#### 2018 Y6 H2 Chemistry Preliminary Exams Paper 3 (Suggested Solutions)

## Section A

#### **Comments**

- Students should follow the pattern given in reaction 1. The OH<sup>-</sup> removes a H<sup>+</sup> on an α carbon (C next to the carbonyl carbon) to form a nucleophile, OHC-CH<sub>2</sub><sup>-</sup>, which can take part in nucleophilic addition with an ethanal molecule. In the same way, when ethanal or propanone are used, OH<sup>-</sup> can remove H<sup>+</sup> from the α carbon in ethanal or propanone to form a nucleophile that reacts with the other or the same carbonyl compound.
- (ii) Since OH<sup>-</sup> is a catalyst, [OH<sup>-</sup>] is constant during each experiment and does not affect the reaction rate.





Since both t<sub>1/2</sub> are approximately the <u>same</u>, the reaction is <u>first order</u> w.r.t. ethanal.

- Students should show the construction lines on the graph and determine the values of at least two half-lives. It is insufficient to find only one half-life.
- Some students read the graph wrongly and obtained a half-life of 4.4 min or 4.8 s.
- Even though either graph can be used to show that reaction is first order with respect to ethanal, the question specified for students to use the graph for expt **I**.

(iii) By drawing tangents at t = 0 min,

For Experiment I, initial rate =  $\left|\frac{1.20 - 0}{0 - 6.8}\right| = \frac{0.176 \text{ mol } \text{dm}^{-3} \text{ min}^{-1}}{0 - 6.8}$ For Experiment II, initial rate =  $\left|\frac{1.20 - 0}{0 - 3.4}\right| = \frac{0.353 \text{ mol } \text{dm}^{-3} \text{ min}^{-1}}{0 - 3.4}$ 

When [OH<sup>-</sup>] doubles, rate doubles. Hence, reaction is <u>first order</u> w.r.t. OH<sup>-</sup>.



#### **Comments**

• The tangent drawn at t=0 should follow the curve for about 2 to 3 small squares. This will better allow students to get a tangent with a gradient within the acceptable range.

• By convention, rate is always positive. Hence, initial rate =  $-\frac{d[rxt]}{dt}$ .

(iv) rate = k[OH<sup>-</sup>][ethanal]

#### **Comments**

- Very well done.
- Only a few students repeated the mistake of writing 'rate equation = k[OH<sup>-</sup>][ethanal]'.

(v) Initial rate method Using Experiment I, 0.1765 =  $k(1.0)(1.2) \rightarrow k = 0.147 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ 

OR

<u>Half-life method</u>  $t_{\frac{1}{2}} = \frac{\ln 2}{k [OH^{-}]}$ Using Experiment I, 4.75 =  $\frac{\ln 2}{k (1.0)}$  →  $k = 0.146 \text{ mol}^{-1} \text{ dm}^{3} \text{ min}^{-1}$ 

- Many students did not realise that the unit for time in this experiment was min. Some converted min to seconds, which is fine, but not necessary.
- Using the half-life method, many students left out [OH<sup>-</sup>] but still obtained the correct answer because in this case, [OH<sup>-</sup>] = 1.0.
- (b) (i) Mechanism:  $\underline{S_N2}$  (or bimolecular nucleophilic substitution)

Let  $RCH_2^-$  represent **A**.



The mechanism should show the following:

- curly arrows to show electron movement
- lone pair on C of nucleophile
- dipoles on C and Br
- inversion of configuration
- all partial charges / charges

#### **Comments**

- Many students mistakenly left out the name of the mechanism.
- The question stated that **A** reacted with an <u>optically active</u> sample of 2-bromobutane to form the product which can <u>rotate plane polarised light</u>. Hence, 3D structure must be shown to illustrate the backside attack by the nucleophile and the inversion of configuration of the chiral carbon for this S<sub>N</sub>2 mechanism.



An increase in temperature from  $T_1$  to  $T_2$  increases the average kinetic energy of the reactant particles. More reactant particles have energy greater than or equal to the activation energy of the reaction.

This results in an <u>increase in effective collision frequency</u> and hence an increase in the rate of the reaction.

- Students need to be familiar with the drawing of the Boltzmann distribution curves to explain the effect of temperature and/or catalyst on the rate of reaction.
- For  $T_2 > T_1$ , the maxima of the curve for  $T_2$  has to be lower than and to the right side of that for  $T_1$  (i.e. as the temperature increases, the peak moves to higher kinetic energy and the distribution broadens out). This is because the total area under the curve (which represents the total number of particles) must remain the same.
- Students should also note the correct shape of the curves and that the curves must start from the origin.
- (iii) The <u>C-Cl</u> bond (BE = 340 kJ mol<sup>-1</sup>) is stronger than the C-Br bond (BE = 280 kJ mol<sup>-1</sup>). Hence it is more difficult to break the C-Cl bond, resulting in a <u>slower</u> reaction for 2-chlorobutane.

# <u>Comments</u>

- Most students did well for this question. A handful of students used atomic radii to substantiate their answer. The use of bond energies is preferred here as it will be a more direct way to show which bond is stronger.
- (iv) Hydroxide ions are less bulky and will experience less steric hindrance when attacking the electron deficient carbon atom.

OR

In **A**, the negative charge is delocalised into the adjacent C=O group. Hence, <u>lone</u> pair on **A** is less available, resulting in a slower reaction.

# <u>Comments</u>

 The electronegativity of an atom in a molecule is a relative measure of its <u>ability to</u> <u>attract bonding electrons</u>. Therefore, it is contradictory to state that the O atom on OHis electronegative and hence its lone pair is more available for donation.



# **Comments**

- Students should note that the final product **D** has one less carbon than **B**. Also, **D** has an ester group which can be formed from the condensation reaction between an alcohol and a dcarboxylic acid. Hence the methyl ketone in **B** can be converted to a carboxylate (reduction of one carbon) via the iodoform reaction.
- (ii) Step 1: <u>I<sub>2</sub>(aq) with NaOH(aq), heat or warm</u> Step 2: (catalytic) <u>conc H<sub>2</sub>SO<sub>4</sub>, heat</u>

## **Comments**

 For step 2, a common mistake was to use H<sub>2</sub>SO<sub>4</sub> (aq), which is <u>dilute</u> H<sub>2</sub>SO<sub>4</sub>. Note that *excess* conc H<sub>2</sub>SO<sub>4</sub> cannot be used as this will cause the alcohol to undergo elimination (dehydration) to form an alkene instead.

# 2 (a) (i) PbF<sub>2</sub>, PbCl<sub>2</sub> and PbBr<sub>2</sub> have giant ionic structure with strong ionic bonds.

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PbF<sub>2</sub>, PbC $l_2$  and PbBr<sub>2</sub> have the same cation and the anions have the same charge. Since the <u>ionic radius increases from F<sup>-</sup> to Br</u>, the <u>interionic distance increases from</u> <u>PbF<sub>2</sub> to PbBr<sub>2</sub></u>. Hence the <u>strength of ionic bond</u> and melting point <u>decreases</u> from PbF<sub>2</sub> to PbBr<sub>2</sub>.

Or since  $|\text{LE}| \propto \left| \frac{q_+ q_-}{r_+ + r_-} \right|$  and the <u>ionic radius increases from F<sup>-</sup> to Br</u>, the LE

become <u>less exothermic</u>, less energy is required to overcome the ionic bond and melting point <u>decreases</u> from  $PbF_2$  to  $PbBr_2$ .

# <u>Comments</u>

- Many students forgot to state the structure of the compounds (i.e. giant ionic structure) although the question asked to explain the melting points in terms of <u>structure</u> and bonding.
- Some students thought that lead(II) halide, PbX<sub>2</sub>, is covalent. As PbX<sub>2</sub> is made up of a metal ion, Pb<sup>2+</sup> (which does not have high charge density) and non-metal halide ion, PbX<sub>2</sub> is ionic. The high melting point of PbX<sub>2</sub> also shows that it is ionic rather than covalent with simple molecular structure.
- Other common mistakes include:
  - $\circ$   $\,$  Using decrease in charge density to explain why LE becomes less exothermic from

PbF<sub>2</sub> to PbBr<sub>2</sub>. As |LE|  $\propto \left| \frac{q_+q_-}{r_+ + r_-} \right|$ , it is the increasing inter-ionic distance (due to

increasing anionic radius) that should be used to explain why LE become less exothermic.

- Using increase in covalent character to explain the decrease in melting point. This is incorrect as melting involves overcoming electrostatic attraction between Pb<sup>2+</sup> and X<sup>-</sup> ions, which is dependent on the ionic bond strength and hence LE.
- (ii) Due to its high charge and small size, Pb<sup>4+</sup> has a <u>high charge density</u> and <u>high polarising power</u>, which causes it to <u>distort the electron cloud of Cl</u><sup>-</sup> to such an extent that PbCl<sub>4</sub> is predominantly a <u>covalent</u> compound.
   (OR: If PbCl<sub>4</sub> is ionic, Pb has to lose 4 valence electrons to form Pb<sup>4+</sup> which is energetically demanding. Instead of losing its valence electrons, Pb shares its 4 valence electrons with 4 Cl atoms to form PbCl<sub>4</sub> which is covalent.)

Hence,  $PbCl_4$ , having a simple covalent/molecular structure, consists of discrete molecules held together by <u>weak instantaneous dipole-induced dipole interactions</u> which requires a <u>small amount of energy</u> to overcome. Thus, it has a low melting point.

## <u>Comments</u>

- Since compounds made of metal and non-metal tend to be ionic, it is necessary for students to explain why PbCl<sub>4</sub> is covalent even though it is made of a metal and non-metal.
- Many students gave Pb<sup>2+</sup> rather than Pb<sup>4+</sup> as the ion that causes the electron cloud of Cl<sup>-</sup> to be distorted so greatly that PbCl<sub>4</sub> is a covalent compound.
- A number of students did not name the specific intermolecular forces of attraction (which is id-id interactions) or gave the wrong intermolecular forces of attraction (pd-pd

interactions). Students should consider the structure and bonding of the compound (in this case  $PbCl_4$  is a simple, non-polar compound) and name the dominant intermolecular forces of attraction between the molecules. Avoid using the term 'Van der Waals forces' of attraction.

(iii)  

$$[I^{-}] = \frac{3.58 \times 10^{-5}}{25.0/1000} = 1.432 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[Pb^{2+}] \text{ in filtrate} = \frac{9.80 \times 10^{-9}}{(1.431 \times 10^{-3})^2} = 4.779 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[Cl^{-}] \text{ from PbC}l_2 \text{ in filtrate} = 4.779 \times 10^{-3} \times 2 = 9.558 \times 10^{-3} \text{ mol dm}^{-3}$$

$$Total [Cl^{-}] \text{ in filtrate} = 9.558 \times 10^{-3} + 0.050 = 0.05956 \text{ mol dm}^{-3}$$

$$K_{sp} = [Pb^{2+}][Cl^{-}]^2 = (4.779 \times 10^{-3})(0.05956)^2 = 1.70 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$$

# **Comments**

mass

mole

• Not a very well attempted question.

Н

0.6

0.6/1.0

= 0.6

≈ 2

- Common mistakes include:
  - o not converting the amount of I<sup>-</sup> to [I<sup>-</sup>] before calculating [Pb<sup>2+</sup>] in the filtrate.
  - not adding the  $[Cl^-]$  from the dissolution of PbC $l_2$  to 0.0500 when calculating  $[Cl^-]$  in the filtrate/reaction mixture before filtration.

(iv)	)

Pb	Cl
59.0	40.4
59.0/207	40.4/35.5
= 0.285	= 1.138
≈ 1	≈ 4

Empirical formula =  $H_2PbCl_4$ Actual formula =  $H_2PbCl_4$ Complex ion = [PbCl\_4]<sup>2-</sup>

## **Comments**

- A small number of students did not work out the <u>simplest ratio</u> (2:1:4) to obtain the empirical formula.
- Some students thought that H is a ligand and gave incorrect formula of complex ions such as [PbH<sub>2</sub>C*l*<sub>2</sub>]<sup>2+</sup>. H<sup>+</sup> is not likely to be a ligand as it does not have a lone pair of electrons to donate to the central metal ion.
- (v) The following equilibrium is established in the saturated solution:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq) -----(1)$$

When concentrated hydrochloric acid is added and the mixture shaken,  $[Cl^-]$  is greatly increased. Pb<sup>2+</sup> ions react with  $Cl^-$  to form the soluble complex,  $[PbCl_4]^{2-}$ , as shown below.

$$Pb^{2+}(aq) + 4Cl^{-}(aq) \rightleftharpoons [PbCl_4]^{2-}(aq) \dots (2)$$

The formation of  $[PbCl_4]^{2^-}$  <u>decreases</u> the  $[Pb^{2+}]$  in the solution. To counteract the decrease in  $[Pb^{2+}]$ , the <u>equilibrium position of reaction (1) shifts to</u> <u>the right</u> i.e.  $PbCl_2$  dissolves. or

<u>[Pb<sup>2+</sup>] decreases</u> due to the formation of [PbC $l_4$ ]<sup>2-</sup>. When <u>ionic product</u>, [Pb<sup>2+</sup>][C $l^{-}$ ]<sup>2</sup> becomes less than the  $K_{sp}$ , all the PbC $l_2$  dissolves.

# **Comments**

- Not a very well attempted question.
- Students should take note that when a common ion of a ppt is added to a reaction mixture containing the ppt, more ppt is expected to precipitate out.

If the ppt dissolves instead, it is likely due to another reaction in which the common ion reacts to form a soluble complex. Equations showing the complex formation and the dissolution of the ppt should be given as part of the answer. Students need to explain the observations using the equations and discussing the shifts in equilibrium position for the two reactions.

**(b) (i)**  $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ 

# **Comments**

- Generally well done.
- A handful of students confused thermal decomposition with combustion.
- (ii) The thermal stabilities of HCl to HI, which is related to the H-X bond strength, increase in the order: HI < HBr < HCl

The stronger the H-X bond, the more thermally stable HX is. Since the <u>bond strength</u> of HI < HBr < HCl, the <u>thermal stability of HI < HBr < HCl</u>.

The energy supplied by the red hot wire <u>was insufficient to decompose HC</u>l, hence there is no observable change; was able to <u>decompose some HBr</u>, resulting in <u>reddish-brown vapour of Br</u><sub>2</sub> formed slowly; and was able to <u>decompose HI readily</u> to result in <u>purple fumes of I</u><sub>2</sub> evolved vigorously.

# **Comments**

- Generally well done.
- Students should make reference to the observations when discussing the rate of decomposition.

(c)



Square planar, 90°

- Many students were careless and forgot to include a square bracket with a negative sign to show the charge of the ion.
- Some students did not use 'o' to represent the additional electron responsible for the overall negative charge.
- Some students described the molecular shape as octahedral, forgetting that lone pairs are not seen and should not be included when describing the shape of a molecule.
- (d)  $C_{l_2} + 2e^- \rightleftharpoons 2Cl^ Mn^{2+} + 2e^- \rightleftharpoons Mn$   $MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$   $MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$   $E^{\ominus} = +1.36 V$   $E^{\ominus} = +1.36 V$   $E^{\ominus} = +1.23 V$  $E^{\ominus} = +1.67 V$

Considering the reaction between  $Cl_2$  and Mn,  $E^{\ominus}_{cell} = +1.36 - (-1.18)$ = +2.54 V (spontaneous)Considering the reaction between  $Cl_2$  and Mn<sup>2+</sup>,  $E^{\ominus}_{cell} = +1.36 - 1.23$ = +0.13 V (spontaneous)

Considering the reaction between  $Cl_2$  and  $MnO_2$ ,  $E^{\ominus}_{cell} = +1.36 - 1.67$ = -0.31 V (not spontaneous)

Thus,  $Cl_2$  will oxidise Mn to Mn<sup>2+</sup> and further oxidise Mn<sup>2+</sup> to MnO<sub>2</sub>. (proven)

Overall eqn:  $2Cl_2 + Mn + 2H_2O \longrightarrow 4Cl^- + MnO_2 + 4H^+$ 

# **Comments**

 Many students left out the calculation of the E<sup>⊕</sup><sub>cell</sub> for the non-spontaneous reaction. This is necessary as you need to show that the highest oxidation state which Mn can be oxidised to is +4 and not +7 (MnO₄<sup>-</sup>). Hence answers need to show:

> Mn to Mn<sup>2+</sup> (positive  $E^{\ominus}_{cell} = +2.54 \text{ V}$ ) Mn<sup>2+</sup> to MnO<sub>2</sub> (positive  $E^{\ominus}_{cell} = +0.13 \text{ V}$ ) MnO<sub>2</sub> to MnO<sub>4</sub><sup>-</sup> (negative  $E^{\ominus}_{cell} = -0.31 \text{ V}$ )

- Some students chose the wrong half-equation, showing the oxidation of  $Mn^{2+}$  to  $MnO_4^-$  ( $E^{\ominus} = +1.52$  V) rather than oxidation of  $MnO_2$  to  $MnO_4^-$  ( $E^{\ominus} = +1.67$  V).
- In general, when answering questions in which the reagent can oxidise/reduce a species to different oxidation states, E<sup>⊕</sup><sub>cell</sub> of each step needs to be calculated so that the final product can be determined.
- Some students gave the overall equation as a reaction between Cl<sub>2</sub> and Mn<sup>2+</sup> rather than the required overall equation for the reaction between Cl<sub>2</sub> and Mn.
- Students should note that only half equations (e.g. reduction and oxidation reactions at the cathode and anode respectively) should contain electrons. However, for an overall balanced equation, no electrons should be present.
- (e)  $PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$

- Generally well done.
- A number of students gave the product as POC*l*<sub>3</sub> rather than H<sub>3</sub>PO<sub>4</sub>. Students should take note that POC*l*<sub>3</sub> is formed only if water is in limited amount. H<sub>3</sub>PO<sub>4</sub> is the expected product when PC*l*<sub>5</sub> is reacted with water, unless otherwise stated in the question.

**3 (a)** 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>5</sup>4s<sup>1</sup>

## **Comments**

- A small number of students failed to recall that the electronic configuration of Cr is anomalous.
- When asked to write the electronic configuration, students need to follow two conventions:
  - (i) Start with 1s<sup>2</sup>..... (Truncated version like [Ar]3d<sup>5</sup>4s<sup>1</sup> is not allowed.)
  - (ii) The subshells must be ordered from the lowest Principal Quantum Shell on the left to the highest on the right, i.e. ......4s<sup>1</sup>3d<sup>5</sup> is not allowed.
- (b) (i) Step I: acid-base (or complexation or complex formation)
  - Step II: oxidation / redox reaction
  - **F**:  $[Cr(OH)_6]^{3-}(aq) \text{ or } [Cr(OH)_4]^{-}(aq)$
  - **G**:  $Cr_2O_7^{2-}(aq)$

## **Comments**

- The types of reaction for steps I and II are generally well done.
- Although ligand exchange was also accepted for step I, the more correct answer would be acid-base reaction. In step I, the aq NaOH removes a proton from each of the H<sub>2</sub>O ligand in Cr(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> (which is simply Cr(OH)<sub>3</sub>), the grey-green ppt, via acid-base reaction to form F, [Cr(OH)<sub>6</sub>]<sup>3-</sup>. Nonetheless, not all complex ion formation involves acid-base reaction.
- For F, students need to note that it is a dark green <u>solution</u>. Hence, F is likely to contain a complex ion. A number of students incorrectly suggested F to be Cr(OH)<sub>3</sub>, which is a grey-green ppt.
- Although the oxidation state of Cr in both CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> are the same (i.e. +6), the colour of CrO<sub>4</sub><sup>2-</sup> is yellow whereas the colour of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> is orange. Hence, G must be Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>.
- (ii) The ability to display <u>variable oxidation states</u> in their compounds. This is due to the <u>close similarity in energy between the 3d and 4s electrons</u>, which thus allows for different number of these electrons to participate in chemical bonding.

OR Ability to form complexes due to availability of low lying vacant orbitals.



Note:

- d<sub>xy</sub> orbital has four lobes with each lobe between the x and y axes.
- d<sub>x2-y2</sub> orbital has four lobes with each lobe **along** the x and y axes.

<u>Comments</u>Generally well done.

(c)

(ii) In an octahedral environment, lone pairs on the ligands approach the central metal ion along the x, y and z axes.

 $3d_x^2 \cdot y^2$  and  $3d_z^2$  orbitals have their <u>greatest electron density along</u> the co-ordinate axes on which the ligands are situated. Hence electrons in these orbitals are pointing towards the lone pairs of ligands, and will be repelled by them.

 $3d_{xy}$ ,  $3d_{yz}$ ,  $3d_{xz}$  orbitals have their <u>greatest electron density in between</u> the co-ordinate axes. Hence the repulsion between electrons in these orbitals and those of the approaching ligands will be <u>less</u> compared to electrons in  $3d_x^{2-y^2}$  or  $3d_z^{2}$  orbitals.

Hence the d-orbitals are split into two different energy levels.

# <u>Comments</u>

- Answers need to be clear in <u>comparing the extent of repulsion</u> between the <u>electrons</u> in the d orbitals and <u>lone pairs</u> of ligands, and <u>explain the difference</u> in the extent of repulsion by referring to the <u>orientation</u> of the d orbitals and <u>direction of approach of ligands</u>.
- (d) (i)  $[Cr(H_2O)_4Cl_2]^+$  $[Cr(H_2O)_5Cl]^{2+}$  $[Cr(H_2O)_6]^{3+}$

# **Comments**

- Generally well done with only a small number of students who gave the formula of the compounds despite the question asking for the <u>complex ion</u> in each compound.
- Note that Cr(H<sub>2</sub>O)<sub>3</sub>Cl<sub>3</sub> is not accepted as this will not give any 'free' chloride in solution to form a white precipitate with aqueous silver nitrate.
- As the question already stated that most of the complex ions formed from Cr<sup>3+</sup> are octahedral in shape, students should not suggest complex ions with more or less than six coordination number.
- (ii) The presence of <u>ligands causes the splitting</u> of the five 3d orbitals in Cr<sup>3+</sup> into two sets of slightly different energy levels. Since the 3d subshell in Cr<sup>3+</sup> are partially filled, electrons from the lower-energy d orbitals can absorb energy and get <u>promoted</u> to the higher-energy d orbitals (d-d transition). The <u>energy absorbed</u> <u>corresponds to certain wavelength from the visible light spectrum</u> and the colour observed is the <u>complement</u> of the colour absorbed.

## <u>Comments</u>

• Generally well done.

(iii) Chloride and water are <u>ligands of different strength</u>. Different proportions of these ligands cause the d orbitals to be split to <u>different extents</u>, creating different <u>energy</u> <u>gaps</u> for different complexes, which in turn <u>absorb energies of different wavelengths</u> <u>from the visible light spectrum</u>, thus displaying different colours.

<u>C</u>	<u>Comments</u>		
•	Generally well done.		

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cis-[Cr(H<sub>2</sub>O)<sub>4</sub>C $l_2$ ]<sup>+</sup>

# **Comments**

- Students must draw the complex ion in an octahedral shape for the cis positioning of the 2 C*l* ligands to be clearly displayed.
- Note that when the H<sub>2</sub>O ligands bind to Cr<sup>3+</sup>, it is the O atom (not the H atom) that donates its lone pair of electrons. Hence, the structure should show clearly the Cr-O bond (not Cr-H bond).
- When drawing complex ions, students should show EITHER the overall charge of the complex ion OR charges on the central metal ion and ligand(s). Do NOT show both the overall charge and the charges on the central metal ion and ligand(s).
- (e) (i) <u>Positive</u> ( $\Delta S > 0$ ). There is increase in disorder/entropy due to <u>increase in number of particles / molecules / species</u> formed.

#### **Comments**

- Students need to state clearly the change in number of particles in the system after the reaction. Note that there are no changes in the number of ions after reaction.
- (ii)  $\Delta H$  value of the forward reaction is close to zero as the <u>type</u> (N $\rightarrow$ Cr coordinate bond) and the <u>number</u> of dative covalent bonds <u>broken and formed are about the same</u>.

#### <u>Comments</u>

 The question already stated that the ∆H value of the forward reaction is close to zero. Hence it is insufficient to say that the total energy absorbed to break the bonds is equal to the total energy required to form the bonds. Students need to elaborate on <u>why</u> they are equal.

## (iii) $\Delta G = \Delta H - T \Delta S$

Since  $\Delta H$  is close to zero and  $\Delta S$  is positive,  $\Delta G$  (for the forward reaction) will be more <u>negative</u> at a <u>higher temperature</u>, hence increasing the yield of complex **H**.

- Students should avoid using words like 'greater', 'smaller', 'increase' or 'decrease' to describe the change in  $\Delta G$ . The same applies for  $\Delta H$ ,  $\Delta S$ , LE and reduction/cell potentials.
- Students need to explain clearly why a higher temperature will increase the yield of H.

# Section B

4 (a) (i) Na<sub>2</sub>O reacts with water to form a <u>strongly alkaline solution</u> (pH  $\approx$  13 – 14). Na<sub>2</sub>O(s) + H<sub>2</sub>O(l)  $\longrightarrow$  2NaOH(aq)

 $SiO_2$  <u>does not dissolve in water</u> because of the strong Si–O covalent bonds in the giant molecular structure. Solution remains <u>neutral</u> (pH = 7).

 $P_4O_{10}$  reacts with water to form an <u>acidic solution</u> (pH ≈ 2).  $P_4O_{10}(s) + 6H_2O(I) \longrightarrow 4H_3PO_4(aq)$ (Note:  $H_3PO_4$  is a weak acid)

## <u>Comments</u>

- Most students could give the balanced equations for the reaction of Na<sub>2</sub>O with water and also of P<sub>4</sub>O<sub>10</sub> with water. However, many failed to describe the reaction in words.
- The question required the description of the reaction of the oxides with water, not why the resulting solution is acidic or alkaline. A common mistake was to explain that NaOH is a strong base because it dissociates completely, without describing the reaction of Na<sub>2</sub>O with H<sub>2</sub>O.
- Many students omitted the pH for the resulting solution when SiO<sub>2</sub> is placed in water.
- Students should pay attention to the correct pH range of the respective solutions formed.
- (ii) (MgO is an ionic oxide which is basic and react with acids. SO<sub>3</sub> is a covalent oxide which is acidic and reacts with bases.)

 $Al_2O_3$  (an amphoteric oxide) reacts with both acids and bases as it is <u>an ionic oxide</u> with covalent character. The covalent character is due to the high charge density/polarising power of  $Al^{3+}$  that polarise and distort the electron cloud of  $O^{2-}$ .

With acid:  $Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$ With base:  $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq)$ 

- The balanced equation for the reaction with acid was generally well done.
- Many students did not know how to balance the equation of Al<sub>2</sub>O<sub>3</sub> with OH<sup>-</sup>, often forgetting that 3H<sub>2</sub>O was required.
- A common mistake was to omit the explanation of why Al<sub>2</sub>O<sub>3</sub> is amphoteric. It must be stated that Al<sub>2</sub>O<sub>3</sub> is ionic with covalent character, not merely that it is partly ionic and partly covalent.
- Some students also went on to explain why a solution of A*l*C*l*<sub>3</sub> is acidic, which is irrelevant to this question.

(b) (i) Step 1: nucleophilic addition

## **Comments**

• Generally well done.

(ii) In primary amides, the lone pair of electrons on the nitrogen atom interacts with the  $\pi$  electron cloud of the adjacent C=O bond and is delocalised. Hence, the lone pair of electrons is not available for donation to the electrophilic carbonyl carbon atom /unable to act as a nucleophile in step 1.

#### **Comments**

- Most students managed to compare and contrast the availability of lone pair of electrons on N between amine and amide so that the N can act as a nucleophile.
- Some students simply regurgitated an answer that was for "why are amides neutral" when this question did not require them to do so. A typical example of this is when students state that "the lone pair of electrons is not available for donation to a proton". Although the reasoning is similar, students must be careful to distinguish between the amide acting as a nucleophile and as a base. Nucleophiles generally attack electron deficient carbons (or other atoms), while bases generally attack protons.
- A handful of students wrote "lone pair of electrons delocalised into O", which is not accepted.
- A handful of students also wrote "electrons from N" instead of "lone pairs on N". Do note that there is a need to specify the words "lone pairs".
- (iii) O H H Br HC -C -C -C -NH H H H H H

Note: All bonds must be shown in the above displayed formula

#### **Comments**

- Not a very well attempted question. Many students were not able to get the structure.
- A common incorrect answer was a structure with an acyl bromide group. This is not possible as the acyl bromide group is highly reactive and would have reacted with the amine (condensation reaction) to form an amide. The resultant product formed will not have any Br atom.
- For those who did get the structure, many forgot to give the displayed formula or were careless (e.g. not showing the two N-H bonds for -NH<sub>2</sub> group)
- (c) (i) Step 1: NaOH(aq), heat

Step 2:  $C_l$  (anhydrous, rtp) Step 3: excess  $CH_3C_l$ , heat

#### <u>Comments</u>

• A common mistake for step 2 was to use the dicarboxylic acid, together with concentrated H<sub>2</sub>SO<sub>4</sub>. While that may form the ester in **P**, the amide will not be formed because the amine will react with the carboxylic acid (-COOH) via acid-base reaction instead.

- Condensed formula for the reagent in step 2 was written wrongly in many cases as C/OCCH<sub>2</sub>COC*l*. Students are reminded to not use the condensed formula, especially when it can be ambiguous. It is always wise to draw the structure out when in doubt.
- A common mistake for step 3 was to omit "excess". Excess CH<sub>3</sub>C*l* is required in this step for polysubstitution to occur to form **R** (quaternary alkylammonium salt).

• Only a minority of students were able to get the structure of **Q**.

(iii) Possible structures for **S** ( $C_6H_{12}BrN$ ):



(or the trans isomers)



(or corresponding cis-trans isomer)

S and T are constitutional / structural / positional isomers.

# **Comments**

- Not a very well attempted question. Students are reminded to use the information given carefully to derive the structures of **S** and **T**. After which, they should check their structures against the given molecular formula.
- Many students gave charged species as the compound, which is incorrect.
- (iv) In **T**, the p orbital of Br overlaps with the  $\pi$  electron cloud of the adjacent C=C bond and the lone pair of electrons in the p orbital of Br delocalises into the C=C bond and results in <u>partial double bond character</u> in the C–Br bond.

Hence, **T** does not undergo nucleophilic substitution and <u>no Br<sup>-</sup> are present</u> to react with Ag<sup>+</sup> to form pale cream ppt of AgBr.

(**S** is an <u>alkyl bromide</u> that can <u>undergo nucleophilic substitution</u> when heated with ethanolic  $AgNO_3$  to form alcohol and  $Br^-$ .  $Br^-$  then forms the pale cream ppt of <u>AgBr</u> with Ag<sup>+</sup>.)

#### <u>Comments</u>

- Generally well done for students who had attempted this question.
- Do note that there is a need to specify the words "lone pairs" instead of using purely "electrons" when referring to that from Br.
- A handful of students wrote that electrons from C=C delocalises into Br, which is incorrect.
- Students are reminded that they should tailor their answers to the questions. Since this question asked for the reason why a pale cream ppt with AgNO<sub>3</sub> was not formed, students should attempt to explain fully, including the fact that since there will be no nucleophilic substitution, no Br<sup>-</sup> would be present to form the pale cream ppt. Most answers simply stopped at "partial double bond character in C–Br".
- 5 (a) Constitutional / Structural / Functional group isomerism

# Generally well done.

(b) R<sub>3</sub>

# **Comments**

- Generally well done.
- A handful of students formed the double bond on the other side of the molecule, without realising that there was no H on the N connected to R<sub>3</sub>.
- (c) (i) Enantiomerism



- Most students managed to give enantiomerism as the type of stereoisomerism.
- Many were penalised for poor drawing of the two enantiomers. A common mistake was to represent the phenyl group as "H₅C<sub>6</sub>" or the ethyl group as "H₅C<sub>2</sub>" or "H<sub>3</sub>CH<sub>2</sub>C".
- A handful of students drew mirror image diagrams with no hash and wedge bonds. Students must understand that the purpose of drawing with hash and wedge bonds is to diagrammatically show the position of the bonds and groups in 3D. To draw structures with only solid lines would either mean:
  - (1) that all bonds present are flat on the plane of the paper (which is not stereochemically possible)
  - (2) it is not important to show the 3D structures (which is clearly not the case for this question).

(ii) Test: To separate samples of **X** and phenytoin, add NaOH(aq) and heat strongly.

Observation: Pungent gas  $(NH_3)$  that turns moist red litmus blue is evolved for the sample containing phenytoin but no pungent gas is evolved for the sample containing **X**.

## <u>Comments</u>

- A common mistake was to use <u>acidic</u> hydrolysis, followed by the observation of ammonia gas. This is incorrect because <u>ammonia gas (basic) will not be produced in an acidic medium</u>. The ammonium salt formed will remain dissolved in the solution.
- Some students wrote free radical substitution as a distinguishing test but this was not accepted because benzene ring could also undergo free radical reaction with halogens under certain conditions.
- (d) (i)  $M_r(J) = 190$

 $n(J) = 5/190 = 0.02632 \text{ mol}; n(H_2) = 2(0.02632) = 0.05264 \text{ mol}$ 

 $\begin{array}{l} pV_{\text{H2}} = nRT \\ (1.0 \ x \ 10^5) \ V_{\text{H2}} = (0.05264)(8.31)(273 \ + \ 150) \\ V_{\text{H2}} = 1.85 \ x \ 10^{-3} \ m^3 = 1.85 \ dm^3 \end{array}$ 

#### **Comments**

• Common mistakes include:

- $\circ$  forgetting to multiply the amount of **J** by 2 to obtain the amount of H<sub>2</sub>
- $\circ~$  using molar gas volumes (22.7 or 24 dm^3) to obtain the volume of H\_2 when the conditions are not s.t.p. or r.t.p.
- substituting 1 bar as 101325 Pa.
   [Note: 1 bar = 100000 Pa, while 1 atm = 101325 Pa]

(ii)	Information / Reaction	Deduction / Explanation
	J has molecular formula,	J is likely to contain a benzene ring due
	$C_{10}H_{10}N_2O_2$	to the relatively high C to H ratio.
	J exhibits optical activity	J contains a chiral centre and/or no
		plane of symmetry.
	<b>J</b> is neutral.	J contains amide and/or –CN group. Or
		J is not carboxylic acid or amine or
		phenol.
	J has no reaction with 2,4-DNPH	J is not aldehyde & ketone / carbonyl
	$H_{r}(\alpha)$ / Ni	Reduction of nitrile.
	$J \xrightarrow{112(g) / 10} K$	Since C=C is absent and there is
		increase of 4 H atoms from J to K, J
		contains –CN group.
		J contains amide/ester/nitrile and
	$J \xrightarrow{H_2SO_4(aq)} CO_2$ + resultant mixture	undergoes acidic hydrolysis.
	distillation	
	residue + distillate L	
	residue base	Residue is an ionic salt. ( <b>M</b> is a base.)





- Many students who attempted this question managed to get marks for deductions made from the information given. Many managed to get the structures of L, M, N, P and Q.
- Students must note that it is generally insufficient to only state type of reactions for their deductions. Deductions on the possible structures or functional groups present should be included in the answers.
- Students should note that it is insufficient to say that "C=O is not present" if a compound does not react with 2,4-DNPH. This is because some functional groups (e.g. esters, amides and acyl halides) other than carbonyl group also contain the C=O bond.
- For the reduction of J to get K, students should make use of the molecular formula to deduce that 4 H have been added so the CN group is present. Some students mistakenly mentioned the presence of 2 C=C (impossible since question already stated that there are no alkene functional group present in J) or the presence of 2 carbonyl groups (impossible since question already stated that J does not react with 2,4-DNPH).
- Students need to avoid writing "methyl alcohol is present" for positive iodoform test because "methyl alcohol" refers to methanol. The term "methyl ketone" is unambiguous, so it is accepted. To avoid ambiguity, students should draw the half structures (e.g. –CH(OH)CH<sub>3</sub>, –COCH<sub>3</sub>) that will give a positive iodoform test.
- A common mistake for **Q** was the wrong positions of NO<sub>2</sub> on the benzene ring or a missing "H" on the "N" of the hydrazone group. Do note that the structure of 2,4-DNPH is in the syllabus.
- Students are reminded of the need for clear presentations of their answers.