acts as acid (proton donor), nitrate acts as base (proton acceptor).

(c) Draw the dot and cross diagram for the NO molecule and hence suggest a reason for the reactivity of NO. [2]



Nitrogen monoxide is quite reactive as it does not have the complete octet configuration around nitrogen atom.

(d) (i) Using relevant data from the *Data Booklet* and the given reaction, calculate the average bond energy of the bond found in the NO molecule.

6

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 $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$; $\Delta H_1 = -906 \text{ kJ mol}^{-1}$

[2]

-906 = 12(390) + 5(496) - 4[BE(NO)] - 12(460)BE(NO) = 636 kJ mol⁻¹

(ii) Suggest a reason for the discrepancy between your answer in part (d)(i) and the experimentally determined value of of 629 kJ mol⁻¹.
 [1]

Data booklet values are only averaged bond energy values.

(e) Using appropriate enthalpy change values given for the Ostwald Process and the following energy cycle, calculate the enthalpy change for reaction (1). [2]



 $\triangle H_1 / 2 = -(-114/2) + (+137)$ $\triangle H_1 = +388 \text{ kJ mol}^{-1}$ (f) State the reagents and conditions used for the formation of glycerol from fats. [1] Aq NaOH, heat

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(g) The molecule of glycerine has the following structure:



(i) State the C–O–N angle (*x*) and the O–N–O bond angle (*y*) as indicated in the diagram above. [2]

3 bond pairs + 0 lone pairs, therefore bond angle of $ONO = 120^{\circ}$

2 bond pairs + 2 lone pairs, therefore bond angle of CON = 105°

(ii) Dynamite is still widely used in many countries for clearing of obstacles and for mining resources. Its potential danger however cannot be underestimated. Calculate the average change in temperature of the surrounding 20 m³ of air around **one** stick of exploding dynamite.
 [Volumetric heat capacity of air = 1.297 kJ m⁻³ K⁻¹]

 $\Delta T = (((1 \times 500 \times 0.8)/227) \times 5.720 \times 10^3 \times 10^3/4) / (0.001297 \times 20 \times 10^6) = 97 \text{ K}$

[Total: 15 marks]

4 *Umpolung* in organic chemistry is the chemical modification of a functional group with the aim of the reversal of polarity of that group. This allows the functional group to undergo reactions that will otherwise not be possible.

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[1]

The reactions below show a classic example of *umpolung* involving dithiane chemistry.



Step I	Condensation	
Step II	Acid-Base	
Step III	Addition	
Step V	Elimination	

(ii) State reagents and conditions to carry out **Step V**.

Al₂O₃, 350°C *Or* conc H₂SO₄, 170°C

- (b) Aldehydes such as ethanal usually undergo attack by negatively charged examiner's species. One example is the reaction of ethanal with HCN, carried out at low use only temperatures in the presence of trace amounts of NaOH.
- (i) Draw a displayed diagram to show the product of the reaction.

[1]

[1]

For

CH₃—C—C≡N

(ii) Suggest the identity of the chemical species attacking ethanal.

CN[−]

(c) In another dithiane reaction, butan-2-one is used instead of cyclohexanone in Step III.



(i) When butan-2-one was used, three different products were obtained after Step V. Draw their structural formulae in the space below. [3]



(ii) Explain why only one product was obtained when cyclohexanone was used. [2]

Cyclohexanone is symmetrical hence only one product structure possible. Trans-isomer is not formed in a cyclic alkene due to ring strain.

(iii) Suggest a simple chemical test that could be carried out to distinguish between *two* of the products. Give the observation for each of the product. [2]

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Heat with acidified KMnO₄.

Effervescence. Gas evolved gives white ppt with limewater.

No effervescence.

[Total: 12 marks]

Section B

Answer **two** of the following three questions. Answer these questions on separate answer paper.

1(a) Chloride ions react with peroxodisulphate ions, $S_2O_8^{2-}$, in a redox reaction. Lead (II) ions are used as catalyst to increase the rate of reaction.

 $S_2O_8^{2-}(aq) + 2C\Gamma(aq) \rightarrow 2SO_4^{2-}(aq) + Cl_2(aq)$

(i) Explain in terms of oxidation numbers whether sulphur is oxidised or reduced in the reaction.

Sulphur is reduced. Its oxidation number decreases from +7 in $S_2O_8^{2-}$ to +6 in SO_4^{2-} .

(ii) Suggest a reason why the uncatalysed reaction is slow.

The reaction involves the collision of two negatively charged ions hence the activation energy is high.

The following graph shows the production of chlorine as the reaction proceeded to completion.



- (iii) The reaction follows *first order* kinetics. Explain the term in *italics*. For an experimentally determined rate equation, rate = k [A] the reaction is 1st order with respect to A.
- (iv) Explain why the experimental results indicate that the overall kinetics are first order.

From graph, the total concentration of CI_2 is 60 × 10⁻³ mol dm⁻³. Graph work

Since $1^{st} t_{\frac{1}{2}} = 2^{nd} t_{\frac{1}{2}} = 1.5$ min, the reaction follows first order kinetics.

So that $S_2O_8^{2-}$ would be the limiting reagent and hence be completely reacted.

OR

So that the concentration of $C\Gamma$ would remain almost constant throughout the experiment. The reaction would appear to be zero order wrt $C\Gamma$.

(b) The following table compares the atomic and ionic radii of sodium and chlorine.

	Atomic radius / nm	Ionic radius / nm
Sodium	0.186	0.095
Chlorine	0.099	0.181

The ionic radius of sodium is smaller than its atomic radius. However, the ionic radius of chlorine is larger than its atomic radius.

Explain the above observations.

[3]

In forming Na^+ ion, Na atom loses its valence electron. Na^+ ion has one electron shell less than Na atom.

In forming $C\Gamma$ ion, CI atom gains one electron. The effective nuclear charge in $C\Gamma$ ion is smaller than in CI atom.

- (c) Beryllium is in Group II of the Periodic Table. It shows a diagonal relationship with aluminium hence they exhibit similar physical and chemical properties.
- (i) Beryllium chloride forms an acidic solution when added to water. Explain the observation, writing equations where relevant.

BeCl₂ dissolves and undergoes <u>hydrolysis</u> in water to form an acidic solution.

BeC $l_2(s)$ + 6H₂O(l) → [Be(H₂O)₆]²⁺(aq) + 2C \overline{l} (aq) [Be(H₂O)₆]²⁺(aq) + H₂O(l) \rightleftharpoons [Be(H₂O)₅(OH)]⁺(aq) + H₃O⁺(aq)

- (ii) Beryllium chloride forms a product with ammonia.
 - State the molar ratio in which beryllium chloride reacts with ammonia.
 - Draw the structural formula of the product formed, showing clearly the type of bonding formed. [5]

Molar ratio of BeC_{l_2} : $NH_3 = 2 : 1$

(d) Ethylbenzene can undergo substitution reaction with chlorine in two ways.



(i) State the conditions needed for reaction I and reaction II. reaction I : Cl_2 , anhydrous FeC l_3 reaction II: Cl_2 , UV light

(ii) Describe a simple test that could be used to distinguish between ethylbenzene and B. Include your observations for each compound.
 Add alcoholic AgNO₃.

B reacts to form a white ppt of AgC*I*. Ethylbenzene does not.

(iii) If the C/ substituent in B is replaced by Br, explain the difference in the rate of reaction with aqueous sodium hydroxide. [6]
 The C Br band is langer and bangs weaker than C Cl band

The C-Br bond is longer and hence weaker than C-Cl bond. Hence, less energy is needed to break the C-Br bond.

The rate of reaction of B with NaOH(aq) is faster.

2 Ethanol can be prepared industrially using ethene as the starting material as shown in Reaction I.

Reaction I: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$

(a) State the conditions required for the industrial preparation of ethanol. [1]

300°C, 60 atm, conc. H₃PO₄

(b) The standard enthalpy change of formation of ethanol, $C_2H_5OH(l)$ can be determined by using the values of the standard enthalpy changes given:

Reaction II: $C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$ $\Delta H_r^{-+} = -44.0 \text{ kJ mol}^{-1}$

	$\Delta H_{\rm f}^{\Phi}$ / kJ mol ⁻¹
$C_2H_4(g)$	+ 52.0
$H_2O(l)$	- 285.8

(i) Define the term *standard enthalpy change of formation* of a compound.

Standard enthalpy change of formation is the energy change when one mole of a compound is formed from its constituent elements in their standard states under standard conditions.

(ii) Calculate the standard enthalpy change of formation of ethanol, $C_2H_5OH(l)$.

 $\Delta H_{f}^{\Phi} = \sum n_{i} \Delta H_{f}^{\Phi} \text{ (product)} - \sum n_{i} \Delta H_{f}^{\Phi} \text{ (reactant)}$ - 44.0 = $\Delta H_{f}^{\Phi} \text{ (} C_{2}H_{5}OH(l)\text{)} - [52.0 - 285.8]$ $\Delta H_{f}^{\Phi} \text{ (} C_{2}H_{5}OH(l)\text{)} = -277.8 \text{ kJ mol}^{-1}$

(iii) Explain why the state symbols for water and ethanol given in reaction II are different from those quoted in the industrial process as seen in reaction I.

Under standard conditions (at 25°C, 1 atm), water and ethanol are both in the <u>liquid state</u> and not the gaseous state.

(c) Ethene can also be used as the starting material for the 3 steps synthesis of propanoic acid.

$$C_2H_4 \rightarrow \mathbf{P} \rightarrow \mathbf{Q} \rightarrow CH_3CH_2COOH$$

Suggest structures for **P** and **Q** and the reagents and conditions required to carry out the above transformations. [5]

P: CH₃CH₂Cl or CH₃CH₂Br
Q: CH₃CH₂CN
HCl or HBr
$$C_2H_4 \longrightarrow P \longrightarrow Q \longrightarrow CH_3CH_2COOH$$

(d) Propanoic acid is a weak acid whereas phosphoric acid, H₃PO₄ can act as a strong monoprotic acid.

Using propanoic acid and phosphoric acid as examples, illustrate, with the help of equations, what is meant by a *strong* acid and a *weak* acid. [2]

Propanoic acid dissociate partially in water $CH_3CH_2COOH + H_2O \rightleftharpoons CH_3CH_2COO^- + H_3O^+$

Phosphoric acid dissociate completely in water. $H_3PO_4 + H_2O \rightarrow H_2PO_4^- + H_3O^+$

(e) (i) Explain what is meant by a *buffer solution*.

A buffer is a solution that is able to resist <u>large</u> changes in pH when <u>small</u> amount of acid or base is added.

(ii) Suggest a suitable compound that can be added to a solution of propanoic acid to make the resulting mixture a *buffer solution*.

sodium propanoate or potassium propanoate

(iii) With the aid of two equations, explain how the *buffer solution* which you suggested in **part (e)(ii)** can control pH. [4]

 $CH_3CH_2COO^- + H^+ \rightarrow CH_3CH_2COOH$ Most of the added H^+ is removed by reacting with the reservoir of $CH_3CH_2COO^-$ conjugate base. Thus the pH remains relatively constant.

CH₃CH₂COOH + OH⁻ → CH₃CH₂COO⁻ + H₂O Most of the added OH⁻ is removed by reacting with the reservoir of CH₃CH₂COOH. Thus the pH remains relatively constant. (f) Information about a commercial cola drink containing phosphoric acid is given in the table below.

	Added acid	Acid concentration in	Volume, at s.t.p., of CO ₂ dissolved in 1 volume of
		drink / g dm ⁻³	drink
cola	Phosphoric acid	0.49	1.12

(i) Calculate the concentration, in mol dm^{-3} , of phosphoric acid, H₃PO₄, in the cola drink. [1]

 $Mr(H_3PO_4) = 3(1.0) + 4(16.0) + 31.0 = 98.0$ $[H_3PO_4] = 0.49 / 98.0 = 0.005 \text{ mol dm}^{-3}$

(ii) Hence, calculate the pH of the cola drink.

 $[H^+] = 0.005 \text{ x } 3 = 0.015 \text{ mol } dm^{-3}$ pH = - lg (0.015) = 1.82

(iii) Calculate the amount of carbon dioxide dissolved in 1 dm³ of cola drink at s.t.p.

[2]

[1]

n(CO₂) dissolved = 1.12 / 22.4 = 0.05 mol

- **3(a)** Ethanoic acid, also known as vinegar, is made by the traditional method of oxidative fermentation of aqueous solutions of ethanol.
 - (i) Construct a balanced equation for the formation of ethanoic acid from ethanol.
 CH₃CH₂OH + 2[O] → CH₃COOH + H₂O
 - (ii) Explain, with the help of a suitable diagram, why the M_r of ethanoic acid in a non polar solvent is approximately 120.



Dimerisation occurs as hydrogen bonds are formed between 2 ethanoic acid molecules.

- (iii) Explain why ethanoic acid is a stronger acid than ethanol.
- Strength of an acid depends on the stability of its conjugate base
- Ethanoate ion (CH₃CO₂⁻) is a more stable conjugate base than ethoxide ion (CH₃CH₂O⁻)

[5]

- (b) A mixture of 0.80 mol of ethanoic acid and 1.30 mol of ethanol was shaken for a long time to reach equilibrium. The mixture was titrated quickly with 2.00 mol dm⁻³ of NaOH and 80 cm³ of alkali was required.
 - (i) Write an equation for the reaction between ethanoic acid and ethanol.

 $CH_{3}COOH + CH_{3}CH_{2}OH \xrightarrow{\frown} CH_{3}CH_{2}COOCH_{2}CH_{3} + H_{2}O$

(ii) Calculate a value for the equilibrium constant K_c for this reaction.

	CH ₃ COOH	+ CH₃CH₂OH ⇐	CH ₃ CH ₂ COOCH ₂ CH ₃	+ H ₂ O
Initial/mol	0.8	1.3	0	0
Change/mol	-0.64	-0.64	+ 0.64	+0.64
Eqm/ mol	0.16	0.66	0.64	0.64

 $\mathrm{Kc} = \frac{0.64 \times 0.64}{0.16 \times 0.66} = 3.88$

- (iii) Deduce what will happen to the value of the equilibrium constant if concentrated sulphuric acid is added to the reaction chamber.
 - No change in K_c . Temperature remains unchanged in the experiment.

[5]

- (c) Sodium is in Period three of the Periodic Table.
 - (i) Write a balanced equation, including state symbols, to show the reaction between sodium and ethanoic acid.

 $2CH_3COOH(aq) + 2 Na(s) \rightarrow 2CH_3COO^-Na^+(aq) + H_2(g)$

- (ii) The elements in third period show a change from metallic to non-metallic nature, which is reflected in the chemical properties of their compounds. Describe the reactions of the oxides of elements sodium to phosphorous with water. Write balanced equations to illustrate your answer. [6]
- $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$
- Na₂O dissolves readily to form strongly alkaline solution (pH 13)
- MgO(s) + H₂O(I) \rightleftharpoons Mg(OH)₂(aq)
- MgO dissolves slightly to form weakly alkaline solution (pH 8)
- Al₂O₃ and SiO₂ are insoluble.
- $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
- P₄O₁₀ reacts with water to form strong acid:
- (d) For the following compounds PCl_3 and $POCl_3$,
 - (i) Draw diagrams to show the shape of each molecule.
 - (ii) Deduce the polarity of each molecule.

[4]





trigonal pyramidal

tetrahedral

PCl3	POCI3
• polar,	• polar,
dipole-moments do	dipole-moments do
not cancel each other	not cancel each
	other

End of Paper