JURONG PIONEER JUNIOR COLLEGE JC2 PRELIMINARY EXAMINATION 2020

CHEMISTRY

Higher 2

Paper 3 Free Response

22 September 2020 2 hours

9729/03

Candidates answer on question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number 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, graphs. Do not use staples, paper clips, glue or correction fluid.

Section A Answer all questions.

Section B Answer one question.

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.

This document consists of 30 printed pages.

2

Section A

Answer all the questions in this section.

1

(a) In a bromine "clock" reaction, solutions of bromate(V) ions, bromide ions, bromine and acid are mixed together with a few drops of red methyl orange.

There are two reactions occurring in the reaction mixture.

 $BrO_3^{-}(aq) + 5Br^{-}(aq) + 6H^{+}(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$ Reaction I $Br_2 + phenol \rightarrow brominated compound$ Reaction II

When a small but constant amount of phenol is added to the reaction mixture, the bromine being slowly produced by reaction I will immediately react with phenol in reaction II, until all the phenol has been used up.

At that point, free bromine will be present in the solution, which will cause a sudden decolourisation of red methyl orange.

| Expt | Volume of 0.350 mol dm ⁻³ KBrO ₃ / cm ³ | Volume of 0.650 mol dm ⁻³ KBr / cm ³ | Volume of 0.250 mol dm ⁻³ H_2SO_4 / cm ³ | Volume of deionised water / cm ³ | Time taken for methyl orange to decolourise /s |
|------|--|--|--|--|--|
| 1 | 5.0 | 5.0 | 10.0 | 10.0 | 82 |
| 2 | 10.0 | 5.0 | 10.0 | 5.0 | 42 |
| 3 | 10.0 | 10.0 | 5.0 | 5.0 | 83 |
| 4 | 5.0 | 5.0 | 20.0 | 0 | 21 |

The time taken for the red methyl orange to decolourise were recorded below.

(i) Explain why the amount of phenol is kept constant in each experiment.

As we are measuring the time taken for a <u>fixed same amount of Br_2 to</u> be used up for the reaction with phenol, so the amount of phenol must be kept constant.

This time is related to the relative rate, $Rate \propto \frac{1}{time}$

(ii) Deduce the order of reaction with respect to [Br⁻], [BrO₃⁻] and [H⁺], explaining your reasoning clearly.

[4]

[1]

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Since <u>total volume of reaction mixture is constant</u>, <u>volume of</u> <u>reactant∞concentration</u> of reactant in the reaction mixture.

Eg. Volume of $KBrO_3 \propto [KBrO_3]$

Rate
$$\propto \frac{1}{time}$$

<u>Comparing expts 1 and 2, [KBr] and $[H_2SO_4]$ are constant, when [KBrO₃] doubled, rate (∞ 1/t) doubled. Thus the reaction is <u>first order w.r.t</u> [KBrO₃].</u>

<u>Comparing expts 1 and 4</u>, [KBrO₃] and [KBr] are constant, when [H₂SO₄] doubled, rate (∞ 1/t) increased by 4 times. Thus the reaction is second order w.r.t [H₂SO₄].

Comparing expts 2 and 3,

Mathematical method

Let a = order of reaction w.r.t [KBr]

 $\frac{[\text{Rate}]_{\text{expt 2}}}{[\text{Rate}]_{\text{expt 3}}} = \frac{[\text{KBrO}_3]^1_{\text{expt 2}} [\text{KBr}]^a_{\text{expt 2}} [\text{H}^+]^2_{\text{expt 2}}}{[\text{KBrO}_3]^1_{\text{expt 3}} [\text{KBr}]^a_{\text{expt 3}} [\text{H}^+]^2_{\text{expt 3}}}$

$$\frac{\frac{1}{42}}{\frac{1}{83}} = \frac{(10)^{1}(5)^{a} (10)^{2}}{(10)^{1}(10)^{a} (5)^{2}}$$

<u>a = 1</u>

(iii) Write a rate equation for the reaction.

Rate = $k[BrO_{3^{-}}][Br^{-}][H^{+}]^{2}$

(iv) Reaction of bromate(V) ions with bromide ions in acidic solution is thought to proceed via the following reaction mechanism:

| step 1: | H⁺ + Br⁻ | fast |
|---------|--|------|
| step 2: | H^+ + $BrO_3^- \rightleftharpoons HBrO_3$ | fast |
| step 3: | $HBr \ + \ HBrO_3 \ \rightarrow \ HBrO \ + \ HBrO_2$ | slow |
| step 4: | $HBrO_2 + HBr \rightarrow 2HBrO$ | fast |
| step 5: | $HBrO \ + \ HBr \ \rightarrow \ H_2O \ + \ Br_2$ | fast |
| | | |

Explain if this reaction mechanism is consistent with the experimentally determined rate equation.

[1]

[1]

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<u>Yes and explanation that intermediate cannot appear in rate equation</u> and the <u>intermediate concentration</u> ([HBr], [HBrO₃]) has to be expressed in terms of the concentrations of the reactants that form it in the previous step.

For the slow step, rate = $k[HBr][HBrO_3]$ --- (*)

From Step 1,
$$K_1 = \frac{[HBr]}{[H^+][Br^-]} \Rightarrow [HBr] = K_1[H^+][Br^-] -- (1)$$

From Step 2, $K_2 = \frac{[HBrO_3]}{[H^+][BrO_3^-]} \Rightarrow [HBrO_3] = K_2[H^+][BrO_3^-] --(2)$

Sub (1) and (2) into (*):

Thus, rate = $k K_1 K_2 [H^+][H^+][Br^-][BrO_3^-] \Rightarrow$ rate = $k_{overall}[H^+]^2[Br^-][BrO_3^-]$

(b) 4-nitrophenol is used to synthesise a derivative of phenacetin, a pain-relieving and fever-reducing drug. In step IV, compound C reacts with phosgene, COCl₂. You may assume that –OCH₂CH₃ is inert.



- Suggest reagents and conditions for step III.
 Step III: <u>Sn, concentrated HCl, heat, followed by NaOH(aq)</u>
- (ii) Suggest why it is necessary to convert 4-nitrophenol to compound A before step II is carried out

To convert <u>phenol to phenoxide a stronger nucleophile</u> to react with halogenoalkane in step II via nucleophilic substitution.

(iii) In step IV, compound C and phosgene reacted in 1:1 molar ratio to form compound D, which has the molecular formula of $C_9H_{10}C/NO_2$. Draw the structure of D.



[1]

[3]

[1]

[1]

(iv) Name and draw the mechanism of the reaction between chloroethane and compound **A** in step **II**.

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For

5

Nucleophilic substitution (S_N2)

Penalty for:

- Missing lone pair
- Missing delta positive and negative charge
- Wrong arrows
- No 3-D/ inversion shown
- Missing by-product
- Wrong product



(v) Compare the reactivities of chloroethane, CH₃CH₂C*l* and ethanoyl chloride, CH₃COC*l* with water. Explain your answer.

Comparing CH₃COC*l* with CH₃CH₂C*l*:

CH₃COC*I*, which is an acyl chloride, undergoes hydrolysis to give CH₃COOH and HC*I*(aq).

- The <u>C atom in -COCl of CH₃COCl is highly electron-</u> <u>deficient</u> or <u>delta positive</u> as it is <u>bonded to two</u> or <u>more</u> <u>electronegative atoms</u> (O and Cl)
- making <u>CH₃COC1 more reactive</u> towards attack by H₂O nucleophile.

CH₃CH₂Cl reacts with H₂O only upon heating

Reactivities: $CH_3COCl > CH_3CH_2Cl$

(c) (i) Use the data in Table 1 to calculate the enthalpy change for the reaction that forms gaseous phosgene, $COCl_2$, ΔH_1 .

$$CO + Cl_2 \rightarrow COCl_2 \quad \Delta H_1$$

| Table 1 | | | |
|-------------|---|--|--|
| compound | $\Delta H_{\rm f}/~{\rm kJ}~{\rm mol}^{-1}$ | | |
| CO(g) | -110 | | |
| $COCl_2(g)$ | -220 | | |

[1]

[1]

 $\Delta H = \Sigma(n\Delta H_{\text{formation}} \text{ products}) - \Sigma(m\Delta H_{\text{formation}} \text{ reactants})$

= -220 - (-110)

<u>= -110 kJ mol⁻¹</u>

(ii) Use the bond energies data in the *Data Booklet* to calculate the enthalpy change of the above reaction, ΔH_1 .

[1]

 $\Delta H = +n\Sigma B.E \text{ bonds broken in reactants - } m\Sigma B.E \text{ bonds formed in products}$ $\Delta H_1 = [BE(C=O) + BE(C$ *l*-C*l*)] - [1BE(C=O) + 2BE(C-C*l*)] --(1)Enthalpy change of reaction = 1077 + 244-[740+2(340)] = -99.0 kJ mol⁻¹

(iii) Suggest a reason for the difference in the values obtained in (c)(i) and (c)(ii).
 The bond energy values in Data Booklet are average values and not the

The bond energy values in Data Booklet are average values and not the true bond energies present in phosgene.

(d) (i) Phosgene reacts with NaOH(aq). It is suggested that the reaction occurs in two stages.

$$\operatorname{COC}_{l_2} \xrightarrow{\operatorname{OH}} \operatorname{COC}_l(\operatorname{OH}) \xrightarrow{\operatorname{Stage 2}} \operatorname{CO}_2 + \operatorname{HC}_l$$

What type of reaction is occurring in stage 1 and stage 2?

[2]

[1]

Stage1:NucleophilicacylsubstitutionReject Nucleophilic substitution

Stage 2: Elimination

(ii) Suggest the structural formula of the organic compound formed when phosgene reacts with methanol.

$$O \rightarrow OCH_3$$
 or $O \rightarrow OCH_3$
 $Cl \rightarrow OCH_3$

[1]

[Total: 20]

2 (a) Direct-methanol fuel cells or DMFCs are a subcategory of proton-exchange fuel cells in which methanol is used as the fuel.

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Direct-methanol fuel cell

 $E^{\oplus}(CO_2 | CH_3 OH) = -0.37 V$

The DMFC relies upon the oxidation of methanol on a catalyst layer. Water and methanol are supplied into the anode. Carbon dioxide is produced.

Air is pumped into the cathode and water is produced at 25°C.

(i) Construct equations for the reactions at the cathode and anode that make up this fuel cell. Hence, write the overall equation for the reaction that occurs in the cell when a current is allowed to flow.

[3]

[1]

Anode: $\underline{CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-}$ Cathode: $\underline{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$ (full arrow) $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$

- (ii) Using data from the *Data Booklet* and the data above, calculate E^{e}_{cell} of the reaction.
- $E^{\bullet}_{cell} = E^{\bullet}_{cathode} E^{\bullet}_{anode} = +1.23 (-0.37) = +\underline{1.60 \text{ V}} \text{ or } +1.6\text{ V} \text{ (exact)}$ (iii) Suggest why the actual e.m.f is lower than what was calculated in (a)(ii). [1] $O_2 + 4H^+ + 4e^- \iff 2H_2O \qquad E^\circ = +1.23\text{ V eqm }^*$

To calculate for **(ii)** was to assume using 1 bar of O_2 but concentration of O_2 is lower than 1 bar in air, equilibrium * shifts to left. $E(O_2/H_2O)$ will be less positive. E_{cell} becomes less positive.

- (iv) Calculate a value of ΔG° for the cell reaction, using your answers in (a)(i) and (ii). [2] $\underline{n = 12 [1]}$ $\Delta G^{\circ} = -nFE^{\circ}_{cell} = -(12 \times 96500 \times 1.6) = -1852.8 = -1850 \text{ kJ mol}^{-1}$ (with
- (v) Suggest a possible advantage of using the methanol fuel cell compared to a hydrogen fuel cell. Liquid methanol takes up less storage space/ is easier to transport/ does not need to keep under pressure as compared to gaseous hydrogen [1]

[1]

correct units)

(b) The use of the Data Booklet is relevant to this question.

When M^{2+}/M half-cell was connected to standard hydrogen electrode (S.H.E), electrons flow from half-cell of M^{2+}/M to standard hydrogen electrode. It was found that the E^{e}_{cell} was +0.26 V.

Draw a fully labelled diagram of how you would determine the standard electrode potential of the $M^{2+}(aq) \mid M(s)$ electrode system. Indicate the cathode and anode on your diagram. Hence, deduce the standard reduction potential of M^{2+} M.



Standard conditions Labelled diagram with salt bridge & inert electrode Label Pt as cathode, M as anode

 $E^{\text{o}}_{\text{cell}} = E^{\text{o}}_{\text{cathode}} - E^{\text{o}}_{\text{anode}} = (0.00) - (-0.26) = +0.26V$ $E^{\text{o}}(\mathsf{M}^{2+}/\mathsf{M}) = -0.26V$ [4]

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(c) Lithium metal reacts with bromoalkanes to give organolithium compounds.

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The carbon-lithium covalent bond in organolithium compounds is polarised ⁶⁻C-Li⁶⁺. These compounds are useful carbon nucleophiles. They react with carbonyl compounds to give lithium alkoxides, which produce alcohols on treatment with dilute acid.



(R is alkyl; R' and R'' are either alkyl or H)

For example, butan-1-ol, can be synthesised from 1-bromopropane and methanal.



The flow-scheme below outlines a synthetic pathway to form compound **U**.



- (i) Suggest the name of reaction for step 1. Nucleophilic addition
- (ii) Draw alcohol R and label with asterisk, *, on the carbon(s) that is/are chiral.

[1]

10



(iii) Deduce the structures of a suitable bromoalkane and a suitable carbonyl compound to synthesise alcohol **R**.

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- RBr + suitable carbonyl compound
- (iv) Deduce the structures of S and T. Give the reagents and conditions for step 2. [3]



Step 2: ethanolic KOH, heat

- (d) (i) Describe the reaction, if any, of Al_2O_3 with water. Include the approximate pH value of any resulting solution. [1] Al_2O_3 is insoluble in water hence pH of solution will remain at $\underline{7}$.
 - (ii) Describe the reactions, if any, of Al_2O_3 with acids and bases. Write equations for any reactions that occur.

| | | [2] | |
|--|---|---------|--|
| | $\underline{Al_2O_3(s) + 2 OH^-(aq) + 3H_2O(l) \rightarrow 2 [Al(OH)_4]^-(aq)}$ | | |
| | <i>Or</i> <u>Al₂O₃(s) + 2NaOH (aq) + 3H₂O(<i>l</i>) → 2Na[A/(OH)₄]⁻(aq)</u> | | |
| | <u>Al₂O₃(s) + 6 H⁺(aq) → 2 Al³⁺(aq) + 3H₂O(l)</u> | | |
| | $Or \underline{Al_2O_3(s) + 6HCl(aq)} \rightarrow 2AlCl_3(aq) + 3H_2O(l)$ | | |
| | State symbols not needed as question did not ask for them. | | |
| | | | |
| | | | |
| | [Tota | al: 22] | |
| | | | |
| | | | |
| | | | |

3 Acids play important and varied roles in our everyday lives.

This question involves some of the important inorganic and organic acids that can be commonly found in the chemistry laboratory.

(a) In 2019, close to 50 million tonnes of phosphoric acid was produced worldwide. 90% of this production was used in the manufacturing of plant fertilisers.

The structure of a molecule of phosphoric acid is given below:



The table below gives the pK_a values of phosphoric acid at 298K.

| Equation | рКа |
|---|------|
| $H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$ | 2.2 |
| $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$ | 7.2 |
| $HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$ | 12.3 |

 (i) Explain why 1 mole of phosphoric acid can lose up to 3 moles of H⁺. [1] Due to the <u>electronegative oxygen</u> atoms, the 3 <u>O-H bonds are polar</u>, which dissociate readily to give 3 mol of H⁺ per mol of the acid.

(either mention electronegative O OR polar O-H bonds to get credit)

(ii) Suggest why the pK_a values of phosphoric acid show an increasing trend.

Increasing *pK*_a means decreasing strength of acid:

 $pK_a: H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$

It gets <u>more difficult_OR_electrostatically unfavourable</u> for additional <u>H⁺ to be removed</u> from an <u>increasingly negatively charged</u> species.

(iii) State the conjugate base of HPO₄²⁻ and calculate its pK_b .

[2]

[1]

PO4³⁻

At 25°C, $pK_a + pK_b = 14$

Hence $pK_b (PO_4^{3-}) = 14 - pK_a (HPO_4^{2-}) = 14 - 12.3$

 pK_b (PO₄³⁻) = 1.7 Note: ecf to be given if student choose wrong pK_a value from the table.

Phosphate buffers are one of the two most important biological buffer systems in most multicellular organisms.

(iv) Explain what is meant by a buffer.

A mixture of a weak acid/base and its salt, which can <u>resist changes in</u> <u>pH when a small amount of acid/base is added</u>, and upon dilution.

(v) One such buffer was prepared in the chemistry laboratory by adding 0.500 g of solid sodium hydroxide to a 150 cm³ of 0.150 mol dm⁻³ Na₂HPO₄ solution.

Using your answer in (a)(iii) or otherwise, calculate the pH of the resulting buffer system.

Amount of NaOH = 0.500 / (23.0 + 1.0 + 16.0) = 0.0125 mol

Amount of Na_2HPO_4 = Amount of HPO_4^{2-} = (150/1000) x 0.150 = 0.0225 mol

 $HPO_4^{2-} + OH^- \rightarrow PO_4^{3-} + H_2O$

Amount of HPO_4^{2-} after reaction = 0.0225 - 0.0125 = 0.0100 mol Amount of PO_4^{3-} after reaction = 0.0125 mol

 $\begin{aligned} \mathsf{pOH} &= \mathsf{pK}_{\mathsf{b}} + \mathsf{lg} \left([\mathsf{HPO}_4^{2\text{-}}] \,/ \, [\mathsf{PO}_4^{3\text{-}}] \right) \\ &= 1.7 + \mathsf{lg} \left\{ (0.0100 / (100 / 1000)) \,/ \, (0.0125 / (100 / 10000)) \right\} \\ &= 1.60 \end{aligned}$

pH = 14 - pOH = 14 - 1.60 = 12.4

(b) Peroxyacids are organic acids of great importance as they are involved in many organic reactions.

One such reaction is the Baeyer-Villiger synthesis, where a ketone is converted into an ester.



(i) State the role of the peroxyacid in the Baeyer-Villiger synthesis.

It serves as an oxidising agent (donates its O atom to the ketone).

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[1]

[1]

The diagram below shows a reaction scheme which involves the Baeyer-Villiger reaction in one of the steps.



(ii) Give the structures of compounds E, F, and G.



(iii) Suggest the reagent and conditions for step III.

[1]

I2, NaOH(aq), heat

[3]

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For Examiner's Use (iv) The product in step III was acidified and the following compound was obtained.



Which of the two acid groups present would have a higher K_a value? Explain your answer.

[2]

The acid group at C2 would have a higher K_a (stronger acid) value.

The conguate base/anion would be more stable due to:

• formation of favourable <u>intramolecular hydrogen bonding</u> within a 6 membered ring for C2 acid compared to 7 membered ring for C1 acid which experiences <u>more ring strain</u>.

OR

- <u>electron-withdrawing</u> -OH group is <u>nearer</u> to C2, hence helps to <u>disperse the negative charge on the -COO⁻ better</u> compared to C1.
- (c) It is known that both Group 2 carbonates and nitrates undergo thermal decomposition. However, the thermal decomposition of nitrates produces two gases: a colourless odourless gas that relights a glowing splint; a brown gas that is a component of acid rain.
 - (i) Suggest and write a balanced equation for the thermal decomposition of magnesium nitrate.

[1]

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Use

 $Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + 1/2 O_2$

(ii) Would barium nitrate decompose at a higher or lower temperature than magnesium nitrate? Explain your answer.

[3]

Barium nitrate decomposes at a <u>higher</u> temperature than magnesium nitrate.

This is because:

- Ba²⁺ has a lower charge density than Mg²⁺ (✓)
- polarise NO_3^- anion to a smaller extent (\checkmark)
- N-O covalent bond in NO₃ weakened to lesser extent/ more difficult to break (✓) (not necessary to state N-O bond)
- more energy required to break(\checkmark) the N-O bond

4(✓): 2 marks 3(✓): 1 mark 0-2 ticks: 0 mark

[Total: 18]

Section B

Answer **one** question from this section.

-4

(a) △H^e_{iso}, the standard enthalpy change of isomerisation, is the enthalpy change when 1 mole of a *cis*–alkene isomerises to 1 mole of the corresponding *trans*–alkene under standard conditions. This enthalpy change, however, cannot be measured directly by experiment. For Examiner's Use

A chemist aimed to determine the standard enthalpy change of isomerisation of *cis*-pent-2-ene to *trans*-pent-2-ene using their standard enthalpy changes of combustion, ΔH_c^{e} . Both alkenes are volatile liquids at 298 K.





The chemist found the ΔH_c^{Θ} of *cis*-pent-2-ene to be -3343 kJ mol⁻¹ from literature review. However, the ΔH_c^{Θ} of *trans*-pent-2-ene was not available.

To determine ΔH_c^e of *trans*-pent-2-ene, the chemist carried out the flame calorimetric experiment using a metal can as shown in the set up below.



His results were shown below.

| increase in temperature of water | 5.2 °C | |
|---|--------|--|
| change in mass of spirit lamp with trans-pent-2-ene | 0.22 g | |

From a previous calibration experiment, he found out that the heat capacity, C, of the calorimeter set-up (*i.e. metal can and water*) is 2.00 kJ K⁻¹.

(i) Using the results above, calculate a value for ΔH_c^{Θ} of *trans*-pent-2-ene.

Heat change, $q = C \times \Delta T = 2.00 \times 5.2 = \frac{10.4 \text{ kJ}}{10.4 \text{ c}}$ $\Delta H_c^{\Theta} \text{ of trans-pent-2-ene} = -\frac{q}{n} = -\frac{10.4}{\left(\frac{0.22}{70.0}\right)} = -3309 = \frac{-3310 \text{ kJ mol}^{-1}}{2000 \text{ c}^{-1}}$

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(ii) Using results from (a)(i) and any relevant data given in (a), calculate the standard enthalpy change of isomerisation, ΔH^{e}_{iso} , of *cis*-pent-2-ene to *trans*-pent-2-ene. [1] $\Delta H^{e}_{iso} = \Delta H^{e}_{c} [cis-pent-2-ene] - \Delta H^{e}_{c} [trans-pent-2-ene]$

= (-3343) - (-3309)= (-3343) - (-3309) = <u>-34.0 (or 33.0)</u> kJ mol⁻¹ Award ecf based on (i) answer

(iii) Suggest a reason why the ΔH_{iso}^{o} of *cis*-pent-2-ene to *trans*-pent-2-ene is exothermic. [1]

trans-pent-2-ene is lower in energy than cis-isomer as the bulky <u>alkyl</u> <u>groups are spaced out minimising repulsion</u> between the electron clouds. OR there is less overcrowding in trans-isomer.

(b) (i) 2-pentyne, C_5H_8 is a liquid hydrocarbon whose structure is given below.



2-pentyne, C₅H₈

Lindlar catalyst is a special catalyst consisting of palladium coated with $CaCO_3$ and lead acetate.

2-pentyne, C_5H_8 undergoes partial reduction with H_2 in the presence of Lindlar catalyst to form pent-2-ene, C_5H_{10} .

$$C_5H_8(l) + H_2(g) \rightarrow C_5H_{10}(l) \qquad \Delta H_1$$

Using relevant data from the Data Booklet, together with the following data, construct a fully labelled energy cycle relating the reactants and products of this reaction to their **gas phase atoms**. Use your energy cycle to calculate the enthalpy change of the reaction, ΔH_1 .

standard enthalpy change of vaporisation of $C_5H_8(l)$ +28.0 kJ mol⁻¹ standard enthalpy change of vaporisation of $C_5H_1(l)$ +26.0 kJ mol⁻¹



Correct energy cycle with 5 balanced eqns including correct state symbols for all reactants and products, each eqn correctly labelled with enthalpy value/ symbol

 $\Delta H_1 = +28.0 + 5609 - 5760 - 26.0 = -152 \text{ kJ mol}^{-1}$

(ii) 2-pentyne reacts with Br₂ in tetrachloromethane to give a product with molecular formula C₅H₈Br₂ which exists as two isomers.

Draw the isomers of the product and state the type of isomerism displayed.



[3]

(c) Alkenes (C=C) and alkynes (C=C) undergo reduction in a similar way. The following reactions illustrate reductions using two different reducing agents, NaBH₄ in methanol and H₂ and Ni at high temperature.





P and **Q** both react with PCl_5 . Suggest the identities of **P** and **Q**.





- 18
- (d) Phosphorus pentachloride, PCl_5 , is a solid which melts at 162 °C.

Describe what you would see when a sample of $PCl_5(s)$ is added to a solution of litmus in water. Write an equation for the reaction that occurs.

 $\underline{PCI_5(s) + 4 H_2O(l) \rightarrow H_3PO_4(aq) + 5 HCI(aq)}$

state symbols not required as not stated in question

Purple litmus solution turns red

(e) 2-methyl-but-2-ene is an alkene that is used as a free radical scavenger in chlorinated solvents.

A method to form alcohols from alkenes is the hydroboration reaction as shown below, using 2-methyl-but-2-ene.

This involves the addition of a B-H bond of borane, BH_3 to an alkene, to yield an organoborane intermediate, RBH_2 in step **1**. RBH_2 then undergoes oxidation by H_2O_2 to form the alcohol in step **2**.



- (i) This process can be viewed as an electrophilic addition reaction with borane, BH₃, as the attacking electrophile. Explain why BH₃ can behave as an electrophile to form organoborane. The boron atom is <u>electron deficient</u> and is able to accept an electron pair from the C=C bond.
- (ii) Using the above information, deduce the structure of alkene **Q** that would enable you to form the following alcohol using the hydroboration method.



Draw the diene which can be used to prepare diol P.

[1]

[1]

[1]



(f) State how the reactivity of the halogens X_2 (X=C*l*, Br and I) as oxidising agents varies down the group, and relate this variation to relevant E° values.

19

Down the group, $\underline{E^{e}(X_{2}/X^{-})}$ becomes less positive(\checkmark), implying that the tendency of X₂ to be reduced decreases(\checkmark). Hence, the oxidising power of X₂ decreases down the group.

[Total:20]

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Reaction 1: $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$

(i) Write an expression for the K_c for reaction **1**.

$$K_{c} = \frac{[I_{3}^{-}]}{[I_{2}][I^{-}]}$$

(ii) When 0.0254 g of solid iodine is dissolved in 150 cm³ of 0.500 mol dm⁻³ of sodium iodide, and allowed to reach equilibrium at 25 °C, the final $[I_3^-(aq)]$ is found to be 6.653 x 10⁻⁴ mol dm⁻³.

Calculate the equillibrium values of $[I_2(aq)]$ and $[I^-(aq)]$ in this solution and hence calculate the value for K_c .

$$n_{\text{I}_2,\text{inital}} = \frac{0.0254}{2(126.9)} = 1.001 \times 10^{-4} \text{ mol}$$
$$[\text{I}_2]_{\text{initial}} = \frac{1.001 \times 10^{-4}}{\left(\frac{150}{1000}\right)} = 6.672 \times 10^{-4} \text{ mol}$$

| | I ₂ (aq) | + | I⁻(aq) | ⇒ | I₃⁻(aq) |
|--|--------------------------|---|----------------|---|---------|
| Initial concentration/ mol dm ⁻³ | 6.672 × 10 ⁻⁴ | | 0.500 | | 0 |
| Change in concentration/ mol dm ⁻³ | -x | | - x | | +x |

Eqm concentration/ mol dm⁻³ $6.672 \times 10^{-4} - x$ 0.500 = x x Since the value of x is given to be 6.653×10^{-4} ,

 $[I_2(aq)] = 6.672 \times 10^{-4} - 6.653 \times 10^{-4} = 0.000001900 \text{ mol dm}^{-3}$

 $[I^{-}(aq)] = 0.500 - x = 0.500 - 6.653 \times 10^{-4} = 0.4993 \text{ mol} \text{ dm}^{-3}$

both [I2]eqm and [I⁻] eqm (ecf for wrong [I2]initial)

$$\mathcal{K}_{c} = \frac{[6.653 \times 10^{-4}]}{[6.672 \times 10^{-4} - 6.653 \times 10^{-4}][0.50 - 6.653 \times 10^{-4}]} = 700 \ (3 \ \text{s.f})$$

(iii) The relationship between the magnitude of the equilibrium constant, K_c , for reaction 1 and temperatures was investigated and the results are recorded below.

| Temperature/ K | Kc |
|----------------|-----|
| Т | 700 |
| T + 200 | 350 |

Deduce the sign for the enthalpy change of the forward reaction for reaction **1**. Explain your reasoning.

[2]

For Examiner's Use

[1]

By Le Chatelier's principle, when temperature increases, the system will $% \left\| {{{\mathbf{x}}_{i}}} \right\| = {{\mathbf{x}}_{i}}$

- <u>favour the endothermic reaction</u> / <u>absorb the excess heat</u> / <u>lower</u> <u>the temperature</u>(✓), reducing the disturbance.
- Since the magnitude of K_c decreases as the temperature is increased from T K to (T+200) K, this means that the backward reaction is favoured and position of equilibrium shifts to the left/ back. (✓)
- (b) At 288 K, an aqueous solution containing 0.00600 mol dm^{-3} of I_2 was found to be in equilibrium with a solution in heptane containing 0.240 mol dm^{-3} of I_2 . The partition coefficient, is given by the following.

partition coefficient =
$$\frac{\left[I_2(\text{heptane})\right]}{\left[I_2(\text{aq})\right]}$$

Calculate the partition coefficient of I2 between heptane and water.

partition coefficient = $\frac{0.240}{0.00600} = 40.0$

(c) To determine the equilibrium constant of Reaction 1 at 288 K, a solution of I_2 dissolved in 5.00 × 10⁻³ mol dm⁻³ aqueous potassium iodide, KI, was shaken with heptane until equilibrium was reached.

Reaction 1: $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$

The heptane layer contained 0.0150 mol dm⁻³ of I₂. The aqueous layer was found to contain I_2 and I_3^- at a total combined concentration of 1.70×10^{-3} mol dm⁻³.

(i) Use the value of the partition coefficient calculated in (b) to determine the concentration of I_2 in the aqueous layer.

[1]

 $40 = \frac{0.0150}{[I_2(aq)]}$ $[I_2(aq)] = 3.75 \times 10^{-4} \text{ mol dm}^{-3}$

(ii) Calculate the concentrations of I_3^- and I^- in the aqueous layer. [2] $[I_3^-(aq)] = 1.70 \times 10^{-3} - 3.75 \times 10^{-4} = 1.33 \times 10^{-3} \text{ mol dm}^{-3}$

 $[I^{-}(aq)] = 5.00 \times 10^{-3} - 1.33 \times 10^{-3} = 3.67 \times 10^{-3} \text{ mol dm}^{-3}$

(iii) Hence, using your answers in (c)(i) and (c)(ii), calculate the value of K_c for reaction 1 at 288 K. [1]

$$K_{\rm c} = \frac{[{\rm I}_3^-]}{[{\rm I}_2][{\rm I}^-]} = \frac{1.33 \times 10^{-3}}{\left(3.75 \times 10^{-4}\right) \left(3.67 \times 10^{-3}\right)} = 966 \text{ mol}^{-1} \text{ dm}^3$$

- (d) Silver chloride is sparingly soluble in water. Describe and explain how the solubility of AgC*l* is affected by
 - adding NH₃(aq),
 - adding NaCl(aq)

 $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq) ---(1)$

When NH_3 is added, stable $[Ag(NH_3)_2]^+$ complex was formed and hence, $[Ag^+]$ decreases. This causes the position of equilibrium 1 to shift right and hence, the solubility of AgC*l* increases.

When <u>NaCl</u> is added, [Cl⁻] increases and this causes the position of equilibrium 1 shift left so as to remove some Cl^- . Hence, the <u>solubility of AgCl</u> decreases.

[2]

[2]

(e) In the *Wurtz* reaction, two iodoalkanes react with sodium metal in dry ether, to form a new carbon–carbon bond, resulting in the formation of a new alkane.

 $R-I + R'-I + 2Na \rightarrow R-R' + 2NaI$

It is given that this *Wurtz* reaction occurs in two steps as shown below.

Step 1: $R-I + 2Na \rightarrow R^- + 2Na^+ + I^-$ Step 2: $R'-I + R^- \rightarrow R - R' + I^-$

(i) Reaction of a single iodoalkane with sodium metal in dry ether via *Wurtz* reaction will give a good yield of symmetrical alkane product.

Draw the organic product formed when (iodomethyl)benzene reacts with sodium metal in dry ether.

CH₂I (iodomethyl)benzene

[1]

(ii) A student decided to produce an assymetrical alkane, **W**, by reacting (iodomethyl)cyclohexane and iodomethane with sodium metal in dry ether.



The student found that the use of *Wurtz* reaction to produce W is not desirable as the yield of the desired product W was very low. This is due to the presence of large amount of two organic side products.

Suggest the identity of **one** of these organic side products.

OR

[1]

CH₃CH₃

(f) The following reaction scheme can be used to synthesise 2-methyl-2-hydroxypentanoic acid from 2-iodopentane.



The intermediates W and X were found to react with aqueous alkaline iodine solution to give a yellow precipitate.

State the reagents and conditions for steps 1, 2, 3 and 4. Draw the intermediates W, X and Y.

[4]

- Step 1: NaOH(aq), heat
- Step 2: KMnO₄(aq), H₂SO₄(aq), heat OR
- $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat Step **3:** Traced NaCN/ NaOH, HCN, 10 °C
- Step 4: $H_2SO_4(aq)$, heat

(g)



Alkane **Z** reacted with bromine in the presence of ultraviolet light to form only two monobrominated compounds.

Draw the structures of the two monobrominated structural isomers formed and predict their relative ratio. [2]



End of paper