## 2015 Year 6 H2 Chem Preliminary Examination Paper 3 (Suggested Solutions)

Answer any four questions on writing paper.

1 (a) (i)

• The difference in ionic radius/ size between the cation and anion is large. This leads to poor packing of the ions in the solid state.

The cationic radius is large which results in a low magnitude of the lattice energy/ less exothermic lattice energy.

<u>OR</u> the dispersion of charge of the cation due to resonance weakens the ionic bonds /interaction.

$$\sim N \sim N$$
  $\sim N \sim N$   $\sim N \sim N$ 

- (ii) A large amount of energy is required to overcome the strong ionic bonds/ interaction in [emim]BF<sub>4</sub> hence they have high boiling point.
- (iii) It allows volatile organic compounds to be easily removed from the ionic liquids by simple distillation.

They can be used as a medium for reactions involving ionic reagents since ionic reagents can dissolve readily in it.

(b) Let the equilibrium partial pressure of NO be 2x.

	N <sub>2</sub> (g) +	$O_2(g) =$	≃ 2NO (g)
Initial partial	0.80	0.80	0
pressure/atm			
Change in partial	-x	-x	+2x
pressure/atm			
Equilibrium partial	0.8 – x	0.8 – x	2x
pressure/atm			

$$K_p = \frac{(P_{NO})^2}{(P_{N2})(P_{O2})}$$

 $0.40 = \frac{4x^2}{(0.8-x)^2}$ x = 0.1922 P<sub>02</sub> = P<sub>N2</sub> = 0.80 - 0.1922 = 0.608 atm P<sub>N0</sub> = 2 x 0.1922 = 0.384 atm

Note: Since the moles of reactants : products is 1 : 1, total pressure remains unchanged as volume of flask is fixed at 1 dm<sup>3</sup>.  $P_{02} + P_{N2} + P_{N0} = 0.80 \times 2 = 1.60$  atm.



- (d) The catalyst will increase the rate of both the forward and the reverse reactions hence equilibrium will be established more quickly. This means that the same equilibrium partial pressure of  $N_2$  and NO will be established before 30 minutes. The rate of change of partial pressure for  $N_2$  and NO will also be faster OR the graphs have steeper gradients. The equilibrium partial pressure of all species will stay unchanged.
- (e)  $\Delta H = B.E.$  (bonds broken) B.E. (bonds formed)

= 994 + 496 - 2(607)= +276 kJ mol<sup>-1</sup> > 0

Since  $\Delta H$  of the fwd reaction is endothermic, equilibrium will shift forward when temperature increases.



HO HO L: HO

0.2 mol of L undergoes redox with Na to form 0.2 mol of H<sub>2</sub> gas  $\Rightarrow$  There are 2 alcohol groups in L

L turns moist red litmus paper blue  $\Rightarrow$  It contains a basic group/ it is basic/ it contains an amine group.

L has a higher  $pK_b$  than  $(CH_3CH_2)_2NH$  but a lower  $pK_b$  than  $C_6H_5NH_2$ 

 $\Rightarrow$  L is less basic than (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH but more basic than C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>.

 $\Rightarrow$  Lone pair of N atom in L less available than that of  $(CH_3CH_2)_2NH$  due to the electron withdrawing alcohol groups.

 $\Rightarrow$  Lone pair of N atom in L more available than that of C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> as there is no delocalisation of the lone pair on N for L.

 $\Rightarrow$  L has pK<sub>b</sub> of 4.0 (accept any value between 3.1 – 9.4)

2 (a)

$$\left[\operatorname{Ca}\right]^{2+} 2 \left[ \begin{array}{c} \operatorname{Ca} \\ \operatorname{C$$

**(b)** (i) 
$$2 Ca(IO_3)_2 (s) \rightarrow 2 CaO (s) + 2 I_2 (g) + 5 O_2 (g)$$

(ii)

cation	Cationic size/nm
Ca <sup>2+</sup>	0.099
Ba <sup>2+</sup>	0.135

The charge density (  $\alpha \frac{\text{charge}}{\text{ionicradius}}$  ) of Ba<sup>2+</sup> is smaller than Ca<sup>2+</sup>.

Hence, polarizing power of  $Ba^{2+}$  is smaller and the electron cloud of the iodate ion is polarized to a smaller extent by  $Ba^{2+}$ .

The iodine–oxygen bond in the iodate ion becomes less weakened by  $Ba^{2+}$  and more energy is required to break the bonds. Thus, barium iodate(V) is thermally more stable.

(g)

(f)

(c) When iodine reacts with the alkene, electrophilic addition occurs.  $M_r$  of the original alkene is 310 - 2(127) = 56 => the alkene has 4 carbon atoms. le C<sub>4</sub>H<sub>8</sub>. For the alkene to have geometric isomerism, it is but—2–ene.



Liquid cylcohexane is non-polar, iodine is also non-polar. Iodine vapour simply dissolves in liquid cyclohexane as it is able to form favourable van der Waals forces of attractions with cyclohexane as the weak van der Waals attractions between iodine molecules is similar in strength with the weak van der Waals in cyclohexane.

(d) (i)

$$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$$
  
= +80000 - (273+25)(152)  
= 34 704 J mol<sup>-1</sup>

 $\Delta G^{\theta} = -2.303 \text{ RT Ig } K_{sp}$ 34 704 = -2.303 (8.31)(298) Ig  $K_{sp}$   $K_{sp} = 8.22 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9}$ 

(ii)

$$2IO_3^- + 12H^+ + 10e^- \Longrightarrow I_2 + 6H_2O \qquad E^{\ominus} = +1.20 V$$
$$O_2 + 2H^+ + 2e^- \Longrightarrow H_2O_2 \qquad E^{\ominus} = +0.68 V$$

 $E_{\text{cell}}^{\ominus} = 1.20 - 0.68 = +0.52 \text{ V} > 0$ . Hence reaction is feasible.

Equation:  $5H_2O_2 + 2IO_3^- + 2H^+ \rightarrow I_2 + 6H_2O + 5O_2$ 

Observation: colourless solution turns brown (with black iodine solids) and effervescence of oxygen gas seen.

(e) (i)



$$\begin{array}{cccc} \operatorname{Fe}^{3+} + e^{-} & \Longrightarrow & \operatorname{Fe}^{2+} & +0.77 \\ \operatorname{I}_{2} + 2e^{-} & \rightleftharpoons & 2\Gamma^{-} & +0.54 \\ \operatorname{Fe}^{2^{+}} + e^{-} & \rightleftharpoons & \operatorname{Fe} & -0.44 \end{array} \right\} \quad \text{Quote 3 } E^{\ominus} \text{ ; 2 } E^{\ominus}$$

- $E_{\text{cell}}^{\ominus} = E_{\text{cell}}^{\ominus}(\text{Fe}^{2+}/\text{Fe}) E_{\text{cell}}^{\ominus}(\text{I}_2/\text{ I}) = -0.44 (+0.54) = -0.98 \text{ V} < 0$
- Oxidation of  $\Gamma$  by Fe<sup>2+</sup> is a non–spontaneous reaction.
- Thus, there is no reaction between I<sup>-</sup> and Fe<sup>2+</sup> when solutions of iron(II) sulfate and potassium iodide are mixed.
- $E^{\ominus}_{\text{cell}} = E^{\ominus}(\text{Fe}^{3+}/\text{Fe}^{2+}) E^{\ominus}(\text{I}_2/\Gamma) = +0.77 (+0.54) = +0.23 \text{ V} > 0$  $\Rightarrow$  This is a spontaneous reaction.
- I<sup>-</sup> is oxidised by Fe<sup>3+</sup> to form I<sub>2</sub> while the Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup> if solutions containing Fe<sup>3+</sup> and I<sup>-</sup> are mixed.

- $Ag^+(aq) + SCN^-(aq) \longrightarrow AgSCN(s)$
- (ii)
- The red colouration is due to the formation of  $[Fe(H_2O)_5SCN]^{2+}$  complex.

(iii)

 $\begin{array}{rcl} \mathsf{Ag}^{+}(\mathsf{aq}) + \mathsf{SCN}^{-}(\mathsf{aq}) & \mathchoice{\longrightarrow}{\leftarrow}{\leftarrow}{\leftarrow} & \mathsf{AgSCN}(\mathsf{s}) & \mathsf{K}_{1} \\ [\mathsf{Fe}(\mathsf{H}_{2}\mathsf{O})_{\mathsf{6}}]^{3+}\left(\mathsf{aq}\right) + \mathsf{SCN}^{-}(\mathsf{aq}) & \Huge{\longrightarrow}{\leftarrow}{\leftarrow}{\leftarrow} & [\mathsf{Fe}(\mathsf{H}_{2}\mathsf{O})_{\mathsf{5}}\mathsf{SCN}]^{2+}\left(\mathsf{aq}\right) & \mathsf{K}_{2} \end{array}$ 

- Equilibrium constant for the formation of AgSCN,  $K_1$ , is much larger than equilibrium constant for the formation of [Fe(H<sub>2</sub>O)<sub>5</sub>SCN]<sup>2+</sup>,  $K_2$ .
- $[Fe(H_2O)_5SCN]^{2+}$  is formed only after the precipitation of AgSCN is completed.
- Any excess SCN<sup>-</sup> subsequently added after the end-point reacts with Fe<sup>2+</sup> in the analyte solution to form the red complex.
- (iv) The solubility and hence the solubility product of CH<sub>3</sub>CO<sub>2</sub>Ag varies with temperature.
  - The silver nitrate sodium ethanoate mixture is kept at 25 °C, so that the [Ag<sup>+</sup>] in the filtrate corresponds to the amount of solid CH<sub>3</sub>CO<sub>2</sub>Ag dissolved at 25 °C.
  - Titration involves the precipitation of AgSCN, whose solubility varies with temperature.
  - Thus, the titration mixture should also be kept at 25 °C to ensure that the endpoint is accurately determined.
- (v) The titration must be carried out in acidic solution to prevent the precipitation of  $Fe^{3+}$  as  $Fe(OH)_3$ .
- (c)(i) Graph I is a titration curve of pAg against volume of KSCN.
  - At the beginning of the titration, Ag<sup>+</sup> is in excess.
  - As KCN (titrant) is added, [Ag<sup>+</sup>] decreases. This corresponds to increasing pAg values.

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(ii) Let s be the equilibrium concentration of Ag<sup>+</sup>.

 $AgSCN(s) \implies Ag^{+}(aq) + SCN^{-}(aq)$ eqm [] / mol dm<sup>-3</sup> - s s s  $\mathcal{K}_{sp}(AgSCN) = [Ag^{+}][SCN^{-}]$ 1.03 × 10<sup>-12</sup> = s<sup>2</sup>  $\Rightarrow s = 1.01 \times 10^{-6} \text{ mol dm}^{-3}$   $\therefore pAg = pSCN = -\log_{10}(1.01 \times 10^{-6}) = 5.99$ 

(iii) • Equivalence point occurs at the point at which Graphs I and II intersect.

(iv) In the saturated solution of  $CH_3CO_2Ag$ ,  $[Ag^+] = [CH_3CO_2^-] = \frac{(8.8)(0.10)}{20.0} = 0.0440 \text{ mol dm}^{-3}$ Thus,  $K_{sp}(CH_3CO_2Ag) = [Ag^+][CH_3CO_2^-]$ 

 $\therefore$  Volume of KSCN needed = 8.8 cm<sup>3</sup>

 $\begin{aligned} \text{hus,} \quad \mathbf{A}_{\text{sp}}(\text{CH}_{3}\text{CO}_{2}\text{Ag}) &= [\text{Ag}^{+}][\text{CH}_{3}\text{CO}_{2}] \\ &= (0.0440)^{2} \\ &= 1.94 \times 10^{-3} \text{ mol}^{2} \text{ dm}^{-6} \end{aligned}$ 

(d) • Solid residue obtained by filtration of titration mixture is AgSCN.

	Ag	С	Ν
Mass / g per 100 g sample	80.6	8.96	10.5
No. of moles	$\frac{80.6}{108} = 0.746$	$\frac{8.96}{12.0} = 0.747$	$\frac{10.5}{14.0} = 0.750$
Ratio of atoms	1	1	1

• Empirical formula of Q is AgCN.

Let  $(AgCN)_n$  be the formula of Q. (108 + 12.0 + 14.0)n = 268 $\therefore n = 2$ 

- Q has a formula of  $Ag_2C_2N_2$  or working above.
- Precipitation of Q occurs when Ag<sup>+</sup> is mixed with [Ag(CN)<sub>2</sub>]<sup>-</sup>.
- Thus, white solid Q is likely to be Ag[Ag(CN)<sub>2</sub>], which contains one cation and one anion.

AgSCN(s)		Ag⁺(aq) + SCN⁻(aq)	 (1)
AgI(s)	$\rightleftharpoons$	Ag⁺(aq) + I⁻(aq)	 (2)
Ag⁺(aq) + 2CN⁻(aq)	$\longrightarrow$	Ag(CN)2 <sup>-</sup> (aq)	 (3)

In the presence of excess CN<sup>-</sup>, Ag<sup>+</sup> forms soluble complex anion, [Ag(CN)<sub>2</sub>]<sup>-</sup>, which decreases [Ag<sup>+</sup>]. By Le Chatelier's Principle, equilibrium position for reaction (1) & (2) shifts right to increase [Ag<sup>+</sup>] and AgSCN and AgI dissolve.

4(a)(i)  

$$\begin{bmatrix} Cu(H_2O)_6 \end{bmatrix}^{2+} (aq) + 2OH^- (aq) \implies Cu(OH)_2 (s) + 6H_2O (l) \\ \begin{bmatrix} Cu(H_2O)_6 \end{bmatrix}^{2+} (aq) + 4NH_3 (aq) \implies \begin{bmatrix} Cu(NH_3)_4 \end{bmatrix}^{2+} (aq) + 6H_2O (l) \end{bmatrix}$$

- (ii) Copper has a higher nuclear charge and more electrons than calcium. The additional electrons enter penultimate 3d orbitals of copper. However 3d electrons provide a poor shield between outermost 4s electrons and the nucleus. Hence, 4s electrons of copper are still strongly attracted by the nucleus. Higher effective nuclear charge experienced by 4s electrons of copper results in smaller atomic radius for copper.
- (b) (i) In the presence of a ligand, the degenerate d orbitals are split into 2 groups of orbitals with different energy level. However, d–d transition is not possible for copper(I) ion as it is a d<sup>10</sup> system with all d orbitals fully filled.
  - (ii) Copper(II) chloride salt is predicted to be more soluble in water. The lattice energy of copper(I) chloride is expected to be less exothermic than the lattice energy of copper(II) chloride since copper(I) ion has lower per unit charge than copper(II) ion and copper(I) ion has a larger ionic radius than copper(II) ion. However, the enthalpy change of hydration for copper(II) ion is more exothermic than that of copper(I) ion as copper(II) ion has larger charge density. The enthalpy change of hydration may be exothermic enough to compensate for the breaking of the lattice structure in order for dissolution to occur.



(iii) Addition



(d)

Observation: Red/reddish-brown precipitate observed



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- 5 (a) Due to the partially filled 3d orbitals in the chromium catalyst [Ar]3d<sup>5</sup>4s<sup>1</sup>, the ethene molecules can form temporary bonds on the catalyst surface. Ethene molecules are also concentrated on the surface.
  - Bonds within these reactant (ethene) molecules are weakened, hence lowering the activation energy of the reaction. Number of these molecules with energy greater or equal to E<sub>a</sub> increase and hence the rate increases.
  - (b) **B** undergoes further oxidation with dichromate to give **C**. Hence **B** is an aldehyde, and A has a primary alcohol group. **C** is therefore a carboxylic acid.

**B** and **C** undergo oxidative cleavage with  $KMnO_4$  to give  $CH_3CO_2H$ . Loss of 2 carbon atoms. Hence **B** and **C** contains alkene/ C=C group, i.e.  $CH_3C=C$  group.

From the molecular formula of A,

**A**:  $CH_3CH=CHCH_2OH$ 

**B**: CH<sub>3</sub>CH=CHCHO

**C**:  $CH_3CH=CHCO_2H$ 

**B** undergoes reduction of alkene group and aldehyde group with hydrogen, while **C** undergoes reduction of the alkene group only.

**D**:  $CH_3CH_2CH_2CH_2OH$ 

**E**: CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H

(c)(i)



analogue of procaine

I: acidified KMnO<sub>4</sub>, reflux II: CH<sub>3</sub>CH<sub>2</sub>OH, conc H<sub>2</sub>SO<sub>4</sub>, reflux III: Sn in conc HCl, heat followed by aq NaOH, r.t.

- (ii) The lone pair of electrons on N<sub>a</sub> atom bonded to benzene ring is delocalised with the  $\pi$  electron cloud of the benzene ring. This decreases the availability of the lone pair on N<sub>a</sub> atom for forming a dative bond with H<sup>+</sup>.
- (iii) At pH = 10, 4-aminobenzoic acid acts as an alkaline buffer.  $H_2NC_6H_4COO^- + H_2O \implies H_3^+NC_6H_4COO^- + OH^-$

When a small amount of acid is added,  $H_2NC_6H_4COO^- + H^+ \rightarrow {}^+H_3NC_6H_4COO^$ excess  $H^+$  is removed by the base (anion) as the conjugate acid (zwitterion). Thus pH of solution remains approximately constant.

When a small amount of base is added,  $^{+}H_{3}NC_{6}H_{4}COO^{-} + OH^{-} \rightarrow H_{2}NC_{6}H_{4}COO^{-} + H_{2}O$ excess  $OH^{-}$  is removed by the conjugate acid (zwitterion) as the base (anion). Thus pH of solution remains approximately constant.

I  $[OH^{-}] = \sqrt{K_b xc} = \sqrt{4.00x10^{-4}x0.04}$ = 0.004 mol dm<sup>-3</sup> pH = 14 - pOH = 14 + lg(0.004) = 11.6

II 
$$pOH = pK_b + lg \frac{[salt]}{[base]}$$
  
 $4 = -lg(4.00x10^{-4}) + lg \frac{[salt]}{[0.04]}$   
[salt] = 0.16 mol dm<sup>-3</sup>

(d) Add in Tollen's reagent into each compound separately and warm.

A silver mirror/ grey ppt is formed with (II) but no silver mirror is formed with (I).

