ANDERSON SERANGOON JUNIOR COLLEGE

2022 JC 2 PRELIMINARY EXAMINATION

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CHEMISTRY

Paper 2 Structured Questions

9729/02 14 September 2022 2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number 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.

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

For Examiner's Use		
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This document consists of 21 printed pages and 3 blank pages.

Answer **all** the questions.

- 1 (a) Calcium, magnesium, and zinc are three minerals that are vital to several bodily processes. Though they occur naturally in a variety of food, many people take supplements that contain these minerals usually found in the +2 oxidation state.
 - (i) State and explain how the second ionisation energy of calcium compares with that of magnesium.

(ii) By quoting relevant data from the *Data Booklet*, suggest how the thermal stability of ZnCO₃ compares with that of MgCO₃ and CaCO₃. Explain your answer.

- (b) Beryllium exhibits physical and chemical properties that are anomalous to the rest of the Group 2 alkaline earth metals. Due to the similarities in electronegativity, beryllium shares many physical and chemical properties with aluminium in Group 13 instead.
 - (i) Beryllium forms a complex ion in aqueous solutions with the following structure, $[Be(H_2O)_4]^{2+}$.

Suggest an equation to show the hydrolysis of beryllium ions in water.

.....[1]

(ii) Beryllium oxide is amphoteric.

Write two chemical equations, with state symbols, showing its reaction with aqueous NaOH and dilute HC*l* respectively.

.....[2]

(iii) Explain why beryllium chloride is not ionic.

.....[1]

(iv) When beryllium chloride is heated, it sublimes and forms gaseous Be₂Cl₄ dimers.



By considering the numbers and type of electron pairs, explain the change in shape and bond angle about the Be atom during the dimerisation of beryllium chloride.

 	 	 [2]

[Total: 10]

(a) Both lactic acid, CH₃CH(OH)CO₂H, and ethanoic acid are colourless liquids at 298 K.

Lactic acid dissociates in water to form its conjugate base, lactate ion CH₃CH(OH)CO₂⁻.

 $CH_3CH(OH)CO_2H + H_2O \implies CH_3CH(OH)CO_2^- + H_3O^+$

An intramolecular hydrogen bond can be formed in the lactate ion.

(i) Draw the structure of the lactate ion showing the intramolecular hydrogen bond formed.

[1]

(ii) Hence, suggest how the K_a of lactic acid would differ from that of ethanoic acid. Explain your answer.

(b) Nicotinamide adenine dinucleotide (NAD⁺) is a coenzyme responsible for carrying electrons from one reaction to another in living cells.

The electrode potential for the reduction of NAD⁺ in a biological system, E(pH 7), in which the conditions are at 1 mol dm⁻³, 25 °C and pH 7, is as shown. The reduced form of NAD⁺ is represented as NADH.

NAD⁺ + H⁺ + 2e⁻
$$\implies$$
 NADH $E(pH 7) = -0.320 V$

The Nernst equation can be used to calculate the electrode potential of the above system when [NAD⁺] and [NADH] change.

$$E = E(pH 7) - (\frac{0.0592}{n}) \log_{10} \frac{[NADH]}{[NAD^+]}$$

where n is the number of moles of electrons transferred in the system.

(i) Using the Nernst equation given, determine the ratio $\frac{[NADH]}{[NAD^+]}$ when E = -0.350 V.

2

(ii) Hence, calculate the percentage of NAD⁺ in the NAD⁺–NADH mixture when E = -0.350 V.

[1]

During intense exercise where there is insufficient supply of oxygen, pyruvic acid, CH_3COCO_2H , is converted to lactic acid.

This process involves the conjugate bases of the two acids and the conversion of coenzyme NADH to NAD⁺, as shown below. The standard cell potential of this reaction is measured at 25 $^{\circ}$ C and pH 7.

 $\begin{array}{ll} \mathsf{CH}_3\mathsf{COCO}_2^- + \mathsf{NADH} + \mathsf{H}^+ \to \mathsf{CH}_3\mathsf{CH}(\mathsf{OH})\mathsf{CO}_2^- + \mathsf{NAD}^+ & E_{\mathsf{cell}}(\mathsf{pH}\ 7) = +0.135\ \mathsf{V} \\ \mathsf{pyruvate} & \mathsf{lactate} \end{array}$

(iii) Write the half-equation for the reduction of pyruvate to lactate in an acidic condition and calculate its standard electrode potential at 25 °C and pH 7.

(iv) Calculate $\triangle G$ for the anaerobic metabolism of pyruvate at pH 7.

[1]

(c) The standard enthalpy change of combustion of lactic acid can be represented as shown.

 $CH_3CH(OH)CO_2H(I) + 3O_2(g) \rightarrow 3CO_2(g) + 3H_2O(I)$

(i) What do you understand by the term *standard enthalpy change of combustion of lactic acid*?



(ii) Using the data in Table 2.1, calculate standard enthalpy change of combustion, ΔH_c^{o} , of lactic acid.

Table 2.1

Species	∆ <i>H</i> ^e _f / kJ mol⁻¹
CH ₃ CH(OH)CO ₂ H(I)	-483.2
CO ₂ (g)	-393.5
H ₂ O(I)	-285.8

[1]

(iii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of lactic acid.

[2]

(iv) Apart from average bond energy values found in the *Data* Booklet, suggest one other reason for the difference in your answers in (c)(ii) and (c)(iii).

.....[1] [Total: 12]

7 BLANK PAGE

3 (a) Methionine is an essential amino acid in humans. It plays a critical role in the metabolism and health of humans because it is the precursor of other amino acids such as cysteine and taurine.



Methionine

The p K_a values associated with methionine are 2.28 and 9.21.

(i) Calculate the pH of 0.15 mol dm⁻³ solution of methionine, ignoring the effect of the second pK_a value.

[1]

(ii) Draw the structure of the zwitterionic form of methionine.

[1]

(iii) Write two equations to describe how a solution containing the zwitterionic form of methionine can act as a buffer.

[2]

(iv) When 10 cm³ of 0.15 mol dm⁻³ of protonated methionine was titrated against aqueous sodium hydroxide, the first equivalence point was reached when 15 cm³ of the 0.10 mol dm⁻³ NaOH was added.

At the first equivalence point, only the zwitterionic form of methionine exists.

With the use of relevant equilibrium constant values, explain if the pH of the solution at the first equivalence point is less than, equal to or more than 7.

(v) Using the value and information from (a)(i) and (a)(iv), as well as the pK_a values provided, sketch the pH–volume added curve you would expect to obtain when 30 cm³ of 0.10 mol dm⁻³ NaOH is added to 10 cm³ of 0.15 mol dm⁻³ protonated methionine.

[2]

(vi) Suggest a suitable indicator for the first equivalence point in the above titration.

.....[1]

(b) Fig. 3.1 shows the four-step synthesis of an amino acid from an aldehyde, via an intermediate **G**.



Fig. 3.1

(i) State the types of reaction that occur during each of the steps 1 and 2.



(ii) Suggest the structure of compound **G**.

[1]

(iii) Draw the displayed formula of a suitable starting aldehyde that can be used to synthesise methionine.

[1]

(c) Chymotrypsin is an enzyme that hydrolyses proteins into smaller peptides and amino acids. It specifically hydrolyses the peptide bond on the carboxyl side of a residue that contains an aromatic ring. For example, the tripeptide J produces two compounds K and L as shown.



The following shows part of a short amino acid sequence found in human protein.



Draw the two dipeptides formed when the above amino acid sequence is hydrolysed by chymotrypsin.

[Total: 15]

4 (a) Table 4.1 shows the pK_a values for some chlorine-containing organic acids.

Table 4.1

acid	р <i>К</i> а
CH ₃ CHC/CO ₂ H	2.80
CH ₃ CCl ₂ CO ₂ H	1.74
CH ₂ C/CH ₂ CO ₂ H	X

(i) Explain the relative pK_a values of CH₃CHC*l*CO₂H and CH₃CC*l*₂CO₂H.

(ii) Suggest a value for *x* and explain your answer. [2]

(iii) An equilibrium is set up between CH₃CHC*l*CO₂H and CH₃CC*l*₂CO₂H in the aqueous medium.

 $\mathsf{CH}_3\mathsf{CHC}/\mathsf{CO}_2\mathsf{H} + \mathsf{CH}_3\mathsf{CC}/_2\mathsf{CO}_2^- \rightleftharpoons \mathsf{CH}_3\mathsf{CHC}/\mathsf{CO}_2^- + \mathsf{CH}_3\mathsf{CC}/_2\mathsf{CO}_2\mathsf{H}$

Using the data in Table 4.1, calculate K_c for the above equilibrium.

- 13
- (b) (i) The following reagents are added to separate samples of compound S.

Draw the structure of each of the organic products, T, U and V.



[3]

(ii) LiA/H₄ is a source of H⁻ and widely used as a reducing agent in organic chemistry.

Identify the functional group, other than alkane, in compound **S** that is not reduced by LiA/H_4 . Suggest why.

(iii) Determine the change in oxidation number of C^a when compound S is reduced to T.
[1]
[1]

14 BLANK PAGE **5** (a) The kinetics of the chlorination of methane is studied.

 $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

The first two steps of the mechanism of the reaction are shown below.

step 1
$$Cl_2 \stackrel{k_{\rm f}}{\underset{k_{\rm r}}{\longrightarrow}} 2Cl \bullet$$

step 2
$$Cl \bullet + CH_4 \xrightarrow{k_2} HCl + \bullet CH_3$$
 slow

(i) The rate equation for the reverse of step 1 is rate = $k_r [Cl \bullet]^2$.

At equilibrium, the rates of the forward and reverse reactions in step 1 are equal.

Write the rate equation for the forward reaction of step 1 and hence write an expression for the concentration of the intermediate $Cl \bullet$ radicals.

.....[2]

- (ii) Write the rate equation for the forward reaction of step 2.
 -[1]
- (iii) Use your answer to (a)(i) and the rate equation for step 2 to write the overall rate equation for the chlorination of methane.

Hence, deduce the orders of reaction with respect to the concentration of the species in the overall rate equation and the overall order of the reaction.

 (b) When chlorine and bromine react with methane, light of different energy and wavelength is required for stage 1 of the reaction.

stage 1
$$X_2 \rightarrow 2X \bullet$$
 $(X = Cl, Br)$

Light of longer wavelength is lower in energy than light of shorter wavelength.

This relationship between the energy and wavelength of light is shown in the equation below.

$$E = \frac{hc}{\lambda}$$

Where:

ere: *E* is the energy of the light of certain wavelength in Joule (J)

h is Planck constant = 6.63×10^{-34} J s

c is the speed of light = $3.00 \times 10^8 \text{ m s}^{-1}$

 $\boldsymbol{\lambda}$ is the wavelength of light in metre (m)

(i) Bond energy is the energy required to break **one mole** of a covalent bond in the gaseous state.

Using the *Data Booklet* and the equation $E = \frac{hc}{\lambda}$, determine the wavelength of light required to break **one** Cl-Cl bond.

Leave your answer in nanometres (nm). One nm is equivalent to 10^{-9} m.

[2]

(ii) Using Table 5.1, identify the colour of light that provides the minimum energy for the reaction between chlorine and methane.

Colour	Wavelength / nm
Violet	380 - 450
Blue	450 – 495
Green	495 – 570
Yellow	570 – 590
Orange	590 – 620
Red	620 – 750

.....[1]

(iii) Hence, explain why the bromination of methane can be carried out with yellow light. (Calculation is not required)

 	 [1]

(c) Fig. 5.1 shows four possible monohalogenoalkanes that can be formed from the reaction of 2-methylbutane with chlorine or bromine. (X = Cl or Br)



(i) State the expected ratio of products **A**, **B**, **C** and **D** in the mixture, assuming equal rate of substitution of all the H atoms.

```
.....[1]
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(ii) The ratio of the isomeric products is more accurately determined if the relative rates of substitution of different H atoms by different halogen atoms are taken into account.

The types of hydrogen atoms in alkanes, together with their relative rates of substitution by Cl and Br atom, are shown in Table 5.2.

Types of H atoms	Structure	Relative rate of substitution by C/ atom	Relative rate of substitution by Br atom
Primary	H 	1	1
Secondary	H 	3	80
Tertiary	R" R—C—H R'	5	1600

Table 5.2

By taking into account the relative rates of substitution of H atoms given above, show that:

- the monochlorinated forms of products **A**, **B**, **C** and **D** are formed in the ratio of 6:5:6:3.
- the monobrominated forms of products **A**, **B**, **C** and **D** are formed in the ratio of 6:1600:160:3.

(iii) 2-methylbutan-2-ol may be synthesised from 2-methylbutane by using the reaction scheme as shown.



Using the ratios given in (c)(ii), explain if chlorine or bromine is a better choice of reagent in this synthesis.

 [1]

(d) One of the possible termination steps in the free radical substitution reaction is the reaction between two alkyl radicals to form an alkane.

The equation shows the collision of two propyl radicals in the termination step of a reaction between propane and chlorine.

$$2 \bullet C_3 H_7(g) \rightarrow C_6 H_{14}(g)$$
 $\Delta S^{\circ} = -190 \text{ J K}^{-1} \text{ mol}^{-1}$

(i) Use the data in Table 5.3 to calculate the enthalpy change for this termination step at 298 K.

species	$\Delta H_{\rm f}^{\rm e}$ / kJ mol ⁻¹
•C ₃ H ₇ (g)	+103
C ₆ H ₁₄ (g)	-167

(ii) Explain how the values of △H^o and △S^o relate to the changes that occur at the molecular level for this termination step.
[2]
(iii) Calculate △G^o for this termination step at 298 K and explain the effect on the spontaneity of this reaction of increasing the temperature above 298 K.
[2]
[2]
(iii) Calculate 100 minutes in the temperature above 298 K.

[1]

6 (a) Iron(II) ions catalyse the reaction between iodide ions and peroxodisulfate ions $(S_2O_8^{2-})$ in aqueous solution.

 $S_2O_8^{2-}(aq) + 2I^{-}(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

(i) With reference to relevant E° values from the *Data Booklet*, show that the uncatalysed reaction between iodide ions and peroxodisulfate ions (S₂O₈²⁻) would occur.

[1]

(ii) Explain why the uncatalysed reaction between iodide ions and peroxodisulfate ions $(S_2O_8^{2-})$ is kinetically slow.

 	[1]

(iii) With the aid of a sketch of the Boltzmann distribution, explain why the addition of iron(II) ions speeds up this reaction.

 (iv) Explain why iron(II) ion is able to act as homogeneous catalyst while Ca²⁺ is unable to do so.

(b) Many iron-containing complexes are coloured. X and Y are two examples of such complexes.

The colour of a compound is due to the absorption of light at specific wavelengths. The colour observed is the complement of the colour absorbed.

Table 6.1 shows the colours absorbed for these two iron-containing complexes.

Table 6.1

iron complex	colour absorbed
X	red
Y	yellow

(i) Suggest the observed colours of X and Y.

(ii) Using the information provided in Table 5.1 on page 17, deduce the relative size of d-orbital splitting in the two iron complexes in Table 6.1.

.....[2]

[Total: 10]

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