

NANYANG JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION Higher 2

CANDIDATE NAME		
CLASS	TUTOR'S NAME	
CHEMISTRY		9729/02

Paper 2 Structured Questions

9729/02 12 September 2023 2 hours

Candidates answer on the Question Paper.

Additional Materials: 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. You may use an HB pencil for any diagrams or graphs. Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. The use of an approved scientific calculator is expected, where appropriate. 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	/11				
2	/20				
3	/20				
4	/24				
Total	/75				

This document consists of **21** printed pages.

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

1 Nitrosyl chloride, NOC*l* decomposes at temperatures above 100 °C to form nitrogen monoxide and chlorine as shown in the equation below.

 $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$

(a) (i) A sample of NOC*l* was allowed to decompose at 150 °C and 125 atm. Assuming that NOC*l* behaves ideally, show that its initial concentration is 3.60 mol dm^{-3} .

[1]

(ii) A student pointed out that the assumption in (a)(i) that NOC*l* behaves ideally is not valid. Suggest and explain **two** possible reasons why this may be so.

[2]

(b) (i) In order to determine the rate equation for this reaction, an investigation was carried out at constant temperature for each experiment. The following results were obtained.

initial rate / N m ⁻² s ⁻¹	16.2	47.2	78.8	124	172
$\rho_{NOCl}/N m^{-2}$	0.30	0.50	0.66	0.82	0.95
$(\rho_{NOCl})^2 / N^2 m^{-4}$	0.09	0.25	0.44	0.67	0.90

Use these data to plot a suitable graph on the grid below to determine the order of reaction with respect to $\rho_{\text{NOC}\textit{/}}$

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(ii) Hence, deduce the order of reaction with respect to ρ_{NOCI} .

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(iii) Construct the rate equation for the decomposition of NOC*l* and state the units of the rate constant.

[1]

(c) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect on a rate constant of increasing temperature from T_1 to T_2 .

[2]

(d) The reverse of the decomposition reaction can also occur such that NOCl is formed from NO and Cl_2 .

Given that a possible mechanism for the reaction is as shown below, suggest the rate equation for the reaction.

Step 1: NO + NO \exists \exists N_2O_2 Step 2: Cl_2 + N_2O_2 \xrightarrow{slow} 2NOC l

.....[1]

[Total: 11]

2 The theoretical value of lattice energies can be estimated using a pure ionic model represented by the Kapustinskii equation as shown, where z_{+} and z_{-} are the charges on ions, r_{+} and r_{-} are the ionic radii in nm, v is the number of ions in the formula unit, and k is a constant with a value of 107.9 nm kJ mol⁻¹.

$$\Delta H_{\text{latt}} = \frac{k \ v \ z_{+} \ z_{-}}{r_{+} + r_{-}}$$

Table 2.1 shows the theoretical lattice energies calculated from the Kapustinskii equation and experimental lattice energies obtained from the Born-Haber cycle for silver chloride, AgC*l*, and silver iodide, AgI.

compound	experimental value / kJ mol ⁻¹	theoretical value / kJ mol ⁻¹
AgC <i>l</i>	-916	-729
AgI	-889	-618

(a) (i) Define the term *lattice energy*.

(ii)	Use the <i>Data Booklet</i> to explain why the theoretical value of lattice energy for AgC <i>l</i> is more exothermic than AgI.
(iii)	Suggest a reason for the difference in the theoretical and experimental values of lattice energy for AgC <i>l</i> .
(iv)	Suggest a reason for the larger difference in the theoretical and experimental values of lattice energy for AgI as compared to AgC <i>I</i> .

(b) Calcium and chlorine forms $CaCl_2$ but not CaCl even though the enthalpy change of formation of CaCl is exothermic. CaCl does not exist as it will undergo disproportionation reaction readily to form $CaCl_2$ and calcium.

 $2CaCl(s) \rightarrow Ca(s) + CaCl_2(s)$

(i) Use the *Data Booklet* and the Kapustinskii equation to calculate the theoretical value of lattice energy for CaCl and $CaCl_2$.

Assume the ionic radius of Ca^+ to be 0.133 nm.

[2]

(ii) Using the answer in (b)(i) and data from Table 2.2, together with data from the *Data Booklet*, construct a Born-Haber cycle to calculate the enthalpy change of formation of CaC*l*.

Table 2.2

	$\Delta H / \text{kJ mol}^{-1}$
standard enthalpy change of atomisation of Ca(s)	+178
electron affinity of chlorine, $Cl(g) + e^- \rightarrow Cl^-(g)$	-349

equation	reaction	$\Delta H / \text{kJ mol}^{-1}$
1	$2CaCl(s) \rightarrow Ca(s) + CaCl_2(s)$	$\Delta H_{eqn1} = y$
2	$Ca(g) \rightarrow Ca(s)$	$\Delta H_{eqn2} = -178$
3	$Ca^{2+}(g) + 2Cl^{-}(g) \rightarrow CaCl_2(s)$	∆ <i>H</i> _{eqn3} from (b)(i)
4	$Ca^+(g) + Cl^-(g) \rightarrow CaCl(s)$	∆ <i>H</i> _{eqn4} from (b)(i)
5	$Ca(g) \rightarrow Ca^{+}(g) + e^{-}$	$\Delta H_{eqn5} = +590$
6	$Ca^+(g) \rightarrow Ca^{2+}(g) + e^-$	$\Delta H_{\rm eqn6} = +1150$

Table 2.3

[3]

(c) Silver chloride, AgC*l*, and silver iodide, AgI, are sparingly soluble in water. Table 2.4 shows the solubility and the solubility products of AgC*l* and AgI at 298 K.

Table 2.4

salt	solubility / mol dm ⁻³	solubility product / mol ² dm ⁻⁶
AgC <i>l</i>	1.4 × 10 ⁻⁵	2.0×10^{-10}
AgI	8.9 × 10 ⁻⁹	8.0 × 10 ⁻¹⁷

(i) Explain, in terms of the interaction formed with water molecules, why the solubility of AgC*l* in water is higher than AgI.

(ii) When a precipitate is formed, ΔG_{ppt}^{e} , in J mol⁻¹, is given by the following expression.

 ΔG^{Θ}_{ppt} = 2.303 RT log K_{sp}

Use the data in Table 2.4 to calculate ΔG^{e}_{ppt} , in kJ mol⁻¹, for the formation of the precipitate AgC*l*(s).

[1]

(iii) The standard enthalpy change of formation of the precipitate AgC*l*(s) is $-66.0 \text{ kJ mol}^{-1}$. Use your answer in (c)(ii) to calculate $\Delta S^{\circ}_{\text{ppt}}$ for the formation of the precipitate AgC*l*(s).



[1]

(iv) Explain the significance of the sign in your answer in (c)(iii).

.....

(v) Explain how the solubility of AgCl(s) will change when the temperature is increased.

[Total: 20]

- **3** Biomolecules are compounds found in cells and living organisms. Biomolecules come in a wide range of sizes and structures, perform a vast array of functions, and are critical for healthy functioning of the human body.
 - (a) An important biomolecule is sucrose, otherwise known as table sugar. Sucrose is formed from two simple sugars: glucose and fructose. Other common sugars in our daily diet are lactose and maltose.



Sucrose is the standard to which all other sugars are compared for determining sweetness. To commercially determine sweetness in products such as ice-cream, relative sweetness (also known as theoretical sweetness) is first used to express sweetness of individual sugars relative to sucrose, which has a reference value of 1.

Table 3.1 shows the relative sweetness and prices of selected sugars.

sugar	sweetness relative to sucrose	estimated price in SGD / kg	price per unit of relative sweetness
Sucrose	1	_	_
Glucose	0.75	\$8.63	
Fructose	1.15	\$25.70	
Lactose	0.20	\$15.49	
Maltose	0.50	\$13.87	

Table	3.1
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*Source: Mullan, M. (n.d.). How do you get the sweetness of ice cream or gelato just right? https://www.dairyscience.info/index.php/ice-cream/220-ice-cream-sweetness.html#2

Overall relative sweetness of a food product such as ice-cream is calculated by first taking the relative sweetness of individual sugar and multiplying this value by their usage measured in grams per 100 grams of ice-cream mix. The relative sweetness of individual sugar used are then summed to give the overall relative sweetness of the food product.

(i) Calculate the overall relative sweetness of a 150 g serving of ice-cream that contains the following sugars by percentage mass.

3% sucrose, 7% glucose, 1.4% lactose and 8.5% maltose

[2]

(ii) To help control cost when producing their ice-cream products, manufacturers can adjust the ratio of the different sugars used. Manufacturers would calculate the price per unit of relative sweetness of individual sugar when making decision on how much of each sugar to use.

Complete Table 3.1 and hence explain why manufacturers would try to minimise use of lactose while maintaining overall relative sweetness in their products.

In a bid to help Singaporeans lead healthier lifestyle, the Health Promotion Board of Singapore has launched the Nutri-Grade mark to help consumers make more informed and healthier food choices. Fig. 3.1 shows the Nutri-Grade mark that is used to assign a grade to food product based on the total amount of sugar and saturated fat within the product.





Source: Measures for Nutri-Grade Beverages. (n.d.). Health Promotion Board. https://hpb.gov.sg/healthy-living/food-beverage/nutri-grade#

(iii) A student would like to determine the assigned grade for the serving of ice-cream in (a)(i) based on sugar content alone. Determine the Nutri-Grade for the serving of ice-cream, assuming that density of the ice-cream is 0.5 g ml⁻¹ and volume of ice-cream remains the same after melting.

[2]

(b) Sugars are sweet because they contain OH groups with a particular orientation that can interact with the taste receptors for sweetness in our tongue. Humans can recognise sweetness in about 1 or 2% sucrose solution.

After being consumed into the body, sucrose breaks down into simpler biomolecules, glucose and fructose. Glucose and fructose then pass through the intestinal wall and enter the bloodstream to be converted into energy or stored as fatty acids for later use.



(i) State the type of reaction that occurs when sucrose breaks down into glucose and fructose.

.....[1]

(ii) The flavour of food is due to a combination of aroma and taste sensations and no single molecule supplies it. Food scientists sometimes describe glucose and fructose as constituents of food which contribute to the taste but not the smell of food. Explain, in terms of structure and bonding, why this is so.

[2]

(iii) When Tollens' reagent is added to glucose solution placed in a test-tube and warmed gently, silver mirror is observed after some time. What does this suggest about the nature of glucose?

.....[1]

(c) Glucose exists in two different structures, α -glucose and β -glucose, that can achieve dynamic equilibrium after some time at a constant temperature.



When plane polarised light is passed through an aqueous solution of glucose, the angle of rotation is dependent upon the structure of the molecule present in the solution. A solution of pure α -glucose has a rotation of +113.4° and a solution of pure β -glucose has a rotation of +19.0°.

When 1 dm³ of freshly prepared α -glucose solution is left to stand at a constant temperature, the measured angle of rotation of plane polarised light gradually decrease to +52.2° and then stays unchanged.

(i) Explain what is meant by *dynamic equilibrium*.

[1]

(ii) Determine the percentage of the α -glucose left in the equilibrium mixture. Hence calculate the value for K_c for the interconversion of α -glucose to β -glucose.

[2]

(iii) State and explain the effect of increasing temperature on the composition of the equilibrium mixture.

[1]

(iv) The conversion of α -glucose to β -glucose is sped up by the presence of acids. A new sample of 1 dm³ freshly prepared α -glucose solution with some dilute sulfuric acid added is left to stand at a constant temperature. Suggest how the measurement of optical rotation in this new α -glucose solution would differ from a α -glucose solution with no acid added. Explain your answer.



(d) Amino acids are a class of biomolecules that serve as building blocks for proteins. The structures of two amino acids, aspartic acid and alanine, are shown.







Aspartic acid has pK_a values of 2.1, 3.9 and 9.8. Fig. 3.2 shows the graph obtained when protonated aspartic acid was titrated with sodium hydroxide.



Fig. 3.2

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(i) Complete Table 3.2 to show the major species present in the solution of aspartic acid at the following pH values.

рН 1	pH 7	pH 11

Table J.Z

(ii) From the graph in Fig. 3.2, suggest at which point, X, Y or Z, would the species present not move under the influence of an external electric field. Explain your answer.

	 	 	 [1]

(iii) Draw the structure of the dipeptide, asp-ala.

[1]

[2]

[Total: 20]

4 (a) Conjugate acid-base pairs differ from each other by one proton. Table 4.1 shows examples of conjugate acid-base pairs.

acid	conjugate base	$K_{\rm a}$ of acid / mol dm ⁻³	pK_b of conjugate base
H H H-C-C-OH H H	$ \begin{array}{cccc} H & H \\ $	1.26 × 10 ⁻¹⁶	
ethanol	ethoxide		
ОН	0-	1.12 × 10 ⁻¹⁰	
phenol	phenoxide		

Table 4.1

- (i) Complete Table 4.1 by calculating the pK_b values of ethoxide and phenoxide ions at 25 °C.
- (ii) Explain the difference in pK_b values of ethoxide and phenoxide ions.



(iii) Suggest why the hydrogen atom in the O-H bond of both ethanol and phenol is acidic but not the hydrogen atom in C-H bond.

.....

(b) The Michael reaction involves a carbonyl compound, such as ethanal, and an alkene of an α,β-unstaturated carbonyl compound, such as 2-methyl-4-hexen-3-one, as shown in Fig. 4.1. The reaction takes place with a small amount of CH₃CH₂O⁻Na⁺ at room temperature.



Fig. 4.1

The three stages of Michael reaction are described in Table 4.2.



Table 4.2

The enolate ion, **B**, can be represented by two different structures as shown in Fig. 4.2. The arrow \leftrightarrow indicates that the actual structure of the enolate ion is somewhere in between these two structures.



Fig. 4.2

(i) State the type of reaction shown in Fig. 4.1.

.....

(ii) D undergoes the Michael reaction to form E.



Suggest a possible structure of **D**.

[1]

(iii) Stages 1 and 2 are acid-base reactions.

State the type of acid-base behaviour shown by ethanal and ethoxide in stage 1, and enolate \bf{B} and 2-methyl-4-hexen-3-one in stage 2.

(iv) Alpha (α) hydrogens are hydrogen atoms bonded to carbon atoms adjacent to carbonyl functional groups.



With reference to Fig. 4.2, explain why the α hydrogen of ethanal is acidic.

 (v) Suggest two reasons why the α hydrogen of 3-aminopropanal is more acidic than ethanal.



- (vi) In Table 4.2, draw the mechanism for stages 2 and 3. Show all relevant lone pairs and the movement of electron pairs by using curly arrows.
- (vii) Using the concepts of electronegativity, electronic and steric effects, and delocalisation, suggest why enolate **B** reacts with the alkene carbon but not the carbonyl carbon in stage 2.

(viii)	Deduce if A in Fig. 4.1 formed via the mechanism in Table 4.2 shows any optical activity. Explain your answer.

 (c) An oxonium ion is a cation containing an oxygen atom that has three bonds and 1+ charge.

F is an example of oxonium ion and can be represented by two different structures as shown in Fig. 4.3.





(i) Suggest why **F** is more stable than **G**.

(ii) Explain why the oxygen atom in \mathbf{F} is sp² hybridised.



Fig. 4.4

(iii) In the mechanism of the reaction shown in Fig. 4.4, an oxonium ion is formed in one of the steps. Suggest the mechanism of the reaction shown in Fig. 4.4. Show all charges, relevant lone pairs and the movement of electron pairs by using curly arrows.

(iv) The reaction between **H** and $C_6H_5O^-Na^+$ proceeds by a similar mechanism. Suggest the effect on the rate of reaction if $CH_3CH_2O^-Na^+$ is replaced with $C_6H_5O^-Na^+$. Explain your answer.

.....

[Total: 24]

loses its optical activity at the end of the reaction.