## 2015 SH2 H2 Chemistry Prelim Paper 2 Suggested Answers with Examiners' Comments

#### 1(a) Procedural format

Divide the unknown into 5 separate portions

- Warm a portion with Fehling's solution: if brick red ppt forms, unknown is ethanal.

- If no ppt, warm another portion with Tollen's reagent: if silver mirror forms, unknown is **benzaldehyde**.

- If no silver mirror, warm another portion of sample with aq  $I_2$  + NaOH(aq): if yellow ppt forms; unknown is **1-iodopentan-2-one**.

- If no yellow ppt, warm another portion with NaOH(aq) and test gas with moist red litmus paper: if litmus paper turns blue, unknown is **propanamide**.

- If no alkaline gas, add  $Br_2(aq)$  to last portion: if orange  $Br_2(aq)$  decolourises & white ppt forms, unknown is **phenylamine**.

Another example of plan:





1(bi)

**1(bii)** 1. Suggest **suitable quantities** of ethanal and 2,4-DNPH to prepare the solid derivative (hydrazone).

2. Filter solid derivative and then dissolve in **minimum volume of hot solvent** (non-polar or organic) ... use **fluted filter paper / pre-heated funnel / Buchner funnel** to remove insoluble impurities

3. Cool solution to form crystals ... Then filter purified crystals using Buchner funnel.

4. **Wash** crystals with **minimum cold solvent** and **dry the solid** (in desiccator / press between filter papers / low temperature oven).

5. Find melting point of pure and dry crystals (m.p 165 °C).

- 1(c) As organic compounds are flammable, there should be NO Bunsen flame or naked flame. / Heat or warm reaction mixture in a water bath when conducting experiments.
- **2(ai)** P:  $1s^2 2s^2 2p^6 3s^2 3p^3$  S:  $1s^2 2s^2 2p^6 3s^2 3p^4$
- 2(aii) 1<sup>st</sup> IE of S is lower than that of P:

All 3*p* electrons in P are unpaired. <u>Two of the 3*p* electrons are paired</u> in S with <u>inter-</u> <u>electronic repulsion</u> between the paired electrons. Thus less energy is required to remove the 1<sup>st</sup> paired electron in S

4<sup>th</sup> IE of S is lower than that of P:

<u>4<sup>th</sup> e in S is removed</u> from <u>3p subshell</u>; while <u>4<sup>th</sup> e in P is removed from 3s subshell</u>; **3p subshell is further** from the nucleus (at a higher E level) with weaker nuclear attraction. Thus less energy is required to remove this electron in S.

2(bi)  

$$p = \frac{(1)(8.31)(298)}{(0.50 \times 10^{-3} - 5.68 \times 10^{-5})} - \frac{(1)^2 (0.687)}{(0.50 \times 10^{-3})^2}$$

$$= 2.84 \times 10^6 \text{ Pa}$$

2(bii) Using the ideal gas equation,

$$p = nRT/V = \frac{(1)(8.31)(298)}{(0.5x10^{-3})} = \frac{4.95 \times 10^6}{2} Pa$$
 or

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$$p_{ideal} = p + \frac{n^2 a}{V^2} = 2.84 \times 10^6 + \frac{1 \times 0.687}{(0.50 \times 10^{-3})^2}$$
  
= 2.84 x 10<sup>6</sup> + 2.748 x 10<sup>6</sup> = 5.59 x 10<sup>6</sup> Pa

**2(biii)** Actual pressure exerted by SO<sub>2</sub> is <u>lower</u> than that calculated from ideal gas equation. This is due to significant <u>intermolecular forces of attraction</u> between <u>polar SO<sub>2</sub></u> and thus less forceful collisions against the walls of container.

# 2(ci) L Metallic bonding

- M Ionic bonding
- N Covalent bonding
- 2(cii) I: average electronegativity for Ge and O =  $\frac{2.01 + 3.61}{2}$  = 2.81 (accept 2.60 - 3.00) difference in electronegativity for Ge and O = 3.61 - 2.01 = 1.60 (accept 1.40 - 1.80) each + correctly determined and plotted the coordinates for GeO<sub>2</sub> The nature of the oxide of germanium is <u>acidic</u>.

II: Oxide of germanium has a <u>lower</u> melting point (giant covalent compound)

Ge is below Si in Group IV with a **<u>bigger atomic size</u>**; overlap of the atomic orbitals of Ge and O will be **<u>less effective</u>** than those of Si and O; the covalent bonds between Ge and O are weaker.

**3(a)** Squaric acid dissociates fully in water to form <u>ions which form ion-dipole interactions</u> with water molecules.

**Energy released** in the formation of these interactions can **<u>compensate</u>** the <u>energy</u> **<u>required</u>** to break the <u>intermolecular hydrogen bonds in squaric acid and in water</u>.



 $C_4H_2O_4 + 2NaOH \rightarrow Na_2C_4O_4 + 2H_2O$ 

**3(bii)** Amt of excess OH<sup>-</sup> in 25.0 cm<sup>3</sup> = 
$$\frac{29.7}{1000} \times 0.100 = 2.97 \times 10^{-3}$$
 mol  
Amt of excess OH<sup>-</sup> in 100 cm<sup>3</sup> = 2.97 x 10<sup>-3</sup> mol x  $\frac{100}{25.0}$  = 1.188 x 10<sup>-2</sup> mol  
Amt of OH<sup>-</sup> that reacted with squaric acid in sample =  $\frac{100}{1000} \times 0.250 - 1.188 \times 10^{-2}$   
= 1.312 x 10<sup>-2</sup> mol  
Amt of squaric acid = 1.312 x 10<sup>-2</sup> /2 = 6.56 x 10<sup>-3</sup> mol  
Mass of pure squaric acid = 6.56 x 10<sup>-3</sup> x 114 = 0.7478 g  
% purity by mass =  $\frac{0.7478}{4} \times 100 = 18.7\%$ 

**3(c)** The dianion can undergo resonance, whereby <u>the lone pair of electrons on O<sup>-</sup> and  $\pi$ </u> <u>electrons of C=C and C=O can delocalise between the p orbitals of all the C and O</u> to give a symmetrical resonance hybrid with identical C-C bond lengths.

OR

The lone pair of electrons on O<sup>-</sup> can delocalise into the  $\pi$  electrons clouds of C=C and C=O to give a symmetrical resonance hybrid with identical C-C bond lengths.

4(ai) 
$$Hg(CNO)_2 (s) \rightarrow Hg(l) + N_2 (g) + 2CO(g)$$

4(aii)  $\Delta H_r^{\theta} = \Sigma m \Delta H_f^{\theta} (\text{products}) - \Sigma n \Delta H_f^{\theta} (\text{reactants})$ = 2 x  $\Delta H_f^{\theta} (\text{CO}) - \Delta H_f^{\theta} (\text{Hg}(\text{CNO})_2)$ = 2 x (-111) - (+386) = -608 kJ mol<sup>-1</sup>

4(aiii)  $\Delta S^{\circ}$  is positive as there is an increase in the number of gaseous molecules in the process.

 $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ , since  $\Delta H^{\circ} < 0$  and  $\Delta S^{\circ} > 0$ ,  $\Delta G^{\circ}$  is always < 0; decomposition of Hg(CNO)<sub>2</sub> is energetically feasible at all temperatures.



By Hess's law,

L.E. = 
$$-(+ 64 + \frac{1}{2} (496) + 1007 + 1810 + (-142) + 844) - 91$$
  
=  $-3922 \text{ kJ mol}^{-1}$   
=  $-3920 \text{ kJ mol}^{-1}$ 

- **4(bii)** Hg<sup>2+</sup>, same for both compounds, <u>-2 charge of O<sup>2-</sup> is higher in magnitude than -1 of</u> <u>F</u>, but <u>r- of O<sup>2-</sup> bigger than r- of F</u> (both are isoelectronic, but F has a higher NC) The effect of increase in charge product <u>outweighs</u> that of interionic distance, since  $|LE| \propto \left| \frac{q_+q_-}{r_++r_-} \right|$ , the <u>magnitude of lattice energy of HgO is likely greater than</u> <u>HgF\_2</u>.
- 4(ci) I: acid base reaction or neutralisation



II: condensation



4(cii) C=O and N-H bond



- 5(ai)  $Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$
- 5(aii)  $\begin{bmatrix} Ni(NH_3)_6 \end{bmatrix}^{2+} \\ Ni(OH)_2(s) + aq \implies Ni^{2+}(aq) + 2OH^{-}(aq) \\ \begin{bmatrix} Ni(H_2O)_6 \end{bmatrix}^{2+} + 6NH_3 \implies \begin{bmatrix} Ni(NH_3)_6 \end{bmatrix}^{2+} + 6H_2O$
- 5(aiii) Ligand exchange reaction

**5(bi)** [R]  $Cu^{2+} + 2e \rightarrow Cu$ [O]  $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$   $E_{red}^{\Theta} (Cu^{2+}/Cu) = +0.34 \text{ V}$   $E_{red}^{\Theta} (S_4O_6^{2-}/S_2O_3^{2-}) = +0.09 \text{ V}$ 

Overall equation:  $Cu^{2+} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + Cu$   $E_{cell}^{\Theta} = +0.25$  V > 0 The redox reaction is energetically feasible; blue  $CuSO_4$  solution would decolourise and a pink solid of Cu is formed.

Alternative accepted answer (in fact,  $Cu^+$  is unstable in aq medium) Overall equation:  $2Cu^{2+} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2Cu^+$   $E_{cell}^{\circ} = +0.06 \text{ V} > 0$ The redox reaction is energetically feasible, blue  $CuSO_4$  solution would become colourless  $Cu^+(aq)$ .

**5(bii)** 
$$\begin{bmatrix} \mathsf{R} \end{bmatrix} \quad \begin{bmatrix} \mathsf{Cu}(\mathsf{NH}_3)_4 \end{bmatrix}^{2^+} + 2e \to \mathsf{Cu} + 4\mathsf{NH}_3 \quad \mathsf{E}^{\Theta}_{\text{red}} \left( \begin{bmatrix} \mathsf{Cu}(\mathsf{NH}_3)_4 \end{bmatrix}^{2^+} / \mathsf{Cu} \right) = -0.05 \text{ V} \\ \begin{bmatrix} \mathsf{O} \end{bmatrix} \quad 2\mathsf{S}_2\mathsf{O}_3^{2^-} \to \mathsf{S}_4\mathsf{O}_6^{2^-} + 2e \qquad \mathsf{E}^{\Theta}_{\text{red}} \left( \mathsf{S}_4\mathsf{O}_6^{2^-} / \mathsf{S}_2\mathsf{O}_3^{2^-} \right) = +0.09 \text{ V}$$

Overall equation:  $[Cu(NH_3)_4]^{2+} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + Cu + 4NH_3$   $E_{cell}^{\Theta} = -0.14 \text{ V} < 0$ The redox reaction is not energetically feasible, deep blue  $[Cu(NH_3)_4]^{2+}$  would remain.

- **5(ci)**  $NH_3$  acts as a Bronsted base as it accepts H<sup>+</sup> from DMGH to produce DMG<sup>-</sup> ligands and  $NH_4^+$ .
- **5(cii)** Coordination number = 4 (The total number of dative bonds contributed by the ligands to the cation.)



Benzoic acid has a lower  $pK_a$  value; is a stronger acid than phenylethanoic acid.

The conjugate base of benzoic acid is <u>more stable</u> than that of phenylethanoic acid: <u>negative charge on O<sup>-</sup> is dispersed to a greater extent as electrons of O<sup>-</sup> can delocalise over 2 highly electronegative O atoms in -COO<sup>-</sup> and further into the <u>benzene ring</u>.</u>

**Dissociation of benzoic acid** into its conjugate base and H<sup>+</sup> is **more favourable** than that of phenylethanoic acid. Hence **benzoic acid is a stronger acid**.

#### Alternative answer

The <u>conjugate base of phenylethanoic acid is less stable</u> than that of benzoic acid, the <u>negative charge on O<sup>-</sup> is intensified</u> as the <u>-COO<sup>-</sup> is directly bonded to an</u> <u>electron donating alkyl</u> group.

6(bi) Lactic acid (acid with pK<sub>a</sub> value closest to the desired pH of 3.55)

6(bii) For buffer system,

$$pH = pK_a + lg \frac{[salt]}{[acid]}$$

$$3.55 = 3.86 + lg \frac{[salt]}{[acid]}$$

$$lg \frac{[salt]}{[acid]} = -0.31$$

$$\frac{[salt]}{[acid]} = 0.4898 \approx 0.490 (3 \text{ s.f.})$$

6(biii) Amount of acid  $= 0.5 \times 0.2 = 0.1 \text{ mol}$ 

Let amount of NaOH added be a mol

	HA	+	OH⁻	$\rightarrow$	$A^-$	+	H <sub>2</sub> O
Initial amount /mol	0.1		а		0		
Final amount /mol	0.1– a		0		а		







 $C_{10}H_{11}Br$  is produced through the following intermediate:



6(di)

Electrophilic addition



Based on the data on electronegativity, B is  $\delta$ + and H is  $\delta$ - (B is less electronegative than H). Thus BH<sub>2</sub><sup>+</sup> is the electrophile.

 $6(dii) \begin{array}{l} \text{Oxidation number of C* in: } Y \text{ is } -3; \text{ Z is } -1 \\ \text{Role of } H_2O_2\text{: as oxidising agent} \end{array}$ 

7(a) cys-ser-val

7(bi)



- Illustrate at least 2 H-bonding between C=O and N-H of different peptide
- Label partial charges on N-H and C=O and lone pair electron on O
- R-groups pointing outwards from the helix
- Label 3.6 amino acids per turn

7(bii) When proline is in the alpha helix structure, this is the structure of the polypeptide:



The N atom of the peptide bond of proline lacks an H atom to form hydrogen bonding at regular intervals, hence it disrupts the regular coiling of the alpha helix structure.

### Alternative answer:

The rigid ring structure of the R group of proline would hinder the twisting and coiling of the alpha helix structure.