## H2 Chemistry Prelim Exam Answers

#### Paper 3 Answers

- 1 (a) (i) Electronegativity increases across the period and decreases down the group. Hence, beryllium and aluminium have similar electronegativity and have similar properties.
  - (ii) BeC $l_2$  has simple molecular structure consisting of weaker instantaneous dipoleinduced dipole attraction between BeC $l_2$  molecules while BeO has a giant ionic structure consisting of stronger ionic bonds between Be<sup>2+</sup> and O<sup>2-</sup>.

Less energy is required to overcome the weaker instantaneous dipole–induced dipole attraction than the stronger ionic bonds. Hence, the boiling point of  $BeCl_2$  is lower than that of BeO.

(iii) BeCl<sub>2</sub> undergoes hydration in water to give  $[Be(H_2O)_4]^{2+}$  which hydrolyses to give an acidic solution. Due to the high charge density of Be<sup>2+</sup>, it can polarise and weaken the O–H bond in the coordinated H<sub>2</sub>O molecules, releasing H<sup>+</sup> into the solution.

Hence, a weakly acidic solution is formed and causes a beaker of litmus solution to change from purple to red.

BeCl<sub>2</sub>(s) + 4H<sub>2</sub>O(l) → [Be(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>(aq) + 2C $\Gamma$ (aq) [Be(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>(aq) + H<sub>2</sub>O(l)  $\rightleftharpoons$  [Be(H<sub>2</sub>O)<sub>3</sub>OH]<sup>+</sup>(aq) + H<sub>3</sub>O<sup>+</sup>(aq)

(b) (i) Since the  $A_r$  of Pb is 207.2, compound **A** can only contain one Pb.

% by mass of Pb in  $\mathbf{A} = \frac{207.2}{290} \times 100 \% = 71.45 \%$ 

element	Pb	Be	F
% by mass	71.45	3.08	25.47
amount / mol	$\frac{71.45}{207.2} = 0.3448$	$\frac{3.08}{9.0} = 0.3422$	$\frac{25.47}{19.0} = 1.341$
simplest ratio	1	1	4

% by mass of F in A = 100 - 71.45 - 3.08 = 25.47 %

Hence, the empirical formula of **A** is  $PbBeF_4$  and thus, x = 1 and y = 4.

(ii)

(c) (i)



(ii) AlCl<sub>3</sub> is acting as a catalyst since it reacted in step 1 and was regenerated in step 4. AlCl<sub>3</sub> is also acting as a Lewis acid since it accepted a lone pair of electrons from O atom of phenyl ethanoate via dative bond formation.

(iii)



- (iv) Neutral  $FeCl_3(aq)$ If 2-hydroxyacetophenone is formed, violet coloration is formed.
- (v) 18  $\sigma$  bonds and 8  $\pi$  electrons
- (vi) Electron-withdrawing -CO<sub>2</sub>H reduces the electron density of benzene and makes the benzene ring less electron-rich, causing B to be less reactive toward electrophilic attack. Hence, the rate of Fries rearrangement is slower for B compared to phenyl ethanoate.

# **2 (a) (i)** Zn and Cu.

Density = mass / volume

- Zn and Cu have higher relative atomic mass as compared to Mg and AI.
- Zn and Cu also have smaller atomic radius.

Hence Zn and Cu have higher densities than Mg and AI.

- (ii)  $Cu^{2+} + 2e \prod Cu + 0.34 V$   $2H^{+} + 2e - \prod H_2 \quad 0.00 V$   $E_{cell} = 0.00 - (+0.34) = -0.34 V$  (<0, not feasible)  $E_{cell}$  calculation & concluding it's not feasible Cu is the residue.
- (b) (i) When precipitation occurs, ionic product of the hydroxide =  $K_{sp}$

For precipitation of Cu(OH)<sub>2</sub>:  $[Cu^{2+}][OH^{-}]^2 = K_{sp}$ (1.0)  $[OH^{-}]^2 = 2.20 \times 10^{-20}$ •  $[OH^{-}] = 1.48 \times 10^{-10} \text{ mol dm}^{-3}$ 

For precipitation of A/(OH)<sub>3</sub>:  $[A\beta^{+}][OH^{-}]^{3} = K_{sp}$ (0.0044)  $[OH^{-}]^{3} = 4.60 \times 10^{-33}$ •  $[OH^{-}] = 1.01 \times 10^{-10} \text{ mol dm}^{-3}$ 

- Since the [OH<sup>-</sup>] required for both precipitates to form is similar, it does not allow for the separation of the two metal ions.
- (ii) When NaOH(aq) is added gradually, a white ppt of Al(OH)<sub>3</sub> is formed and blue ppt of Cu(OH)<sub>2</sub> is formed.
  - $Al^{3+}(aq) + 3OH^{-}(aq) \rightleftharpoons Al(OH)_{3}(s)$  ......(1)
  - $Cu^{2+}(aq) + 2OH^{-}(aq) \rightleftharpoons Cu(OH)_{2}(s)$
  - When excess OH<sup>-</sup> is added, white ppt of Al(OH)<sub>3</sub> dissolves to give a colourless solution due to the formation of complex ion, Al(OH)<sub>4</sub><sup>-</sup>.
  - $Al^{3+}(aq) + 4OH^{-}(aq) \rightleftharpoons Al(OH)_{4}^{-}$ ...... (2)
  - As [Al<sup>3+</sup>] falls, the position of equilibrium of (1) shifts to the left, causing the white precipitate to dissolve, while the blue ppt of Cu(OH)<sub>2</sub> remains.
- (iii) In the presence of ligands, the partially filled 3d orbitals of  $Cu^{2+}$  split into two energy levels, with a small energy gap,  $\Delta E$ .
  - An electron in the lower energy d orbital absorbs energy in the visible spectrum corresponding to ∆E and becomes excited to a vacant d orbital at the higher energy level (d-d transition).
  - Unabsorbed wavelengths are transmitted and the colour observed is complementary to the colour absorbed.

- (c)
- $Ag^+ + e^- \rightleftharpoons Ag$ (+0.80V) $Cu^{2+} + 2e^- \rightleftharpoons Cu$ (+0.34V) $Zn^{2+} + 2e^- \rightleftharpoons Zn$ (-0.76V)

The operating voltage is carefully regulated so that it is sufficient for Cu to be oxidised.

## At anode

Cu is preferentially oxidised to  $Cu^{2+}$  and dissolve in the electrolyte. Zn will be oxidised to  $Zn^{2+}$  and dissolve in the electrolyte as well since  $E^{\theta}(Zn^{2+}/Zn)$  is more negative than  $E^{\theta}(Cu^{2+}/Cu)$ .

Ag will not be oxidised to  $Ag^+$  as  $E^{\theta}(Ag^+/Ag)$  is more positive than  $E^{\theta}(Cu^{2+}/Cu)$  and will be collected as anode sludge.

At cathode

 $Cu^{2+}$  is preferentially reduced to Cu and deposited at the cathode as  $E^{\theta}(Cu^{2+}/Cu)$  is more positive than  $E^{\theta}(Zn^{2+}/Zn)$ .  $Zn^{2+}$  will remain dissolved in the electrolyte.

(d) (i) 
$$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$$

- (ii) Ionic radius of the Zn<sup>2+</sup> (0.074nm) is larger than radius of Mg<sup>2+</sup> (0.065nm) but ionic charge remains the same (2+). The charge density of Zn<sup>2+</sup> is lower than charge density of Mg<sup>2+</sup>, and its polarising power is also lower.
  - The cation is less able to polarise the electron cloud of the CO<sub>3</sub><sup>2-</sup>ion in ZnCO<sub>3</sub>.
  - The C–O bonds in CO<sub>3</sub><sup>2-</sup> is polarised and weakened to a smaller extent. More energy is needed to break the C–O bond.
  - Hence thermal decomposition is more difficult for ZnCO<sub>3</sub> and a higher temperature is needed before it decompose.
- (e) Both MgO and  $A_{2}O_{3}$  react with acids. MgO(s) + 2H<sup>+</sup>(aq)  $\rightarrow$  Mg<sup>2+</sup>(aq) + H<sub>2</sub>O(l)  $A_{2}O_{3}(s)$  + 6H<sup>+</sup>(aq)  $\rightarrow$  2A<sup> $\beta$ +</sup>(aq) + 3H<sub>2</sub>O(l)

Both  $P_4O_{10}$  and  $Al_2O_3$  react with bases.  $P_4O_{10}(s) + 12NaOH(aq) \rightarrow 4Na_3PO_4(aq) + 6H_2O(l)$  $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$ 

 $Al_2O_3$  has a giant ionic lattice structure with strong electrostatic forces of attraction between  $Al^{\beta^+}$  and  $O^{2^-}$  ions. The high charge density of  $Al^{\beta^+}$  allows the electron cloud of  $O^{2^-}$  to be polarised, resulting in partial covalent character in the ionic bond.  $Al_2O_3$  is hence amphoteric, exhibiting both acidic and basic properties.

(f)	(i)	$F_2 + 2e^-$ 2 $F^-$	+2.87 V
		$Cl_2 + 2e^-$ 2 $Cl^-$	+1.36 V
		Br <sub>2</sub> + 2e <sup>-</sup> 2Br <sup>-</sup>	+1.07 V
		$I_2 + 2e^ 2I^-$	+0.54 V

 $E_1(X_2/X^-)$  becomes less positive down the group. This means that halogens are less easily reduced down the group, and so the oxidising power of the halogens decreases down the group.

(ii) The relative oxidising ability of bromine and iodine can be illustrated with the reaction with  ${\rm Fe}^{2+}$ 

$$\begin{array}{cccc} {\sf Fe}^{3+} + e^- & {\sf Fe}^{2+} + 0.77 \\ {\sf Br}_2 + 2e^- & {\sf 2Br}^- + 1.07 \\ {\sf I}_2 + 2e^- & {\sf 2I}^- + 0.54 \end{array}$$

Bromine is a stronger oxidising agent than iodine as bromine is able to oxidise  $Fe^{2+}$  to  $Fe^{3+}$  (as  $E_{cell} > 0$ ), but iodine is unable to do so.

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\begin{array}{ll} \text{Br}_2 + 2\text{F}e^{2+} \rightarrow 2\text{Br}^- + 2\text{F}e^{3+} & \text{E}_{\text{cell}} = +1.07 - (+0.77) = +0.30 \text{ V} > 0 \\ \text{I}_2 + 2\text{F}e^{2+} \rightarrow \text{No reaction} & \text{E}_{\text{cell}} = +0.54 - (+0.77) = -0.23 \text{ V} < 0 \end{array}
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# 3 (a) (i) Free radical substituition



(ii) 
$$\Delta H_{rxn} = (+193 + 410) - (+280 + 366) = -43 \text{ kJ mol}^{-1}$$

(iii) The brief exposure to bright light produces chlorine radicals that initiate chain reactions of the propagation step to produce more radicals for reaction to proceed.

The exothermic reaction results in an increase in temperature, hence rate of reaction increases.

- (iv) There is a decrease in ON of  $C_1$  atom from -1 in  $CH_3CH_2Br$  to -3 in  $CH_3CH_2Li$ .
- (v) Cu<sup>2+</sup> + 2e<sup>-</sup> ≈ Cu +0.34V Li<sup>+</sup> + e<sup>-</sup> ≈ Li -3.04V

The  $E^{\theta}(Cu^{2+}/Cu)$  is more positive. Cu undergoes oxidation less readily, hence is a much weaker reducing agent.





Ketone in C undergoes condensation with 2,4-DNPH to form orange precipitate D.

Ketone in **F** undergoes condensation with 2,4-DNPH to form orange precipitate.

<u>No aldehyde</u> in **C** to undergo <u>oxidation</u> with Tollens' reagent to form a silver mirror.

<u>Alkene</u> in **C** undergoes <u>electrophilic addition</u> with  $Br_2(aq)$  to form bromohydrin in **E**.

<u>Phenylamine</u> in **C** undergoes <u>electrophilic substitution</u> with  $Br_2(aq)$  to form a white precipitate, **E**.

Phenylamine in F undergoes electrophilic substitution with Br<sub>2</sub>(aq)

the system, from a less disordered solid phase to a more disordered liquid phase. This give rise to a greater disorder. Hence, entropy of the system increases.

- (ii) In presence of moisture,  $PCl_5$  undergoes hydrolysis giving white fumes of HCl.  $PCl_5(s) + 4H_2O(I) \rightarrow H_3PO_4(aq) + 5HCl(g) pH = 1-2$
- (b) (i)



Cl is arranged in a <u>tetrahedral</u> arrangement with respect to P in PCl<sub>4</sub><sup>+</sup>.



Cl is arranged in an <u>octahedral</u> arrangement with respect to P in  $PCl_6^-$ .





Each C atom has two sp hybridised orbitals and two unhybridised p orbitals. The two C atoms are bonded to each other by a  $\sigma$  bond through head-on overlap of two neighbouring sp hybrid orbitals and two  $\pi$  bond through the side-on overlapping of the two unhybridised p orbital of each C atom, forming two C=C double bond.

(c) (i) O

(ii)  $\Delta H = 390 + 340 - 305 - 431 = -6 \text{ kJ mol}^{-1}$ 

(iii) nucleophilic sibstitution  $(S_N^2)$  [1] name + first step to form TS



- (ii) Only the cis isomer exists for both. The trans isomer for both products will experience ring strain, hence unlikely to be formed.
- (iii) Isomer L is more basic.

The N atom in isomer **K** is sp<sup>2</sup> hybridised. The p-orbital of N atom overlaps with the  $\pi$  electron cloud of the C=C. The lone pair of electrons on N atom is delocalised into C=C, thus making it less available for dative bonding with a proton.

The N atom in isomer L is sp<sup>2</sup> hybridised. The p-orbital of N atom is used for  $\pi$  bonding with the neighbouring C atom. The lone pair of electrons on N atom thus resides sp<sup>2</sup> hybridised orbital, thus making it available for dative bonding with a proton.

- As number of protons increases, nuclear charge increases
- As successive electrons are added to the same outermost shell, shielding effect remains approximately the same.
- Hence, effective nuclear charge increases and attraction between the nucleus and outermost electron increases.
- More energy is required to remove the outermost electron.

1<sup>st</sup> I.E. of A*l* is lower than that of Mg.

Less energy is required to remove the 3p electron in A*I* as it experiences increased shielding provided by the filled 3s subshell.

1<sup>st</sup> I.E. of S is lower than that of P.

Less energy is required to remove the paired  $3p_x$  electron in oxygen as it experiences inter-electronic repulsion.



- (iii) H<sub>2</sub>/Ni, heat
- (iv) Y is ethanol  $/CH_3CH_2OH$

- (c) (i)  $\text{LiAIH}_4 + 4H_2O \rightarrow 4H_2 + \text{LiOH} + Al(OH)_3$  $\text{LiOH} + Al(OH)_3 + 4H^+ \rightarrow \text{Li}^+ + Al^{3+} + 4H_2O$ 
  - (ii)

$$V = \frac{nRT}{p} = \frac{4(1.80/37.9) \times 8.31 \times (25+273)}{101325}$$
  
= 0.004643 m<sup>3</sup>  
= 4.64 dm<sup>3</sup>

- (d) (i) The reaction is a nucleophilic substitution. The C–Br bond is weaker than C-Cl bond. Hence the  $CH_3NH_2$  nucleophile will react more readily with the electron deficient C bonded to Br.
  - (ii) The reaction is a nucleophilic acyl substitution. N is less electronegative than O atom, and the lone pair on N atom is more available than the lone pair of electron on O atom. -NH<sub>2</sub> is a stronger nucleophile than –OH, and the amine group will attack the electron deficient acyl carbon more readily.
  - (iii) AlCl<sub>3</sub> is electron deficient (a Lewis acid) and accepts a lone pair from phenylamine (a Lewis base), forming a dative bond. Hence AlCl<sub>3</sub> will not be present to act as a catalyst to generate the CH<sub>3</sub><sup>+</sup> electrophile for electrophilic substitution to take place.

#### (e)

- initial  $n(salt) = n(C_4H_9N_2O_4SNa) = 4.50/204.1 = 0.022048 \text{ mol}$
- n(HC/) added = 0.200 50.0 / 1000 = 0.0100 mol (limiting)
- $\therefore$  final n(salt) = n(C<sub>4</sub>H<sub>9</sub>N<sub>2</sub>O<sub>4</sub>SNa) = 0.022048 0.0100 = 0.012048 mol
- final n(acid) formed = n(ACES) = 0.0100 mol

$$pH = pK_a + lg \frac{[salt]}{[acid]}$$
$$= 6.88 + lg \left(\frac{0.012048/0.250}{0.0100/0.250}\right) = 6.88 + 0.08091$$
$$= 6.96$$