2021 Raffles Institution H2 Chemistry Prelim Paper 2 – Suggested Solutions 1(a)(i) Heat gained by water = 4.18 x 10.0 x 300 = 12540 J Heat gained by copper can = $0.384 \times 10 \times 250 = 960 \text{ J}$ Total heat gained = 12540 + 960 = 13500 J = 13.5 kJ 1(a)(ii) Amt of ester = 0.980 / 74.0 = 0.0132 mol Theoretical heat energy released = 0.0132 x 1592 = 21.1 kJ 1(a)(iii) Method 1 - Find % heat loss to surroundings 13.5 kJ (expt) / 21.1 kJ (theoretical) = 64% of heat energy transmitted (36% heat loss)Amt of ethyl ethanoate = 0.948 / 88.0 = 0.010773 mol Heat transferred = 4.18 x 11.5 x 300 + 0.384 x 11.5 x 250 = 15525 J = 15.5 kJ Theoretical heat released = 15525 / 0.64 = 24257 J = 24.3 kJ $\Delta H = -24.3 \text{ kJ} / 0.01077 = -2252 = -2250 \text{ kJ mol}^{-1}$ Method 2 - Find thermal capacity of apparatus OR by proportion Thermal capacity = theoretical energy released / observed temperature change Thermal capacity = $21.1 \text{ kJ} / 10 \text{ K} = 2.11 \text{ kJ} \text{ K}^{-1}$ Theoretical heat produced from combustion = $2.11 \text{ kJ K}^{-1} \times 11.5 \text{ K} = 24.3 \text{ kJ}$ Amt of ethyl ethanoate = 0.948 / 88.0 = 0.010773 mol $\Delta H = -24.3 \text{ kJ} / 0.01077 = -2252 = -2250 \text{ kJ mol}^{-1}$ 1(b)(i)





A (C₃H₄O₂)

B (C₆H₈O₄)

1(b)(ii) pK_a for **P** will be smaller.

The conjugate base for **P** CH₃CH(OH)COO⁻ is more stable than CH₃CH₂COO⁻. The –OH group is electron-withdrawing and disperses the negative charge on O of –COO⁻ to a large extent. Hence, **P** is a stronger acid than propanoic acid.

1(b)(iii) [H⁺] = $10^{-2.43}$ = 3.72 x 10^{-3} mol dm⁻³ $K_a = (3.72 \times 10^{-3})^2 / (0.10 - 3.72 \times 10^{-3}) = 1.43 \times 10^{-4}$ mol dm⁻³ $pK_a = -\log 1.43 \times 10^{-4} = 3.84$

> Note: Since [H⁺] is known, no need to make assumption here. With assumption, K_a is 1.38 x 10⁻⁴ mol dm⁻³ and p K_a is 3.86.

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mixture of three isomeric alkenes (C₁₀H₁₆)

1(c)(iii) Both nucleophile and base have a pair of electrons available for donation.

A nucleophile attacks an electrophile (or an electron-deficient species) to form a bond, as shown in reaction 1.

A base accepts a H^+ (proton) as shown in reaction 2.

1(c)(iv) reaction 1: <u>aqueous</u> KOH, <u>heat</u> reaction 2: KOH in <u>ethanol</u>, <u>heat</u> **1(c)(v)** Nucleophilic substitution S_N1



- **2(a)(i)** sp²
- **2(a)(ii)** Since the boron atom is sp² hybridised and it only has 6 valence electrons around boron, there is an empty unhybridised p orbital which can accept a pair of electrons and thus, is an electrophile.
- **2(b)(i)** Since B is less electronegative than H, B would develop δ^+ while H would be δ^- .



2(b)(ii) The more stable tertiary carbocation is formed if the electron deficient B atom forms a bond with the doubly bonded carbon with more hydrogen atoms.

The H atom of BH_3 is therefore bonded to the doubly bonded carbon with fewer hydrogens, forming a product which does not follow Markovnikov's rule.



2(c)(i)

or any correct conformations of this stereochemistry.

compound V

2(c)(ii) Compounds **W** is formed when BH₃ attacks the alkene from the bottom of the plane of the alkene. **V** and **W** are <u>enantiomers</u>.



3(a) Both VSO₄ and $V_2(SO_4)_3$ have giant ionic lattice structure with strong ionic bonds.

The ionic bond strength is dependent on lattice energy (LE)

 $\left| \text{ lattice energy } \left| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right| \right| \right|$

Since V³⁺ has a higher charge and smaller cationic radius than V²⁺ and they have the same anion, the lattice energy of V₂(SO₄)₃ is more exothermic / magnitude of lattice energy of V₂(SO₄)₃ is larger than that of VSO₄. More energy is required to overcome the stronger ionic bonds in V₂(SO₄)₃ and thus it has a higher melting point.

3(b)(i) $VO_2^+ + 2H^+ + e \rightleftharpoons VO^{2+} + H_2O$ $E^{\ominus} = +1.00 V$ $V^{3+} + e \rightleftharpoons V^{2+}$ $E^{\ominus} = -0.26 V$

 $E_{\text{cell}}^{\ominus} = 1.00 - (-0.26) = +1.26 \text{ V}$

3(b)(ii) $VO_2^+ + 2H^+ + e \Rightarrow VO^{2+} + H_2O$ $E^{\ominus} = +1.00 \text{ V}$

If the battery is allowed to run at higher pH, [H⁺] would decrease and position of equilibrium for the above equilibrium would shift to the left.

 $E(VO_2^+/VO^{2+})$ would become less positive, causing E_{cell} to become less positive.

3(b)(iii) Tank **A**: the solution turns from grey (violet-green) to green. Tank **B**: the solution turns from green to blue. © Raffles Institution 2021 9729/02/S/21

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3(b)(iv) H⁺ ions flow from Tank **A** towards Tank **B**.

To maintain electrical neutrality. As the reaction proceeds, the electrolyte in Tank **A** becomes increasingly positive (due to a more highly positively charged ion being formed) while the electrolyte in Tank **B** becomes decreasingly positive (due to consumption of H^+).

OR To maintain/replenish [H⁺] as it is being used up in Tank **B**.

- **3(b)(v)** The porous electrodes would allow liquid to pass through, thus <u>increasing the surface area</u> for contact, allowing the exchange of electrons to occur faster.
- **3(c)(i)** $V^{3+} + VO^{2+} + H_2O \rightarrow VO_2^+ + V^{2+} + 2H^+$
- **3(c)(ii)** $\Delta G^{\ominus} = -nFE^{\ominus}$ = - (1)(96500)(-1.26) = +1.22 x 10⁵ J mol⁻¹
- **4(a)(i)** The concentration of dissolved Cl^{-} increases linearly as the time of electrolysis increases.

4(a)(ii) The reactions at the cathode and anode remove water.
With less water in the mixture, the concentration of dissolved
$$Cl^{-}$$
 increases.

- **4(a)(iii)** A white solid of NaC*l* will be observed at the bottom of the setup.
- **4(a)(iv)** A greater proportion of chlorine gas will be produced.
- **4(a)(v)** Increasing the concentration of NaOH increases the concentration of the common ion, Na⁺. This causes the position of equilibrium of NaC*l*(s) \Rightarrow Na⁺(aq) + C*l*⁻(aq) to shift to the left, precipitating NaC*l*(s), reducing the concentration of dissolved NaC*l*.
- **4(a)(vi)** 1. The oxidation of OH^- is favoured over the oxidation of Cl^- at the anode since $E^{\ominus}(O_2/OH^-)$ is less positive than $E^{\ominus}(Cl_2/Cl^-)$.

 $\begin{array}{ll} \mathsf{C}l_2 + 2\mathsf{e}^- \rightleftharpoons 2\mathsf{C}l^- & E^\ominus = +1.36 \ \mathsf{V} \\ \mathsf{O}_2 + 2\mathsf{H}_2\mathsf{O} + 4\mathsf{e}^- \rightleftharpoons 4\mathsf{O}\mathsf{H}^- & E^\ominus = +0.40 \ \mathsf{V} \end{array}$

- 2. The concentration of chloride in solution is significantly decreased, causing $E(Cl_2/Cl^-)$ to become much more positive, preventing Cl^- from being oxidised.
- **4(b)(i)** Amount of Fe = 0.04(15000)/55.8 = 10.75 mol Amount of O₂ consumed by Fe = 0.75(10.75) = 8.06 mol

Amount of $NaClO_3 = 0.88(15000)/(106.5) = 123.9$ mol Amount of O₂ produced from $NaClO_3 = 1.5(123.9) = 185.9$ mol

Overall amount of O_2 produced = 185.9 - 8.06 = 177.8 mol Volume of O_2 produced = 177.8 (24.0) = 4267 dm³ = 4270 dm³ (to 3 sf)

4(b)(ii) With 3 bond pairs and 1 lone pair around each P atom, the bond angle should be 107° . The bond angle in P₄ is 60° , leading to increased bond pair-bond pair repulsion, which makes the molecule less stable and more reactive.

4(b)(iii) P₄, S₈ and Cl₂ are <u>simple covalent molecules</u> with <u>instantaneous dipole-induced dipole (id-id)</u> interactions between their molecules.

The <u>electron clouds of P_4 and S_8 are larger and more polarisable</u> than that of Cl_2 . More energy is required to overcome the <u>stronger id-id interactions in P_4 and S_8 compared to Cl_2 .</u>

4(b)(iv) 1st ionisation energy of P > 1st ionisation energy of S. The valence electron to be removed from S is a paired 3p electron which experiences additional inter-electronic repulsion, requiring less energy for removal.

 1^{st} ionisation energy of S < 1^{st} ionisation energy of C*l*. More energy is required to remove the valence electron of chlorine which experiences a higher nuclear charge but approximately constant shielding compared to sulfur.

- 4(c)(i) Br
- **4(c)(ii)** Step 1: Br₂(aq) Step 2: Na(s)
- 4(c)(iii)



4(c)(iv) Use an excess of NH₃.

Using an excess of NH₃ increases the probability of ethylene oxide colliding with NH₃ instead of ethanolamine or diethanolamine to form the polysubstituted products.

- 4(c)(v) Methanal
- **4(c)(vi)** H_2 , Ni, heat OR LiA $/H_4$ in dry ether
- **4(c)(vii)** Temperature in chamber **A**: 40 °C Temperature in chamber **B**: 80 °C (**A** cooler than **B**, temperature difference of at least 40 °C)

At a cooler temperature in chamber **A**, larger K_c , the position of equilibrium lies to the right, encouraging ethanolamine to bond with CO_2 to remove CO_2 from the air in the submarine.

At a higher temperature in chamber **B**, smaller K_c , the position of equilibrium lies to the left, liberating CO₂ to be released.

4(d) Ba²⁺ has a larger ionic radius than Ca²⁺, resulting in Ba²⁺ having a lower charge density and polarising power than Ca²⁺.
Ba²⁺ distorts the electron cloud of CO₃²⁻ to a lesser extent than Ca²⁺, leading to less weakening of the covalent bonds within CO₃²⁻.
More heat energy is required to break the covalent bonds within CO₃²⁻ in BaCO₃, leading to a higher temperature for thermal decomposition.