

VICTORIA JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION Higher 1

CT GROUP **……………………………..**

CHEMISTRY 8873/02

2 hours

11 September 2018

Paper 2

Candidates answer on the Question Paper.

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in. Write in dark blue or black pen. You may use a soft pencil for any diagrams or graphs. Do not use staples, paper clips, glue or correction fluid.

Section A Answer **all** the questions.

Section B

Answer **one** question.

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

This document consists of **23** printed pages and **1** blank page.

Section A

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

1 (a) The graph below shows the third ionisation energies of the Period 3 elements from Na to C*l*.

(i) With the aid of an equation, define the 3rd ionisation energy of phosphorous.

It is the energy required to remove 1 mol of electrons from 1 mol of gaseous P^{2+} ions to form 1 mol of gaseous P^{3+} ions.

 $P^{2+}(q) \rightarrow P^{3+}(q) + e^{-}$

(ii) Explain why there is a general increase in the 3rd ionisation energies from phosphorous to chlorine.

Nuclear charge increases from phosphorous to chlorine due to an increase in number of protons. Shielding effect remains relatively constant from phosphorous to chlorine due to the same number of inner shell electrons. Hence, effective nuclear charge increases from phosphorous to chlorine.

More energy is required to remove the 3rd electron that is more strongly held by the nucleus.

[2]

[2]

(iii) Give the full electronic configuration of P2+.

P²⁺: 1s² 2s² 2p⁶ 3s² 3p¹

[1]

(iv) With reference to your answer from (a)(iii), explain why the 3rd ionisation energy of Si is higher than that of P.

Si²⁺: 1s² 2s² 2p⁶ 3s² P²⁺: 1s² 2s² 2p⁶ 3s² 3p¹ The removal of the $3rd$ electron from P is from the 3p subshell compared to the removal from the 3s subshell for Si.

 Since the 3p subshell is further away from the nucleus / is of higher energy, less energy is required to remove the $3rd$ electron from $P²⁺$.

[2]

(b) (i) Sketch a graph on the axes provided to show the pH of the solutions produced when the Period 3 chlorides (from Na to P) are added to excess water.

(ii) Nitrogen is in the same group as phosphorous in the Periodic Table. Suggest whether NCl₅ is able to exist.

NC*l*5 does not exist. N atom does not have energetically accessible vacant orbitals to expand its octet.

[1]

[2]

(iii) Arsenic is in the same group as phosphorous in the Periodic Table. With the aid of an equation, suggest the pH of the solution obtained when arsenic trichloride is added to excess water.

 $AsCl₃ + 3H₂O \rightarrow H₃AsO₃ + 3HCl$

 pH 2 AsC*l*3 undergoes complete hydrolysis in water to produce a strong acid, HC*l*. [*Accept pH 1‒3*]

[2]

(c) The boiling points of the two chlorides of phosphorous are shown in the table below.

(i) Explain the difference in boiling points between the two chlorides of phosphorous.

Due to the greater number of electrons in PC*l*5, more energy is required to overcome the stronger instantaneous dipole–induced dipole interactions in PC*l*5 compared to the permanent dipole–permanent dipole interactions in PC*l*3.

(ii) PC*l*3 is able to react with BF3. State the type of bond formed and draw a diagram to illustrate the shape of the product obtained.

4

[2]

- (d) In the solid state, PC l_5 exists as an ionic lattice with the formula $[PCl_4]^+ [PCl_6]^-.$
	- (i) State the shapes and bond angles of the $[PCI_4]^+$ and $[PCI_6]^-\text{ions}$.

[2]

(ii) Compare the lattice energy of [PC*l*4] +[PC*l*6] ‒ with that of NaC*l*. Explain your reasoning.

Since lattice energy $\propto \left| \frac{q^+q^-}{r^+q^-} \right|$ $\frac{q}{r^*+r}$ and all the ions are singly charged while the radii of [PC/₄]⁺ and [PC/₆]⁻ are larger than that of Na⁺ and C/[−], the lattice energy will be less exothermic for [PCl4]⁺[PCl₆][−].

[2]

[Total: 20]

- **2 (a)** 3–chloropropanoic acid, CH2C*l*CH2CO2H, is a weak Bronsted acid. Solution **A** is a 0.100 mol dm[−]3 CH2C*l*CH2CO2H solution. It has a pH of 2.49.
	- **(i)** Write the expression for the *K*a of 3–chloropropanoic acid, including the units.

CH₂C*l*CH₂CO₂H \Rightarrow CH₂C*l*CH₂CO₂⁻ + H⁺ $K_{a} = \frac{[CH_{2}C/CH_{2}CO_{2}][H^{+}]}{[CH_{2}C/CH_{2}CO_{2}H]}$ mol dm⁻³

[1]

(ii) Hence, calculate the p*K*a of 3–chloropropanoic acid.

Since pH = 2.49, $[H^+]$ = 10^{-2.49} $K_{\rm a} = \frac{[{\rm CH_2C} / {\rm CH_2CO_2}] [H^+]}{[{\rm CH_2C} / {\rm CH_2CO_2} H]}$

$$
= \frac{[10^{-2.49}][10^{-2.49}]}{[0.100]}
$$

= 1.05 × 10⁻⁴

$$
pK_a = -lg(1.05 × 10^{-4})
$$

= 3.98 [2]

5

(iii) When 25 cm3 of 0.0500 mol dm[−]3 KOH was added to 25.0 cm3 of solution **A**, a buffer solution is formed. With the aid of two equations, explain how the buffer solution is able to maintain a relatively constant pH.

When a small amount of acid is added, a large reservoir of CH₂CICH₂CO₂neutralises the acid to maintain a fairly constant pH. CH₂C*l*CH₂CO₂[−] + H⁺ → CH₂C*l*CH₂CO₂H

When a small amount of base is added, a large reservoir of CH₂C/CH₂CO₂H neutralises the base to maintain a fairly constant pH. CH₂C/CH₂CO₂H + OH[−] → CH₂C/CH₂CO₂[−] + H₂O

[3]

(b) 3–chloropropanoic acid can undergo a series of reactions as shown below.

- **(i)** Draw the full structural formula of compound **A** in the box. [1]
- **(ii)** State the reagents and conditions required for reactions **I**, **II** and **III**.

Reaction **I**:

reagents NaOH(alc) condition reflux Reaction **II**: reagents NaOH(aq) condition reflux Reaction **III**:

'unzipped' to form sheets of oxidised graphene as shown in **Figure 1**.

Single-walled

carbon nanotube

6

reagents $KMnO_4(aq)$ or $K_2Cr_2O_7(aq)$, H₂SO₄(aq)

condition reflux [*Allow heat*]

(iii) Draw the structure of one repeat unit of the polymer **B**.

[1]

[3]

(iv) Suggest the structural formula of compound **C**.

[1]

[Total: 12]

3 (a) Single–walled carbon nanotubes behave like cylindrical graphene. Multi–walled carbon nanotubes consist of multiple–rolled layers of graphene.

(i) Plastic is a good replacement for steel because of its low cost. The insertion of carbon nanotubes into plastic has made it at least 10 times stronger than steel.

Describe the structure and bonding of a carbon nanotube. Hence, explain whether a single–walled carbon nanotube or a multi–walled carbon nanotube has higher tensile strength.

Multi-walled

carbon nanotube

Single–walled carbon nanotube is made up of a single layer of carbon atoms, arranged in a hexagonal network with each carbon atom covalently bonded to three other carbon atoms.

 Multi–walled carbon nanotube has higher tensile strength as it has more covalent bonds that need to be broken due to the multiple walls of cylindrical graphene.

(ii) Similar to graphene, carbon nanotubes conduct electricity. They can be

[2]

7

Figure 1

The 'unzipping' of a carbon nanotube to form oxidised graphene at the molecular level is shown in **Figure 2** below.

With reference to **Figures 1** and **2**, explain whether sheets of oxidised graphene can conduct electricity.

The p–orbitals on the carbon atoms in oxidised graphene overlap sideways to form a continuous pi–electron cloud / allow delocalisation of pi–electrons, where the electrons act as mobile charge carriers.

[2]

(iii) We can obtain a sheet of graphene by reduction of oxidised graphene, only if the width is less than 50 nm.

Currently, it is not possible to produce very large sheets of graphene. Suggest how the edges of the graphene sheet pose difficulties to the production of large sheets of graphene.

Edges have carbon atoms that are not fully bonded / edges may curve upwards or downwards causing areas of graphite / multilayer structure formed.

[1]

(b) Geckos are lizards with the remarkable ability to scamper up walls. A shortcoming of synthetic gecko–inspired fibres is that it cannot operate on both wet and dry surfaces.

Researchers have created 'geckel' which is an array of high silicone pillars sitting on a solid substrate. Each cylindrical pillar has dimensions of 400 nm in diameter and 600 nm in height. The surfaces of the pillars are coated with a synthetic adhesive polymer, poly[3,4–dihydroxystyrene]–co–styrene], as shown below. 'Geckel' can be used to create wall–climbing robots.

8

(i) Explain whether each silicone pillar can be considered as a nanomaterial.

No, since each cylindrical pillar has dimensions of 400 nm in diameter and 600 nm in height. Nanomaterials have at least one dimension within the range of 1 nm to 100 nm.

(ii) A wall has been painted with a paint comprising of a mixture of hydrocarbons while another wall has been painted with a paint comprising of a polymer, poly(ethylene oxide).

$$
H_{\uparrow}^{\perp}OCH_{2}CH_{2}^{\perp}OH
$$
\npoly(ethylene oxide)

Explain how the silicone pillars and synthetic adhesive polymer of 'Geckel' enable a wall–climbing robot to support its own weight on both types of paint surfaces.

The silicone pillars of 'Geckel' have large surface areas that are able to come into close contact with the wall surface.

 The molecules of the synthetic adhesive polymer are able to stick to the wall surface through instantaneous dipole–induced dipole interactions for the wall painted with hydrocarbons and hydrogen bonding for the wall painted with poly(ethylene oxide).

[2]

[1]

[Total: 8]

4 (a) The two most common types of nylons used in textile and plastic industries are nylon−6 and nylon**–**6,6. The structure of nylon−6,6 is shown below.

nylon-6,6

(i) Define the term *polymer*.

Polymer is a macromolecule made from monomers with average molecular mass of at least 1000 or at least 100 repeat units.

[1]

(ii) Ropes made of nylon−6,6 are chosen for its high tensile strength. Ropes made from polyesters such as poly(ethylene terephthalate) (PET) are about 90% as strong as that of nylon−6,6.

With the aid of a diagram, showing relevant interactions, explain why nylon−6,6 is stronger than polyester.

There are stronger hydrogen bonds in between nylon polymer chains as compared to permanent dipole–permanent dipole interactions in polyester chain.

[3]

(iii) Rust or grout on toilet tiles can be removed by spraying the tiles with a rust remover (**Figure 3**) before scrubbing the tiles with a brush. Explain whether a brush with nylon bristles or high density poly(ethene) bristles should be used for the scrubbing.

Figure 3

A brush with high density poly(ethene) bristles should be used. The acid would cause hydrolysis of the amide linkage in nylon bristles while poly(ethene) bristles are unaffected.

[2]

(iv) State whether nylon−6,6 is classified as a thermoplastic or thermoset. Hence, explain whether it can be recycled.

Nylon–6,6 is a thermoplastic which is recyclable. It melts upon heating as the hydrogen bonds between the chains can be broken. [2]

(b) Cavone is found in the oils of spearmint. It undergoes a Wittig reaction to yield the monomer, MIMC, which could undergo polymerisation with monomer **X** to form polymer **A**.

(i) State the type of polymerisation that has occurred to form polymer **A**. Hence, draw the constitutional formula of monomer **X**.

[2]

 (ii) Explain why polymer **A** has a more rigid structure as compared to nylon−6,6 in **(a)**.

Polymer A contains C=C double bonds which can crosslink between the polymer chains through covalent bond formation.

[1]

Carvone can also be transformed into dihydrocarvide which undergoes a series of steps to form polymer **B**.

(iii) Write an equation for the base hydrolysis of dihydrocarvide.

(iv) Infra–red spectroscopy can be used to identify functional groups present in organic compounds. For example, the ketone functional group of carvone shows an absorption signal at 1670–1740 cm[−]1.

Polymer **B** shows the following infra-red absorption signals at 1635–1690 cm⁻¹, 1050–1330 cm[−]1 and 1730–1750 cm[−]1.

With reference to the *Data Booklet*, identify the bonds that correspond to the above infrared absorptions.

[1]

(v) With the aid of an equation, define the *enthalpy change of combustion* of carvone, $C_{10}H_{14}O$.

The enthalpy change of combustion is the energy released when one mole of carvone

 is completely burnt in excess oxygen under standard conditions of 298 K and 1 bar.

 Equation: $CH₃$ $10CO₂(q) + 7H₂O(l)$ $130₂(q)$ H_3C `СН. **[***Accept C10H14O used in the balanced equation***]**

[2]

(vi) Draw the structure of compound **Z** in the box for the following synthesis. State the reagents and conditions for step **I** and step **II**.

(vii) Only one of the C=C bonds in the isomer of carvone exhibits *cis–trans* isomerism. Draw the skeletal structures of the *cis–trans* isomers.

trans

[2]

[Total: 20]

cis

12

Section B

Answer **one** question from this section, in the spaces provided.

5 (a) Phosphine has the chemical formula PH3. The kinetics of the reaction between phosphine and sodium chlorate(I) can be investigated by the following method.

(i) Determine the order of reaction with respect to PH3 and NaC*l*O.

Comparing experiments 1 and 3, when the concentration of PH_3 is doubled, the rate of reaction is also doubled. Hence, the order of reaction with respect to PH_3 is 1.

Comparing experiments 2 and 3, $\frac{\text{rate}_2}{\text{rate}} = \frac{\text{[PH}_3]^1 \text{[NaClO]}^x}{\text{max}_{1 \le i \le n} \text{max}_{2 \le i}}$ rate₃ [PH₃]¹[NaC/O]^x $\frac{3.58}{7.36} = \frac{(0.14)^{1}(5.70)^{x}}{(0.48)^{1}(3.50)^{x}}$ $(0.48)^{1}(3.50)^{x}$ Hence, the order of reaction with respect to NaC*l*O is 1. [2]

(ii) Write the rate equation for this reaction.

Rate = *k*[PH3][NaC*l*O]

 $[1]$

(iii) Determine the rate constant for experiment 1 and state its units.

Rate = *k*[PH3][NaC*l*O] 3.68 = *k*(0.24)(3.50) $k = 4.38$ Unit = mol^{-1} dm³ s⁻¹

[2]

(iv) Calculate the initial rate of formation of NaC*l* when the initial concentrations of PH₃ and NaC*l*O are 0.36 mol dm⁻³ and 2.50 mol dm⁻³ respectively.

Initial rate of formation of NaC*l* $= 2 \times$ initial rate of disappearance of PH₃ $= 2 \times 4.38(0.36)(2.50)$ $= 7.88$ mol dm⁻³ s⁻¹

[1]

(v) Determine the concentration of NaC*l* produced after two half-lives for experiment 1.

[NaC*l*]max $= 0.24 \times 2$ $= 0.480$ mol dm⁻³ [NaC*l*] after two half-lives $= 0.75 \times 0.480$ $= 0.360$ mol dm⁻³

[2]

(b) The Appel reaction is used to convert alcohols to alkyl halides while triphenylphosphine, PPh₃, is oxidised to triphenylphosphine oxide, O=PPh₃.

Ph in PPh₃ and O=PPh₃ is a phenyl group, which remains unchanged after the reaction.

$$
PPh_3 + CBr_4 + CH_3CH_2OH \rightarrow O=PPh_3 + CHBr_3 + CH_3CH_2Br
$$

(i) With reference to the *Data Booklet*, calculate the enthalpy change for this reaction.

∆*H* = ΣBE(reactant) – ΣBE(product) $=$ [BE(C–Br) + BE(C–O) + BE(O–H)] – [BE(P=O) + BE(C–H) + BE(C–Br)] $= (280 + 360 + 460) - (540 + 410 + 280)$ = –130 kJ mol[−]¹

 (ii) Using bond energy values from the *Data Booklet*, explain why the rate of reaction is slower when CCl₄ is used in place of CBr₄.

B.E.(C–C*l*) = 340 kJ mol⁻¹ > B.E.(C–Br) = 280 kJ mol⁻¹ Thus, more energy is needed to break the C‒Br bond leading to larger *E*a and slower rate of reaction.

[2]

[2]

(iii) Triphenylphosphine. PPh3 can also be oxidised by oxygen to form triphenylphosphine oxide, $O=PPh_3$ with the use of a catalyst [MoO2C*l*2(DMSO)2].

With the aid of a Maxwell–Boltzmann distribution diagram, explain how the addition of a catalyst speeds up the rate of reaction.

(c) In a titration experiment, 0.100 mol dm[−]**³** NaOH was added to 15.0 cm3 of phosphoric acid as shown below.

15

Phosphoric acid is a tribasic acid, and it dissociates into $PO₄³⁻$ in three steps as shown below.

(i) Calculate the concentration of the phosphoric acid.

Amount of phosphoric acid required $= 0.100 \times 20 \times 10^{-3}$ = 0.00200 mol $[H_3PO_4]$ $= 0.00200 \div (15.0 \times 10^{-3})$ = 0.133 mol dm[−]³

[1]

(ii) With reference to the titration curve and **(c)(i)**, suggest whether phosphoric acid is a weak or strong acid.

For $H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$ From the graph, initial $pH = 1.5$.

 $[H^+] = 10^{-1.5} = 0.0316$ mol dm⁻³ $[H^+]$ < $[H_3PO_4]$

H3PO4 is a weak acid as it dissociates partially.

[2]

(iii) Arrange the three *K*a values of phosphoric acid in decreasing order of acidity. Explain your answer.

*K*a1 > *K*a2 > *K*a3 It is more difficult to remove a positively charged proton from an ion of increasing negative charge, leading to a lower extent of dissociation.

OR The H⁺ ion produced from the first dissociation suppress the subsequent dissociation, leading to a lower extent of dissociation.

[2]

(iv) The table below lists some common indicators found in the college laboratory. With reference to the given titration curve for phosphoric acid, suggest an indicator to detect the second end–point. Hence, state the colour change of your chosen indicator at the second end-point of the titration.

Thymolpthalein

Colour changes from colourless to blue.

[1]

[Total: 20]

- **6 (a)** During an experiment, a student added 3.00 g of solid KOH to 100 cm3 of 1.00 mol dm⁻³ HNO₃ solution. The initial temperature of the HNO₃ solution was 29.2 °C and the highest temperature recorded was $36.5 \,^{\circ}\text{C}$.
	- **(i)** Define the *standard enthalpy change of neutralisation,* Δ*H*^o *neut*.

The energy released when one mole of water is formed when an acid neutralises a base, under standard conditions of 298 K and 1 bar.

[1]

(ii) Calculate the Δ*H*neut of this reaction. You may assume that 4.18 J of energy is required to raise the temperature of 1 g of the solution by 1 \degree C.

 $KOH + HNO₃ \rightarrow KNO₃ + H₂O$

Amount of KOH $= 3.0 \div (39.1 + 16.0 + 1.0)$ $= 0.0535$ mol

Amount of HNO₃ $= 1.00 \times 100 \times 10^{-3}$ = 0.100 mol

 Amount of water formed $= 0.0535$ mol Heat evolved $=$ mc ΔT $= (100)(4.18)(36.5 - 29.2)$ $= 3051.4$ J Δ*H*neut $= -(3051.4) \div 0.0535$ $= -57004$ J mol⁻¹ (negative sign and units) $= -57.0$ kJ mol⁻¹

[2]

(b) Compressed Natural Gas (CNG) has been used as a fuel for vehicles in Singapore since 2001 because it releases less air–borne pollutants. Together with the mandatory catalytic converters installed in vehicles, this helps to maintain the high air quality that Singapore enjoys.

The reaction below takes place in the catalytic converter and it is catalysed by a rhodium catalyst.

$$
2CO(g) + 2NO(g) \rightarrow N_2(g) + 2CO_2(g) \qquad \Delta H < 0
$$

(i) Draw energy profile diagrams for both the catalysed and uncatalysed reactions on the axes below. Label on the diagrams the axes, Δ*H*, activation energies for both the catalysed $(E_a(\text{cat}))$ and uncatalysed (E_a) reactions.

[2]

(ii) Explain in terms of collision theory, how the addition of a catalyst increases the rate of reaction.

A catalyst provides an alternative pathway with a lower activation energy for the reaction. There are more molecules with energy greater than *E*a(cat), leading to a greater frequency of effective collisions.

[1]

(iii) Explain the mode of action of the rhodium catalyst in this reaction.

17

The type of catalysis is heterogeneous catalysis. Adsorption of reactant molecules by forming weak bonds with active sites. This weakens the covalent bonds in the molecules. The surface concentration of reactants increases and reactants have the correct orientation for reaction to occur. After reaction, the products desorb from the surface.

[3]

(c) Natural gas has many impurities such as CH₄ and H₂S, which can react according to the following equilibrium.

$$
CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)
$$

2.0 mol of CH₄, 4.0 mol of H₂S, 2.0 mol of CS_2 and 6.8 mol of H₂ were allowed to reach equilibrium in a 250 cm³ vessel at 800 \degree C. The equilibrium concentration of CH₄ was found to be 3.4 mol dm⁻³.

(i) Calculate the value of K_c , include the units in your answer.

$$
K_{c} = \frac{[CS_{2}][H_{2}]^{4}}{[CH_{4}]H_{2}S]^{2}}
$$

=
$$
\frac{(12.6)(45.6)^{4}}{(3.4)(6.8)^{2}}
$$

= 3.47 × 10⁶ mol² dm⁻⁶

[2]

(ii) Define *Le Chatelier's Principle*.

Le Chatelier's Principle states that when a system at equilibrium is disturbed, the system will counteract the change imposed by shifting the position of equilibrium

in a direction that tends to reduce that change, so as to re–establish the equilibrium.

[1]

(iii) Explain how the position of equilibrium would be affected if the volume of the vessel is changed to 500 cm3.

When the volume of the vessel is doubled, the total pressure is halved. Hence, by Le Chatelier's Principle, the system will counteract the decrease in pressure by favoring the forward reaction to increase the total number of gaseous molecules. The position of equilibrium shifts to the right.

[2]

(iv) Explain how the position of equilibrium would be affected if a catalyst was introduced into the vessel.

A catalyst increases the rates of the forward and backward reactions to the same extent, there will be no shift in the position of equilibrium.

(d) Hydrogen peroxide and iodide ions react in an acidic medium to form water and iodine as shown below.

$$
H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2
$$

The rate of reaction is monitored by measuring the amount of iodine produced with time. The concentration of H_2O_2 remaining is then calculated as shown in the table below.

(i) Plot a graph of [H2O2] against time on the axes below. Hence, determine the order of reaction with respect to $[H_2O_2]$.

Since the three half–lives are approximately constant \approx 325 s, the order of reaction with respect to $[H_2O_2]$ is one.

[3]

(ii) Use the graph to determine the initial rate of the reaction.

Initial rate
= -gradient of tangent at t = 0
=
$$
\frac{0.0200 - 0}{0.460}
$$

= 4.35 × 10⁻⁵ mol dm⁻³ s⁻¹

[2]

[Total: 20]

End of Paper