Raffles Institution (Junior College) 2009 Preliminary Examination H2 Chemistry Suggested Solutions

Question 1

(a)(i) Amount of lactic acid = Amount of NaOH needed for neutralisation

$$\frac{20.00}{1000}$$
 x0.120 = 0.0024 mol

Concentration of lactic acid = $0.0024 \div \frac{25.0}{1000} = 0.0960 \text{ mol dm}^{-3}$

- (ii) $pK_a = pH \text{ at half-neutralisation} = 3.85 \text{ (when } V_{NaOH} = 10 \text{ cm}^3\text{)}$ $K_a = 10^{-3.85} = 1.41 \text{ x } 10^{-4} \text{ mol } \text{dm}^{-3}$ Alternatively, $K_a = \frac{[H^+][A^-]}{[HA]}$ Initially, $[H^+] = [A^-] = 10^{-2.45} = 3.548 \text{ x } 10^{-3} \text{ mol } \text{dm}^{-3}$ $K_a = \frac{3.548 \text{ x } 10^{-3} \text{ x} 3.548 \text{ x } 10^{-3}}{0.0960 - 3.548 \text{ x } 10^{-3}} = 1.36 \text{ x } 10^{-4} \text{ mol } \text{dm}^{-3}$ where HA = lactic acid
- (iii) At equivalence point, the resultant mixture is a solution of sodium lactate, H₃CH(OH)COO⁻Na⁺. Being the conjugate base of a weak acid, lactate ion hydrolyses in water to give OH⁻:

 $CH_3CH(OH)COO^{-}(aq) + H_2O(I) \rightleftharpoons CH_3CH(OH)COOH(aq) + OH^{-}(aq)$ The formation of OH⁻ causes the pH at equivalence point to be greater than 7.



Samples **A** and **B** contain lactic acid but the lactic acid in **B** is the <u>enantiomer/ optical isomer</u> of the lactic acid in **A**. Hence **A** and **B** behave differently towards plane–polarised light.

(ii) Sample C is a <u>racemic mixture</u> of the two optical isomers of lactic acid (contains equal amounts of the two optical isomers of lactic acid) and hence does not exhibit optical activity. Due to the mixture of the optical isomers, the <u>packing of lactic acid molecules</u> in C <u>is not as regular</u> as the packing of lactic acid molecules in A where only one optical isomer of lactic acid is present.

Hence melting point of sample C is lower than that of A.

D does not contain -OH nor -COOH since it does not react with sodium.

It is a di<u>ester</u> formed when –OH and –COOH groups of one lactic acid molecule reacts with the –COOH and –OH groups respectively of another lactic acid molecule.

(d)(i) **E** has a <u>chiral centre</u> as it rotates plane–polarised light. **E** is an <u>aldehyde</u> since it reacts with Fehling's solution to give a reddish brown precipitate. Amount of hydrogen evolved with sodium per mol of $\mathbf{E} = \frac{0.24}{24} \div 0.01 = 1$ mol

Amount of Hydrogen evolved with solidin per motor $\mathbf{L} = \frac{24}{24}$

Hence two displaceable H are present \Rightarrow there are <u>two –OH group</u>.

(ii) E is an alcohol. The stability of its anion is lower than the stability of the anion of lactic acid as the <u>anion is destabilised by the electron-donating</u> -CH₂CH(OH)CHO group. Lactic acid is a much stronger acid as its anion forms <u>two equivalent resonance structures</u> with the negative charge on O delocalised over two electronegative O atoms.



(ii) <u>Intramolecular hydrogen-bonding</u> occurs in maleic acid and thus it has lower melting point as there are <u>less sites for inter-molecular hydrogen bonding</u>.



Question 2

(a)(i) Heat evolved = $\frac{100}{80} \times 200 \times 4.18 \times 46.9 \text{ J} = 49.01 \text{ kJ}$

Amount of cyclobutane used = $\frac{1.00}{12.0x4 + 1.0x8} = 0.01786$ mol

$$\Delta H_{c}[] = -\frac{49.01}{0.01786} = -2.7446 \times 10^{3} \text{ kJ mol}^{-1} = -2.74 \times 10^{3} \text{ kJ mol}^{-1}$$

- (ii) $\Delta H_1 = \Delta H_C[$] $2\Delta H_C[CH_2=CH_2] = -2.745 \times 10^3 2(-1422) = +99 \text{ kJ mol}^{-1}$
- (iii) ΔS of the reaction is greater than 0 since more gaseous molecules are formed in the forward reaction. ΔH is greater than 0 To be spontaneous, $\Delta G = \Delta H - T\Delta S < 0 \Rightarrow \Delta G$ likely to be negative if T is large. Hence reaction is favoured by high temperature.
- (b)(i) Bond energy of X-Y bond is the average energy absorbed when 1 mol of X-Y bonds are broken in gaseous state.
 - (ii) $\Delta H_1 = \Sigma$ (bonds broken) Σ (bonds formed) +99 = 4BE(C-C) + 8BE(C-H) – [2BE(C=C) + 8BE(C-H)] = 4BE(C-C) – 2 x 610 BE(C-C) = 1/4(99+1220) = 330 kJ mol⁻¹

[1]

- (iii) The C-C-C bond angle in cyclobutane is 90° which is <u>much smaller</u> than the normal sp³ -hybridised angle of 109°.
 The <u>angle strain weakens</u> the C-C bond in cyclobutane so that it is lower than the C-C bond energy value (which is the average of C-C bond energy found in compounds) found in the *Data Booklet*.
- (c)(i) To <u>keep the total volume constant</u> so that the concentration of ethene or bromine used is directly proportional to the volume used.
 - (ii) Rate of reaction is <u>inversely proportional to the time taken</u> for the colour of bromine to disappear and <u>directly proportional to the volume of bromine</u> used.

(iii) Rate $\propto \frac{V_{Br_2}}{t}$

Comparing experiments 1 and 2,

[ethene] used in experiment **2** is decreased to $\frac{12}{20} = 0.6 \times [\text{ethene}]$ used in expt **1**.

$$\frac{Rate_2}{Rate_1} = (\frac{V_{Br_2}}{t})_2 \div (\frac{V_{Br_2}}{t})_1 = \frac{20}{25}x\frac{15}{20} = 0.6$$

Since a decrease in [ethene] results in the same decrease in rate, the reaction is first order with respect to ethene.

Comparing experiment 1 and 3,

[Br₂] used in experiment **3** is decreased by $\frac{10}{20}$ =0.5 x [Br₂] used in expt **1**

$$\frac{Rate_3}{Rate_1} = (\frac{V_{Br_2}}{t})_3 \div (\frac{V_{Br_2}}{t})_1 = \frac{10}{15} \times \frac{15}{20} = 0.5$$

Since a decrease in $[Br_2]$ results in the same decrease in rate, the reaction is first order with respect to bromine.

(iv) 15 s

(v) The reaction progresses via electrophilic addition mechanism with the formation of carbocation, CH₂BrCH₂⁺.

Subsequent addition of CH₃OH to the carbocation and loss of H⁺ results in the formation of product as shown:



Question 3

(a) The electronic configuration of V^{3+} is [Ar]3d².

Hence its 3d-subshell is only partially filled.

 $V^{3\scriptscriptstyle +}$ exists as aqua complex, $[V(H_2O_6)]^{3\scriptscriptstyle +}$ in aqueous solution.

H₂O ligand splits the 3d–subshell into two sets of different energy.

Electron in the lower set **absorbs visible light energy** corresponding to the **small** energy gap between the 2 sets of energy and **is promoted to the upper set**.

Since visible light is absorbed, aqueous solutions of vanadium ions are coloured, with the **colour observed being the complementary colour** of the light absorbed.

(b)(i) $SO_2(g) + 2VO_2^+(aq) \longrightarrow SO_4^{2-}(aq) + 2VO^{2+}(aq)$ SO_2 reduces yellow VO_2^+ to blue VO^{2+} . As the reaction proceeds, the presence of both yellow VO_2^+ and blue VO_2^{2+} causes the mixture to appear green until all VO_2^{+} is used up and the solution appears blue due to VO^{2+} .

- (ii) SO₂ can also react with KMnO₄. It must be boiled off completely to ensure that none of it remains so that the KMnO₄ used in titration reacts only with vanadium ions and hence the amount of vanadium ions can then be determined accurately.
- (iii) Amount of vanadium ions = 5 x amount of MnO_4^- used = 5 x $\frac{33.00}{1000}$ x 0.0200 = 3.300 x 10⁻³ mol Mass of vanadium in sample = 3.300 x 10⁻³ x A_r of V = 3.300 x 10⁻³ x 50.9 = 0.1680 g Percentage by mass of V = $\frac{0.1680}{0.300}$ x 100 = 56.0%
- (c)(i) Reaction at electrode A: $VO_2^+(aq) + 2H^+(aq) + e^- \longrightarrow VO^{2+}(aq) + H_2O$ (I) Reaction at electrode B: $V^{2+}(aq) \longrightarrow V^{3+}(aq) + e^ E_{cell}^{\Theta} = 1.00 - (-0.26) = +1.26V$
- (ii) Electrode A is the <u>positive electrode as electrons are consumed</u> in the reaction due to reduction of VO_2^+ to VO^{2+} .
- (iii) To <u>increase the total surface area of the electrodes</u> so that the reactions at the electrodes proceed rapidly.
- (iv) As the reaction proceeds, the <u>electrolyte in tank A becomes increasingly negative</u> (due to consumption of H⁺) while the <u>electrolyte in tank B becomes increasingly positive</u> (due to a more highly positively charged ion being formed). The membrane <u>allows selective ions to pass through</u> (eg H⁺ to migrate via membrane from tanks B to A) to maintain electrical neutrality.
- (v) Spent electrolyte may be replaced by fresh electrolyte so that the battery does not run out of power.
 (Other acceptable answers: Storage of chemicals in conventional battery lead to loss of power/ environment aspect due to battery being thrown away etc.)
- (d) $VO_2^+(aq) + 2H^+(aq) + e^- \longrightarrow VO^{2+}(aq) + H_2O(I)$ Change in amount of VO_2^+ required = (0.90–0.10) x 3 x 2.00 mol = 4.80 mol Amount of electrons needed = 4.80 mol Quantity of electricity required = 4.80 x 96500 C = 4.632 x 10⁵ C Time required = $\frac{Q}{I}s = \frac{4.6320x10^5}{12} \div 3600 h = 10.7 h$

Question 4

(a) Iodine oxidises thiosulfate to tetrathionate resulting in a change of average oxidation number from +2 to +2.5:

$$\begin{split} &I_2 + 2S_2O_3^{\ 2^-} \longrightarrow 2I^- + S_4O_6^{\ 2^-} \\ &\text{Chlorine oxidises thiosulfate to sulfate(VI) resulting in a change of average oxidation number from +2 to +6: \\ &4Cl_2 + S_2O_3^{\ 2^-} + 5H_2O \longrightarrow 8CI^- + 2SO_4^{\ 2^-} + 10H^+ \\ &\text{Since chlorine is able to increase the oxidation state of S in thiosulfate more greatly than iodine, chlorine has higher oxidising power than iodine.} \end{split}$$

(b)(i) NaCl(s) + H₂SO₄(l) \longrightarrow NaHSO₄(s) + HCl(g)

- (ii) Hydrogen iodide formed is oxidised by conc H_2SO_4 to iodine since HI is easily oxidised.
- (iii) Concentrated phosphoric(V) acid.
- (c) O Br reacts with aq NaOH at <u>room temperature</u>, Br reacts with aq NaOH only on warming.

This is because $\underline{C_6H_5COBr}$ undergoes nucleophilic substitution more readily than $\underline{C_6H_{11}Br}$ which requires heating for the reaction with aq NaOH to form $\underline{C_6H_{11}OH}$. $\underline{C_6H_5Br}$ does not react with aq NaOH.

Their differences in reaction with aq NaOH is due to differences in structures which result in different ease of substitution.

Due to the presence of electronegative O attached to the carbonyl C, the carbonyl C in C_6H_5COBr is <u>more partially positive</u> compared to the C to which Br is attached in $C_6H_{11}Br$.

The carbonyl carbon in C_6H_5COBr is also sp^2 -hybridised so that it is <u>less sterically hindered</u> than the sp^3 -hybridised carbon to which the Br atom is attached in $C_6H_{11}Br$.

Due to the overlap of the orbital containing lone–pair of electrons on Br with π –electron cloud of benzene ring, the C–Br has **partial double bond character** so that it is not easily broken and does not react with aq NaOH even on heating.

(d)(i) Ca has a **bigger atomic radius**/ more diffuse electron cloud than Mg so that it does not form strong covalent bond with R and X. Thus, it is not able to form organometallic compounds with halogenoalkanes.

Lithium/ copper gives a similar reaction with halogenoalkane as magnesium.

(v)

- (ii) Being a very strong base, <u>**R** in **RMqX** reacts with water</u> to form an alkane, **RH** which would prevent it from acting as a nucleophile.
- (iii) The reaction between Mg and RX requires breaking of the C-X bond.

C–X bond gets weaker in the order C–F > C–Cl > C–Br > C–I due to <u>decrease in efficiency</u> of overlap of C and X orbitals as valence orbital of X becomes more diffuse as halogen increases in size/ <u>decrease in polarity of C–X bond</u> as X decreases in electronegativity down the group.

Hence reactivity between RX and Mg is in the order: iodoalkane > bromoalkane> chloroalkane > fluoroalkane.



OH

 CH_3



(vi) One mole of RMgBr reacts with one mole of CH₃COBr via nucleophilic substitution mechanism to form one mole <u>of the ketone CH₃COR</u>. The one mole of CH₃COR formed then reacts with another mole of RMgBr to form CH₃CR₂OH. (vii) Ratio of alcohol A: alcohol B: alcohol C

 $= \frac{2}{3}x\frac{2}{3} : 2 \times \frac{2}{3}x\frac{1}{3} : \frac{1}{3}x\frac{1}{3}$ = 4 : 4 : 1

Question 5

(a)(i) F exists as zwitterions so that ionic bonds hold the zwitterions strongly,

resulting in it having higher melting point than **D** which only has weaker <u>hydrogen bonds</u> between its molecules.

D is basic and does not react with aq NaOH. It can only interact with water molecules in NaOH(aq) via hydrogen bonding. The hydrophobic benzene ring further limits its solubiliity in aq NaOH.

F contains the –COOH group and hence reacts with aq NaOH to form an anion:

$${}^{*}H_{3}N \longrightarrow CH_{2}CH_{2}COO^{-} + OH^{-} \longrightarrow H_{2}N \longrightarrow CH_{2}CH_{2}COO^{-} + H_{2}O$$
Or
$$H_{2}N \longrightarrow CH_{2}CH_{2}COOH + OH^{-} \longrightarrow H_{2}N \longrightarrow CH_{2}CH_{2}COO^{-} + H_{2}O$$

The anion interacts with water molecules strongly via ion–dipole interactions so that F is more soluble in NaOH(aq) than D.



(iii)



Or other sensible answers (presence of CH_3CHOH – or CH_3CO – group and absence of amine and –COOH groups.)

(b)	Information	Deduction of structure
	Formula of $\mathbf{G} = C_8 H_{11} O_3 N$	Index of unsaturation
		$= \frac{1}{2}(2x8+2-11+1) = 4$
		(or high C to H ratio)
		\Rightarrow G is likely to contain a benzene ring/ aromatic.
	G rotates plane–polarised light.	G is likely to contain at least one chiral carbon.
	G gives a violet colouration with	G is a phenol with violet colourtion formed by complex
	neutral FeCl ₃ solution	formation.
	G reacts with 2 mol of aq NaOH	There are 2 phenolic–OH group in G , reacting with OH ⁻
		via acid-base reaction .
	G is insoluble in water but dissolves	G is likely to contain an amine group, with $-NH_2$ being
	in dil H₂SO₄.	protonated by H ⁺ .
	G is oxidised by $K_2Cr_2O_7$ to form a	G is a secondary alcohol and is oxidised to a ketone by
	product which reacts with	$K_2Cr_2O_7$.
	2,4–DNPH to give an orange ppt.	
	H is formed by reaction of G with Al_2O_3	H is formed from G by dehydration , it is likely an alkene.
	H reacts with ag Br ₂ to form	The product is likely to be a bromohydrin formed by
	$C_8H_7O_3NBr_4$.	electrophilic addition and electrophilic substitution
		into activated benzene ring.
	G reacts with $C\ell CO-COC\ell$ to form	The phenol, secondary alcohol and amine reacts with
	J which has 3 hexagonal rings.	CCO-COCC via nucleophilic substitution.
		3 hexagonal ring \Rightarrow cyclic esters and amides formed
		with the phenolic –OHs and alcoholic–OH and amine on
		adjacent carbon atoms.



G

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