Pioneer Junior College H2 Chemistry Preliminary Examination Paper 3 Suggested Answers

1 (a) (i) Using pV = nRT(38.9 x 101000)(2.0 x 10⁻³) = n_{total} x 8.31 x (273 + 30) n_{total} = 3.12 mol

	$SO_2Cl_2(g)$	≠	SO ₂ (g)	+	Cl ₂ (g)
Eqm amount / mol	2 – x		Х		х

At equilibrium, $n_{total} = 2 - x + x + x$ = (2 + x) mol

x = 1.12 mol

 $n(SO_2Cl_2) = 2 - 1.12 = 0.88 \text{ mol}$ $n(SO_2) = n(Cl_2) = 1.12 \text{ mol}$

(ii) $[SO_2Cl_2] = \frac{1}{2}(0.88) = 0.44 \text{ mol dm}^{-3}$ $[SO_2] = [Cl_2] = \frac{1}{2}(1.12) = 0.56 \text{ mol dm}^{-3}$

$$K_c = \frac{(0.56)^2}{(0.44)} = 0.713 \text{ mol dm}^{-3}$$

- (iii) Le Chatelier's principle states that when a <u>system in equilibrium</u> is subjected to a change, the system will react in such a manner to <u>counteract the change</u> so as to <u>re-establish the equilibrium</u>.
- (iv) $SO_2Cl_2(g) \Rightarrow SO_2(g) + Cl_2(g)$ ΔH negative

By Le Chatelier's principle, an increase in temperature favours an endothermic reaction. Since the forward reaction is exothermic, the position of equilibrium shifts to the left, resulting in an increase in $[SO_2Cl_2]$ and a decrease in $[SO_2]$ and $[Cl_2]$. Thus, the value of K_c will decrease.

(b) Sodium chloride has a high melting point whereas silicon tetrachloride has a low melting point. Sodium chloride is an ionic compound with giant ionic lattice structure. Strong electrostatic attractions exist between sodium and chloride ions, hence large amount of energy is required to weak the strong ionic bonds during melting. Silicon tetrachloride is a covalent compound with <u>simple molecular structure</u>. Weak van der waals forces (induced dipole – induced dipole) exist between silicon tetrachloride molecules. Lesser energy is required to overcome these intermolecular forces of attractions during melting. (or difference in electrical conductivity) Sodium chloride gives sodium and chloride ions on dissolution in water. Both sodium ion (having low polarising power) and chloride ions (anion of a strong acid) do not undergo <u>hydrolysis</u> thus a solution of sodium chloride is neutral. Silicon tetrachloride, on the contrary, undergoes <u>hydrolysis</u> to give an acidic solution.

NaCl(s) + aq \rightarrow Na⁺(aq) + Cl⁻(aq) SiC $l_4(I)$ + 2H₂O(I) \rightarrow SiO₂(s) + 4HCl(aq)

(c) (i)

$$CH_{3}CH=CH_{2} \xrightarrow{I} CH_{3}CH(OH)CH_{2}Br \xrightarrow{II} CH_{3}COCH_{2}Br \xrightarrow{III} CH_{3}COCH_{2}OH$$

Step I: Br₂(aq)

Step II: $KMnO_4(aq)$, $H_2SO_4(aq)$, heat

Step III: NaOH(aq), heat

- **2 (a) (i)** Standard enthalpy change of neutralisation is the heat evolved when 1 mole of water is formed when an acid reacts with an alkali under the standard conditions of 298 K and 1 atm.
 - (ii) Ethanoic acid is weak acid which undergoes partial dissociation. Some of the energy liberated from the neutralisation is used for the dissociation of the weak acid unlike HC*l* and HNO₃ which dissociate completely.

(iii) $CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+Cl^-$

Heat evolved = mC Δ T = (35.0 + 45.0) x 4.2 x 5.2 = 1747 J = 1.747 kJ

No of moles of salt produced = $35.0/1000 \times 1.0 = 0.0350 \text{ mol}$

 $\Delta H_{reaction} = -1.747.2/0.035 = -49.9 \text{ kJ mol}^{-1}$

(b) (i)
$$CH_3CH_2NH_2 + H_2O \Rightarrow CH_3CH_2NH_3^+ + OH^-$$

[]_{eqm} / mol dm⁻³ 0.10 - x x x

$$K_{b} = \frac{[CH_{3}CH_{2}NH_{3}^{+}][OH^{-}]}{[CH_{3}CH_{2}NH_{2}]}$$
$$4.5 \times 10^{-4} = \frac{x^{2}}{0.10 - x}$$

Since $CH_3CH_2NH_2$ is a weak base, it undergoes partial dissociation. Hence, 0.10 >> x. Thus, 0.10 - x \approx 0.10

$$x = [OH^{-}] = 6.71 \times 10^{-3} \text{ mol dm}^{-3}$$

 $pH = 14 - pOH = 14 - [-lg(6.71 \times 10^{-3})] = 11.8$

(ii) A solution that is equally effective in resisting changes in pH is a buffer at its maximum buffer capacity, i.e. a solution in which [CH₃CH₂NH₂] = [CH₃CH₂NH₃⁺]. This occurs when half of the amount of CH₃CH₂NH₂ is converted to the salt.

Volume of HC*l* required for complete neutralisation = 20.00 cm^3 Volume of HC*l* required to neutralise half the amount of CH₃CH₂NH₂ = 10.00 cm^3 .

At the maximum buffer capacity, $pOH = pK_b$ pOH = -lg(4.5 x 10⁻⁴) = 3.35 pH = 14 - 3.35 = 10.7





(c) phenylamine < 4-methylphenylamine < ethylamine

Ethylamine is the most basic as it contains one electron donating, ethyl group. This makes the lone pair of electrons on N more available to accept a proton. Phenylamine is the least basic as it contains an amine group bonded directly to the benzene ring. As a result, the lone pair of electrons on the N can delocalised into the ring, making the lone pair of electrons on N less available for coordination with proton. 4-methylphenylamine is more basic than phenylamine because it contains –CH₃ group which is electron donating which reduces the extent of the delocalisation of the lone pair of electrons on N.

- (d) (i) CH₃COC*l*, room temperature
 - (ii) Phenol is not a good nucleophile to react with ethanoyl chloride to form the ester.

[Note: To form the ester, phenol is usually treated with NaOH(aq) to form sodium phenoxide. Phenoxide ion is a better nucleophile.]

(iii) NaOH(aq) at room temperature

Product:



NaOH(aq), heat



3 (a) (i) The <u>order of reaction</u> with respect to a reactant is the <u>power</u> to which the concentration of that <u>reactant</u> is raised in the experimentally determined rate equation.

Half-life, t_{γ_2} , is the <u>time taken for the reactant concentration to</u> decrease to half of its original value.

(ii) Let rate= $k[H_2O_2(aq)]^m[I^{-}(aq)]^n$

Compare experiments 1 & 2, keeping $[H_2O_2(aq)]$ constant $\frac{1.2x10^{-4}}{1.5x10^{-4}} = \frac{k(0.020)^m (0.040)^n}{k(0.020)^m (0.050)^n}$ (or use inspection method) n = 1

Rate of reaction is <u>1st order</u> with respect to I(aq) or rate $\alpha[I(aq)]$.

Compare experiments 1 & 3, keeping [I⁻(aq)] constant $\frac{1.2x10^{-4}}{3.0x10^{-4}} = \frac{k(0.020)^{m}(0.040)^{n}}{k(0.050)^{m}(0.040)^{n}} \quad \text{(or use comparing method)}$ m = 1

Rate of reaction is <u>1st order</u> with respect to $H_2O_2(aq)$ or rate α [H₂O₂]

rate= $k[H_2O_2(aq)][I^{-}(aq)]$

- (iii) Using experiment 1, rate= $k[H_2O_2(aq)][I^{-}(aq)]$ 1.2 x 10⁻⁴ = k(0.020)(0.040)k = 0.15 mol⁻¹ dm³ min⁻¹
- (iv) For experiment 4 and 5, since $[I^{(aq)}] >> [H_2O_2(aq)]$, $[I^{(aq)}]$ is approximately constant.

Thus, rate = $k'[H_2O_2(aq)]$ (a pseudo first order reaction) where k' = k[I(aq)] $\ln 2$ $\ln 2$

$$t_{1/2} = = \frac{m_{-}}{k'} = \frac{m_{-}}{k[I^{-}]}$$

 $t_{1/2}$ of H_2O_2 in experiment 4 = 9.2 min (for [I⁻(aq)] = 0.500 mol dm⁻³) $t_{1/2}$ of H_2O_2 in experiment 5 = 4.6 min (for [I⁻(aq)] = 1.00 mol dm⁻³)

(b) (i) The reaction can be quenched by:

- adding NaOH/NaHCO₃/Na₂CO₃ to remove the H⁺(aq)
- sudden <u>cooling</u> of the reaction mixture
- sudden <u>dilution</u> through the addition of large volume of water any of the above method
- (ii) $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

(c) (i) On descending the group, the atomic size of the halogen increases, the number of electrons that can be polarised increases. The strength of the van der Waals' forces (induced dipole – induced dipole interactions) increases (or the effects of a stronger induced dipole – induced dipole interaction outweigh the effect of the permanent dipole – permanent dipole interaction) from HCl to HI. More energy is required to overcome the van der Waals' forces (induced dipole – induced dipole interactions).

Hence, the boiling points of HCl, HBr and HI increase down the Group.

(ii) Thermal stability of the hydrides decreases down from HCl to HI, i.e. thermal stability of HCl > HBr > HI.

On descending the group, the atomic size of the halogen increases, the valence p-orbital of the halogen becomes more diffused. As a result, the overlap the orbitals between hydrogen and the halogen in forming the H – X bond becomes less effective. Hence, the bond length of H – X increases from HC*l* to HI and the H – X bond formed becomes weaker and therefore less energy required to break H – X bond.

(d)

Information given	Deduction		
P , $C_{10}H_{11}O_2Br$, has high C: H ratio, no. of C > 6.	Presence of aromatic ring		
P , C ₁₀ H ₁₁ O ₂ Br, does not undergo acid base reaction with aqueous sodium carbonate	P does not contain a carboxylic acid group.		
P undergoes alkaline hydrolysis and nucleophilic substitution to form Q and $\mathbf{R}(C_7H_8O)$.	 P is an ester. Q is salt of carboxylic acid and contains –OH group. R is an alcohol with aromatic ring. 		
R undergoes oxidation to give benzoic acid.	R Is phenylmethanol.		
Q is optically active.	Q has a chiral carbon with 4 different groups attached.		
Q undergoes nucleophilic substitution with PCl_5 to form steamy fumes of HCl .	Q contains a carboxylic acid and an alcohol group.		



4 (a) (i) $3Mg(NH_2)_2(s) \rightarrow Mg_3N_2(s) + 4NH_3(g)$

(ii) Mg(NH₂)₂ is less thermally stable than Ba(NH₂)₂. Due to a smaller ionic radius, Mg²⁺ has a higher charge density than Ba²⁺ hence it is able to polarise the electron cloud of the amide ion to a greater extent. This weakens the N-H bond in the Mg(NH₂)₂ more and thus a lower temperature is needed to decompose magnesium amide.

(iii)
$$Mg_3N_2(s) + 6H_2O(I) \rightarrow 3Mg(OH)_2(s) + 2NH_3(aq)$$

 $NH_3(aq) + HCl \rightarrow NH_4^+ + Cl^-$

Amount of Mg_3N_2 formed = $\frac{1}{2} \times 0.0060 = 0.0030$ moles

 M_r of $Mg_3N_2 = 100.9$

Mass of $Mg_3N_2 = 0.003 \times 100.9 = 0.303 g$

Percentage of magnesium nitride = 0.303 x 100% = 30.3%

(b) (i) At 298K, $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$ = +71 - 298(174/1000) = +19.1 kJ mol⁻¹

The reaction is not energetically feasible is the ΔG^{θ} is positive.

(ii) Since $\Delta S > 0$ and $\Delta H > 0$, for reaction to be feasible, $\Delta G < 0$, this can only occur at a higher temperature.

(c) Enthalpy



By Hess Law,

$$\Delta H^{\theta}_{lattice} (ZnO) = -657 - 908 - 1730 - \frac{1}{2}(496) - 130 + (-348)$$

 $= -4021 \text{ kJmol}^{-1}$

(d)

Information given in Qn	Deduction		
L , C ₉ H ₈ O, has a high C:H ratio and number of C > 6.	Presence of an aromatic ring present		
Compound L is insoluble in water and aqueous sodium hydroxide.	L does not contain a phenol group.		
L undergoes electrophilic addition with liquid bromine to form M , $C_9H_8OBr_2$.	L contains an alkene group.		
L undergoes oxidation with Tollens' reagent to give a silver mirror but not with Fehling's solution.	L is a benzaldehyde.		
L undergoes oxidation with acidified potassium manganate(VII) to give N, $C_8H_6O_4$ with the loss of 1 C as CO_2 .	L has the C=C is at the terminal position. N is a diacid due to the presence of 4 oxygen atoms.		
Compound N undergoes acid-base reaction with aqueous sodium hydroxide to form a soluble sodium salt.	N contains carboxylic acid groups.		
N undergoes nucleophilic substitution with SOC <i>l</i> ₂ to form two acid chloride groups which undergoes further nucleophilic substitution with ethylamine.	The final product O is a diamide.		

5 (a) surface area of artefact = 800 cm^2

volume of Al ₂ O ₃ deposited	= surface area x thickness = 800 x (0.1/10) = 8.00 cm ³		
mass of Al_2O_3 deposited = 4.0 x 8.00 = 32.0 g			
amount of Al ₂ O ₃ deposited	= 32.0 / [2(27.0) + 3(16.0)] = 0.3137 mol		
During anodising, $2H_2O \rightarrow O_2 + 4H^+ + 4e$			

 $4Al + 3O_2 \rightarrow 2Al_2O_3$

Hence, $2Al_2O_3 \equiv 3O_2 \equiv 12 \text{ e}^ 1Al_2O_3 \equiv 3/2 \text{ } O_2 \equiv 6 \text{ e}^-$

amount of e⁻ needed to deposit 0.3137 mole of $Al_2O_3 = 0.3137 \times 6$ = 1.882 mol

- (b) (i) A complex ion contains a <u>central metal ion bonded to ligands</u> by <u>co-ordinate / dative bonds</u>. An example of a complex ion is [Fe(H₂O)₆]³⁺.
 - (ii) In complex ion, there is repulsion between the electrons in the ligands and the electrons in the d orbitals of the transition metal ion. This raises the energy of the d orbitals and splits them into two sets of different energies. This is known as d-orbital splitting.

When light passes through a solution of the transition complex, light with energy corresponding to the energy difference between the dorbitals can be absorbed to promote an electron from the set of lower energy d orbitals to that of higher energy. This is known as d-d transition.

The colour exhibited by $[Fe(H_2O)_6]^{2+}$ is complementary to the colour of light that is absorbed.

(c) $Fe^{3+}(aq) + e \Rightarrow Fe^{2+}(aq)$ $E^{e} = + 0.77 V$ $I_{2}(aq) + 2e \Rightarrow 2I^{-}(aq)$ $E^{e} = + 0.54 V$ $[Fe(CN)_{6}]^{3-} + e \Rightarrow [Fe(CN)_{6}]^{4-}$ $E^{e} = + 0.36 V$ $2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_{2}$ $E^{e}_{cell} = +0.77 + (-0.54)$ = +0.23 V > 0

Hence, reaction is energetically feasible. lodide is oxidised to iodine which accounts for the reddish brown solution.

$$2[Fe(CN)_6]^{3-} + 2I^- \rightarrow 2[Fe(CN)_6]^{4-} + I_2 \qquad E^{\Theta}_{cell} = +0.36 + (-0.54) \\ = -0.18 \text{ V} < 0$$

The reaction is not energetically feasible.

 $[Fe(CN)_6]^{3-}$ cannot be reduced by I⁻, this is because CN⁻ ligands are able to stabilise the +3 oxidation state of iron (relative to the +2 oxidation).

- (d) Haemoglobin consists of 4 separate polypeptide chains of two types, namely 2 α chains and 2 β chains. Each polypeptide carries a haem group containing Fe²⁺ to form a subunit. Each subunit folds and coils into a compact globular shape and joins together by hydrogen and ionic bonds. The hydrophobic R groups are directed inwards to the centre. They are also involved in holding haemoglobin in its three dimensional shape. The hydrophilic R groups are directed outwards on the surface of the molecules, making it soluble in water.
- (e) (i) Dative bonding in which the lone pair of electrons on the oxygen atom is donated to the vacant orbitals of iron.
 - (ii) The oxidation state of iron remains as +2 as the reaction to form oxyhaemoglobin is a <u>ligand exchange</u> not a redox reaction.



A – Aspartic acid; B – Glycine; C – Lysine