2024 Y6 H2 Chemistry Preliminary Exams Paper 2 – Suggested Solutions

- 1(a)(i) $B^{3+}(g) \longrightarrow B^{4+}(g) + e^{-}$
- 1(a)(ii) B³⁺: 1s² C³⁺: 1s² 2s¹
 C³⁺ has <u>one more electron shell</u> than B³⁺; the 2s electron in C³⁺ is further away from the nucleus than the 1s electron in B³⁺. <u>Shielding experienced</u> by the 2s electron in C³⁺ is <u>greater</u> than the 1s electron in B³⁺. Despite the <u>greater nuclear charge</u> in C³⁺, <u>electrostatic attraction</u> between the nucleus and the 2s electron in C³⁺ is <u>weaker</u> than the 1s electron in B³⁺. Less energy is required to remove the 2s electron in C³⁺ compared to the 1s electron in B³⁺. Thus, B has a higher fourth ionisation energy than C.
- ^{1(b)(i)} H•× B•× H •× H
- 1(b)(ii) shape: <u>trigonal planar</u> bond angle: <u>120°</u>
- **1(b)(iii)** $\Delta H_{\rm r}$ = energy required to break bonds energy released from bonds formed = 3BE(B-H) + $\frac{3}{2}$ BE(O=O) – BE(B=O) – BE(B-O) – 3BE(O-H) = 3(330) + $\frac{3}{2}$ (496) – 837 – 536 – 3(460) = -1019 kJ mol⁻¹ = $\frac{-1020 \text{ kJ mol}^{-1}}{1000 \text{ kJ mol}^{-1}}$ (3 s.f.)
- **1(b)(iv)** The standard enthalpy change of combustion of borane is more exothermic than ΔH_r as energy is released to condense steam to water and to convert B₂O₃ from gaseous to solid state.
- **1(c)(i)** Aluminium in A/Cl_3 has a vacant, low-lying orbital to accept a lone pair of electrons from the chlorine atom of another A/Cl_3 molecule.
- 1(c)(ii) sp² to sp³
- **1(c)(iii)** There is less electron density in each $B-H_b$ bond / fewer shared bonding electrons, hence resulting in weaker attraction to the nuclei.





- **1(d)(ii)** N is <u>more electronegative</u> than B, and this reduces the extent of electron delocalisation (partially delocalised) compared to benzene.
- 1(d)(iii) NO₃⁻ + 10H⁺ + 8e⁻ \rightleftharpoons NH₄⁺ + 3H₂O E^{\ominus} = +0.87 V O₂ + 4H⁺ + 4e⁻ \rightleftharpoons 2H₂O E^{\ominus} = +1.23 V 2(a)(i) E_{cell}^{\oplus} = +1.23 – (+0.87) = +<u>0.36 V</u> > 0 (reaction is spontaneous) 2(a)(ii) The beneficial bacteria provide enzymes which act as biological catalysts to speed up the nitrification process. 2(b)(i) Day 9 or 10 2(b)(ii) Day 29 $[NO_3^-]$ before water change = 35 ppm 2(b)(iii) $[NO_3^-]$ after water change = $\frac{100-25}{100} \times 35 = 26.3 \text{ ppm}$ Using Henderson-Hasselbalch equation, $pH = pK_a + lg(\frac{[NH_3]}{[NH_4^+]})$, 2(b)(iv) $7.4 = 9.25 + lg(\frac{[NH_3]}{[NH_4^+]})$ $\frac{[NH_3]}{[NH_4^+]} = 10^{7.4-9.25} = 0.014125$ $\begin{bmatrix} [NH_3] = 0.014125[NH_4^+] \\ z = \frac{[NH_3]}{TAN} = \frac{[NH_3]}{[NH_3] + [NH_4^+]} = \frac{0.014125[NH_4^+]}{0.014125[NH_4^+] + [NH_4^+]} = \frac{0.014125}{0.014125 + 1} = \frac{0.0139}{0.0139}$ OR Let mole fraction of NH_3 be z, hence mole fraction of $NH_4^+ = 1 - z$ $\frac{z}{1-z} = 0.014125$ $z = \frac{0.014125}{1+0.014125} = 0.0139$ 2(c)(i) When small amount of OH⁻(aq) is added, $HCO_3^{-}(aq) + OH^{-}(aq) \longrightarrow CO_3^{2^{-}}(aq) + H_2O(I)$ When small amount of H₃O⁺(aq) is added, $CO_3^{2-}(aq) + H_3O^+(aq) \longrightarrow HCO_3^-(aq) + H_2O(I)$
- **2(c)(ii)** Tank water with a higher carbonate hardness has a <u>higher buffer capacity</u> to partially offset increase in [H⁺] due to the nitrification process.

2(d)(i) $n(S_2O_3^{2^-}) = 13.40 / 1000 \times 0.0100$ = 0.000134 mol mole ratio of $O_2 : I_2 : S_2O_3^{2^-}$ = 0.5 : 1 : 2 = 1 : 2 : 4 $n(O_2) = 0.000134 / 4 = 0.0000335$ mol $[O_2] = 0.0000335 / 100 \times 1000$ = 3.35 × 10⁻⁴ mol dm⁻³ (within recommended range) 2(d)(ii) Oxidation: N₃⁻(aq) $\longrightarrow \frac{3}{2}N_2(g) + e^-$

Reduction: $N_3^-(aq) \longrightarrow \frac{1}{2} N_2(g) + e^-$ Reduction: $8H^+(aq) + 2NO_2^-(aq) + 6e^- \longrightarrow N_2(g) + 4H_2O(I)$

Overall: $4H^{+}(aq) + 3N_{3}^{-}(aq) + NO_{2}^{-}(aq) \longrightarrow 5N_{2}(g) + 2H_{2}O(I)$

2(e) Decreasing basicity: N(1) > N(2) > N(3)

N(1) is a primary amine. The <u>electron-donating</u> $-CH_2$ - group <u>increases the electron</u> <u>density on N(1)</u>, making the lone pair of electrons on N <u>more readily available to</u> form a dative covalent bond with a proton.

N(2) is an aromatic amine. The <u>orbital containing the lone pair of electrons on the</u> <u>nitrogen atom overlaps with the π electron cloud of the benzene ring and the lone</u> pair of electrons is delocalised and is less available to form a dative covalent bond with a proton.

N(3) is a sulfonamide which has similar basicity as amides. It has the lowest basicity among the three nitrogen-containing groups because the <u>orbital containing the lone</u> pair of electrons on the N atom overlaps with the π electron cloud of the adjacent <u>S=O group</u> and the lone pair of electrons is <u>delocalised</u> to a greater extent, and <u>hence least/not available to form a dative covalent bond with a proton</u>.

3(a)(i)



mirror plane

3(a)(ii) The carbocation that is produced in the reaction is trigonal planar with respect to the positively charged carbon. Cl⁻ can attack the positively charged carbon from either side of the trigonal plane with equal likelihood. This results in the formation of a racemic mixture. The optical activity of each enantiomer cancels out each other. The product mixture is unable to rotate plane-polarised light.



3(b)(i) In this reaction, a secondary carbocation, **F'**, rearranges to form a tertiary carbocation, **G'** which is <u>more stable</u> because it has <u>more electron donating alkyl</u> <u>groups</u> bonded to the positively charged carbon. This helps to <u>disperse the positive</u> <u>charge</u>. **G** will be formed in a larger proportion.



- 3(b)(iii) Although both carbocations are tertiary carbocations, <u>L' is more stable as there is less repulsion between bond pairs of electrons in the cyclopentane ring</u>, compared to K'. L' is formed faster and hence, <u>L is the major product</u>.
- 3(c)(i)

M:

∕___он

Step 2: PCl₅ / PCl₃ / SOCl₂, or dry HCl, ZnCl₂, heat





© Raffles Institution 2024



3(c)(vi) To 1 cm³ of each compound, add 1 cm³ NaOH(aq), followed by 2 to 3 drops of KMnO₄. Heat the solution.

S: Purple KMnO₄ is decolourised. Black solid MnO₂ is formed. **T**: Purple KMnO₄ remains.

- **3(d)(i)** CFCs contain C–C*l* bonds which undergo homolytic fission in the presence of UV light to form <u>chlorine radicals</u> which catalyse the decomposition of ozone.
- **3(d)(ii)** HFCs have higher GWP than CFCs. Hence, HFCs trap more heat and cause global warming to a larger extent than CFCs.
- **4(a)(i)** The <u>order of reaction with respect to a particular reactant</u> is <u>the power to which</u> <u>the concentration of that reactant is raised in the rate equation</u>.

The rate constant, k, is <u>a constant of proportionality in the rate equation</u>. It is constant for a particular reaction at a given temperature.



4(a)(ii) From Fig. 3.1, first $t_{1/2} = 2^{nd} t_{1/2} = 2 \cdot 3 \times 10^{-4} \text{ s}$ ∴ reaction is <u>first order with respect to •OH</u>.

Fig. 3.1

4(a)(iii) $k' = k[CH_3CHO]^n$ A straight line graph with positive gradient passing through the origin is obtained for the graph of k' vs [CH₃CHO], OR <u>k' \propto [CH₃CHO]</u>, OR k' is directly proportional to [CH₃CHO]. The reaction is <u>first order with respect to CH₃CHO</u>.

k = gradient =
$$\frac{(4.0-0.0) \times 10^3}{(4.5-0.0) \times 10^{-7}} = \underline{8.89 \times 10^9}$$

4(a)(iv) rate = $k[\bullet OH] [CH_3CHO]$

- **4(a)(v)** <u>Yes I agree</u>, since equation 1 shows a bimolecular reaction involving $1 \cdot OH$ reacting with 1 ethanal which agrees with the rate equation in **(a)(iv)** showing that the reaction is first order with respect to both $\circ OH$ and CH_3CHO .
- **4(a)(vi)** A catalyst will <u>increase</u> the magnitude of the <u>rate constant</u>, <u>k</u>, and <u>decrease the</u> magnitude of the <u>activation energy</u>, <u>E_a</u>.



progress of reaction

- 4(c)(i) $2H_2O_2 \longrightarrow \bullet OH + HOO \bullet + H_2O$
- **4(c)(ii)** Fe²⁺ is a <u>homogeneous catalyst</u> as it is in the <u>same phase as H_2O_2 </u>. It is <u>used in equation 2 and regenerated in equation 3</u>.
- 4(c)(iii) Add aq, NaOH/aq. Na₂CO₃ to precipitate out Fe(OH)₂ / Fe(OH)₃.
 OR Add aq. NaS₂O₃ (or other known reducing agent of H₂O₂) to react with H₂O₂.
 OR Add a large volume of water (dilution).