2017 C2 Prelims Paper 3 Mark Scheme

1 (a) No. of moles of NaOH = 0.100 x 26.50/1000 = 2.65×10^{-3} mol

No. of moles of H_2SO_4 (in $25cm^3$) = ½ x 2.65×10^{-3}
= **1.325×10^{-3}** mol **[1/2]**

No. of moles of H_2SO_4 (in $250cm^3$) = 1.35×10^{-3} x **250/25.0** **[1/2]**
= 0.01325 mol

No. of moles of H_2SO_4 reacted = (0.425 x 100/1000) **–** 0.01325 **[1/2]**
= 0.02925 mol

No. of moles of $Cu_3(CO_3)_2(OH)_2$ = 0.02925 **x 1/3** **[1/2]**
= 9.75×10^{-3} mol

Mass of azurite = 9.75×10^{-3} **x 344.5** **[1/2]**
= 3.359 g

% by mass of pure azurite in the powdered rock = 3.359/3.70 x 100%
= 90.8% **[1/2]**

(b) (i) x = 2 **[1]**

$[Cu(NH_3)_2]^+$ **[1]**

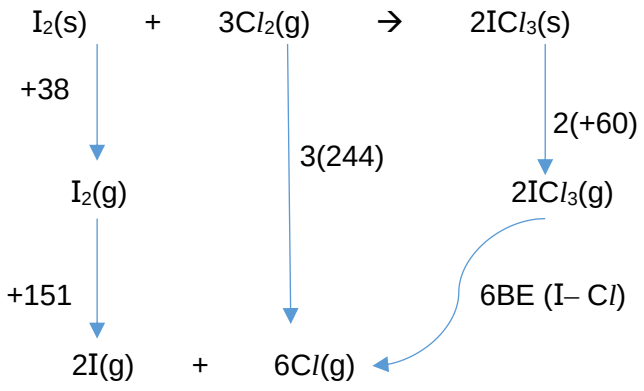
(ii) [O] $[Cu(NH_3)_2]^+ + 2NH_3 \longrightarrow [Cu(NH_3)_4]^{2+} + e^-$

[R] $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Overall: $4[Cu(NH_3)_2]^+ + O_2 + 8NH_3 + 2H_2O \rightarrow 4[Cu(NH_3)_4]^{2+} + 4OH^-$

2 half-equations: **[1/2 each]**
Overall equation: **[1]**

(c) (i)



-162 = +38 + 151 + 3(244) – 6BE(I– C*l*) – 120

BE(I– C*l*) = +160.5 $kJmol^{-1}$

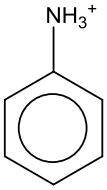
energy cycle: **[2]**
application of Hess's Law: **[1]**
correct stoichiometry coefficients: **[1]**

(ii)

$$\Delta G_f^{\ominus} = \Delta H_f^{\ominus} - T\Delta S_f^{\ominus}$$
$$-40.4 = -81 - 298\Delta S_f^{\ominus}$$
$$\Delta S_f^{\ominus} = -0.136 \text{ kJ mol}^{-1} \text{ K}^{-1}$$
$$= -136 \text{ J mol}^{-1} \text{ K}^{-1}$$ **[1]**

$\Delta S_f^{\ominus}$ is negative as there is a **<u>decrease in the number of gaseous molecules</u>**, resulting in **<u>fewer number of ways</u>** that the particles and the energy can be distributed. **[1]**

(d) (i) Electrophilic substitution, reduction and condensation. **[1 each] x 3**

(ii) 

and CH_3CO_2H **[1/2 each]**

2 (a) (i) $C_nH_{2n+1}SH + 3(n+1)/2\ O_2 \rightarrow n\ CO_2 + SO_2 + (n+1)H_2O$ **[1]**

(ii) $\chi_{SO_2} = \dfrac{\eta_{SO_2}}{\eta_{CO_2} + \eta_{SO_2} + \eta_{H_2O}}$ = 1/(n+1+n+1) = 1/(2n+2) shown **[1]**

(iii) $\chi_{SO_2} = \dfrac{p_{SO_2}}{p_{total}}$

1/(2n+2) = 16900 / 101325

n = 2 **[1]**

(iv) $\eta_{SO_2} = \dfrac{p_{SO_2}V}{RT} = \dfrac{16900(1.65x10^{-3})}{8.31(110+273)} = 0.00876$ mol = $\eta_{ethanethiol}$ reacted **[1]**

Mass of ethanethiol = 0.00876 x 62.1 = 0.544 g **[1]**

(b) (i) As Reaction 1 is effectively complete whereas ethanol does not react with NaOH, this shows that ethanethiol is a stronger acid than ethanol. **[1]**

(ii) Nucleophilic substitution **[1]**

(iii) Reaction 1 was carried out to generate $CH_3CH_2S^-$, a stronger nucleophile than CH_3CH_2SH. **[1]**

(iv) For bromobenzene, the lone pair of electrons on the bromine atom is delocalised into the ring. As a result, there is partial double bond character to the C-Br bond, so its bond strength is higher than a typical C-Br in a halogenoalkane and it is very difficult to break. **[1]**

Sterically, the rear side of the C-Br bond in bromobenzene is blocked by the benzene ring.
Or
The pi-electron cloud of the benzene ring will repel the lone pair of electrons of the incoming nucleophile, rendering attack of the nucleophile difficult. **[1]**

(c) (i) Base **[1]**

(c) (ii) As the equilibrium position lies towards the products (K>1), $\Delta G^{\ominus}$ is negative. **[1]**

As the equilibrium constant for Reaction 1 is a very large number, as $\Delta G^{\ominus}$=-RTlnK, the magnitude of $\Delta G^{\ominus}$ is very large. **[1]**

(iii) A: HNO_3 **[1]**
B: NO_2 **[1]**

(iv) The temperature in the furnace is 400 °C. **[1]** (accept any temperature between 170 °C and 630 °C)

The ionic radii of Cu^{2+}, Pb^{2+} and Ba^{2+} are 0.073nm, 0.120nm and 0.135nm respectively. **[1/2]**

The charge density of the cation decreases from Cu^{2+} to Pb^{2+} to Ba^{2+}. **[1]**

The polarising power of the cation decreases from Cu^{2+} to Pb^{2+} to Ba^{2+}. OR the cation is less able to distort the electron cloud of the nitrate, weakening the N-O bonds within the nitrate anion to a smaller extent. **[1]**
Hence more energy is required to decompose $Pb(NO_3)_2$ compared to $Cu(NO_3)_2$ but less compared to $Ba(NO_3)_2$. **[1/2]** (accept "ease of decomposition" / "decomposition temperature")

(d) **(i)** Reaction (A) is more likely to occur as it is easier to break a C-C bond (350 kJ mol^{-1}) compared to a C-H bond (410 kJ mol^{-1}) **[1]**

(ii) Reactions (C), (D) and (E) **[1]**

(iii) Hydrogen **[1]**

(iv) The $\bullet CH_2CH_3$ radical loses a hydrogen (is oxidised) to form ethene and gains a hydrogen (is reduced) to form ethane. As it is both oxidised and reduced, this is a disproportionation. **[1]**

OR
The average oxidation number of carbon in the $\bullet CH_2CH_3$ radical is -2.5, but -2 in ethene and -3 in ethane. As carbon is both oxidised and reduced, this is a disproportionation. **[1]**

3 (a) (i) Concentration of a solid is constant. **[1]**

(ii) $\eta(C_{18}H_{29}SO_3Na)$ present in 1.00 g of detergent

$= \left(\frac{17.4}{100} \times 1.00\right) \div 348 = 5.00 \times 10^{-4}$ mol

$\therefore [C_{18}H_{29}SO_3^-] = 5.00 \times 10^{-4}$ mol dm^{-3} **[1]**

IP $= (2.50 \times 10^{-4})(5.00 \times 10^{-4})^2 = 6.25 \times 10^{-11}$ mol^3 dm^{-9} **[1]**

Since IP > K_{sp}, a precipitate will form. **[1]**

(iii) For the detergent to be effective, no precipitate is formed

$\Rightarrow$ IP < K_{sp}

$\therefore [Ca^{2+}][C_{18}H_{29}SO_3^-]^2 < 1.20 \times 10^{-17}$

From **(a)(ii)**, $[C_{18}H_{29}SO_3^-] = 5.00 \times 10^{-4}$ mol dm^{-3}

$\therefore [Ca^{2+}] < \frac{1.20 \times 10^{-17}}{(5.00 \times 10^{-4})^2} = 4.80 \times 10^{-11}$ mol dm^{-3}

Maximum $[Ca^{2+}] = 4.80 \times 10^{-11}$ mol dm^{-3} **[1]**

(iv) $K_c = \frac{[CaP_3O_{10}^{3-}]}{[Ca^{2+}][P_3O_{10}^{5-}]}$ **[1]**

(v) $K_c = \frac{[CaP_3O_{10}^{3-}]}{[Ca^{2+}][P_3O_{10}^{5-}]}$

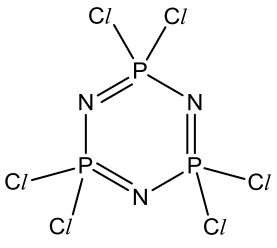
$7.70 \times 10^8 = \frac{0.90}{[Ca^{2+}] \times 0.10}$

$[Ca^{2+}] = 1.17 \times 10^{-8}$ mol dm^{-3} **[1]**

(vi) Since $[Ca^{2+}]$ is **more than 4.80×10^{-11}**, the added solid sodium tripolyphopshate was **insufficient** to make the detergent effective. **[1]**

(b) (i) $3PCl_5 + 3NH_4Cl \rightarrow (Cl_2PN)_3 + 12HCl$ **[1]**

(ii)



[1]

(iii) ($Cl_2PN)_3$ undergoes <u>hydrolysis</u>. **[1]** (Accept nucleophilic substitution)

<u>White fumes</u> of HCl is observed. **[1]**

(iv) From the Data Booklet, atomic radius of P = 0.110 nm, atomic radius of N = 0.074 nm and atomic radius of Cl = 0.099 nm

Atomic radius of N is the smallest as it has <u>one less principle quantum shell</u> than <u>P and Cl</u> and hence their <u>valence electrons are closer to the nucleus</u>. **[1]**

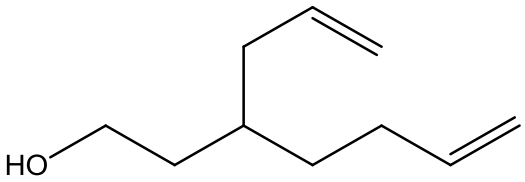
Atomic radius of Cl is smaller than P. Cl has <u>higher nuclear charge / higher proton number</u> but <u>similar shielding effect</u> **[1]** as P. Hence Cl has higher effective nuclear charge and the valence electrons are held closer to the nucleus.

(Idea of valence electron closer to nucleus just need to be mentioned once in answer).

Note: atomic radius of N must be compared to Cl. Explaining atomic radius of N < P and atomic radius of Cl < P does not fully explain the trend atomic radius of N < Cl < P.

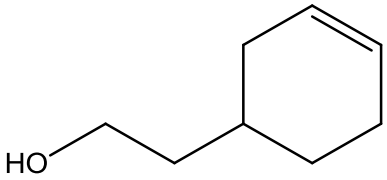
(c) **(i)**

B =



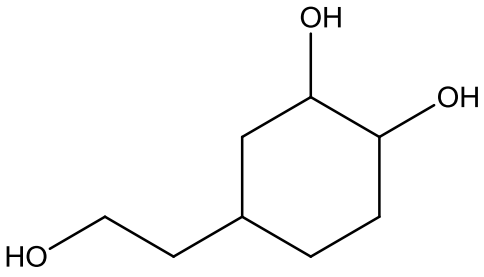
[1]

C =



[1]

D =



[1]

(ii) Step 1: alcoholic KOH, heat or alcoholic NaOH, heat **[1]**

Step 3: $KMnO_4$, NaOH(aq), cold **[1]**

Step 4: excess concentrated H_2SO_4, heat or concentrated H_3PO_4, heat or Al_2O_3, heat **[1]**

4 (a) (i) $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e$ **[1]**

(ii)
- Reactant molecules diffuse towards the catalyst surface and are **adsorbed onto the active sites**.
- The **bonds in the reactant molecules weaken**, and the **activation energy is lowered**.
- Reactant molecules are **brought closer together**, and are **correctly orientated.**
- When the product is formed, it **desorbs** and diffuses away from the catalyst surface **freeing up the active sites**.

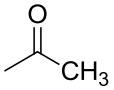
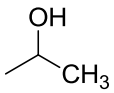
[4]

(iii)
- Correctly drawn CO_2/ ethanol half cell
  - $[H^+]$ and ethanol to 1mol dm^{-3}
  - Temperature and pressure of CO_2 to 298K and 1 bar
  - Electrode: graphite/ metal catalyst/ platinum (coated with metal catalyst)
- Correctly drawn standard hydrogen electrode
  - $[H^+]$ to 1 mol dm^{-3}
  - Temperature and pressure of H_2 to 298K and 1 bar
  - Platinum electrode
- Salt bridge and voltmeter

[1] for each point

(iv)
- When pH increases, **[H+] decreases**. This **favours the oxidation** of ethanol.
- Reduction potential should become **more negative**. **[2]**

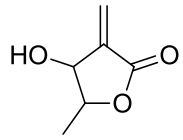
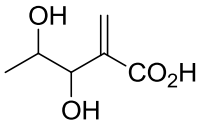
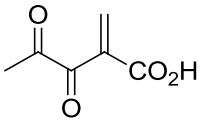
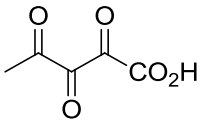
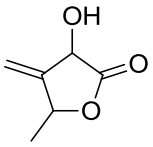
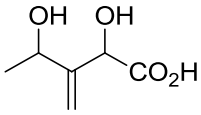
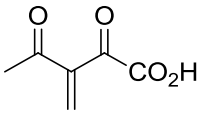
(b) (i) Degree of unsaturation of **A** = 3
Degree of unsaturation of **B** = 2 **[2]**

(ii)
- **Carboxylic acid**
  - reacts with Na_2CO_3 in an acid–carbonate reaction.
- **(Two) 2º alcohol**
  - oxidation with I_2, NaOH(aq), suggest that either  or  is present. Since **B** does not react with 2, 4 – DNPH, a 2º alcohol is present
  - oxidation with $K_2Cr_2O_7$ does not increase the number of oxygen atoms in C. No primary alcohol was oxidized.
- **(Terminal) Alkene**
  - Oxidative cleavage with $KMnO_4$.
  - Oxidative cleavage causes the molecule to lose one carbon.

[3]

(b) (iii) • Since **B** contains a carboxylic acid and alcohol and is formed from the acid hydrolysis of **A**, **A** contains an **ester functional group**. **[1]**

(iv) • Of the two secondary alcohols, it is the secondary alcohol with the CH_3 that forms the ester since **A** does not give a yellow ppt with alkaline I_2(aq)

A	B	C	D
			
			

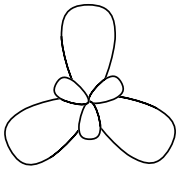
[1] each

5 (a) Histidine exists as zwitterions due to the internal neutralization of amino and carboxylic acid groups. **Zwitterions** are **arranged in an orderly manner** in solid crystalline state. **[1]**

It has a **giant ionic structure with** strong **ionic bonds** between the zwitterions.
[1] both

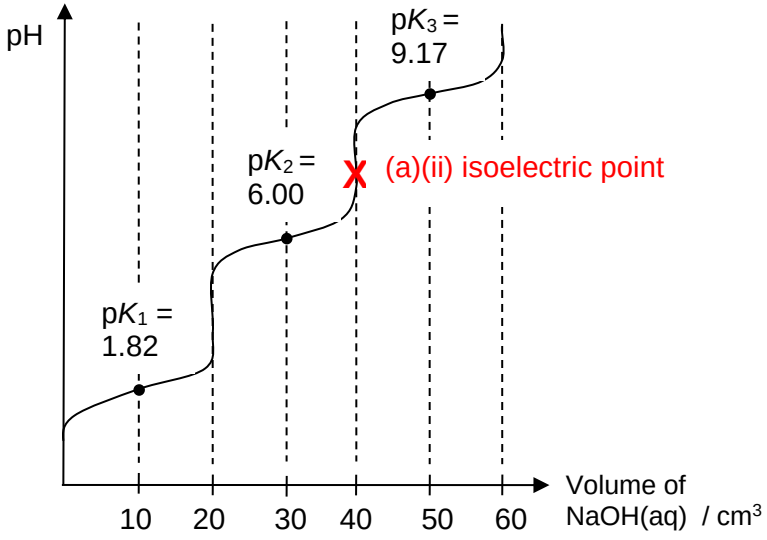
A lot of energy is required to separate the zwitterions due to the **strong** ionic bonds, thus it has high melting point. **[1]**

(b) sp^2 **[1]**



[1]

(c) (i)



[1] axis labels and shape of curve
[1] 3 equivalence points at correct volumes & mark pK_1, pK_2 & pK_3
[1] Mark X at the correct volume

(c) (ii) pH = pK_{a2} + lg [A^-]/[HA]
6 = 6.00 + lg [A^-]/[HA]
[A^-]/[HA] = <u>1</u>

<u>Before addition of OH^-</u>
Amount of histidine present = 0.100 dm^3 x 0.10 mol dm^{-3} = 0.01 mol
Amount of HA = Amount of A^- = $0.01 \times \frac{1}{2}$ = <u>0.00500 mol</u>

<u>On addition of OH^-:</u>
Amount of OH^- added = 0.01 dm^3 x 0.01 mol dm^{-3} = 0.0001 mol

	HA + OH^-(aq) ⇌	A^-(aq) + H_2O
Before adding NaOH	0.00500	0.00500
After adding NaOH	0.00500 – 0.0001 = 0.00490	0.00500 + 0.0001 = 0.00510

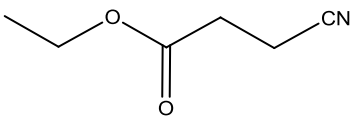
pH = 6.00 + lg (0.00510/0.00490)
= <u>6.017 ≈ 6.02</u>

[1] for original [A^-]/[HA]
[1] for amount of A^- & HA before addition of NaOH
[1] pH with 2 dp

(d) (i) (Alkaline) Hydrolysis **[1] reject acid hydrolysis**

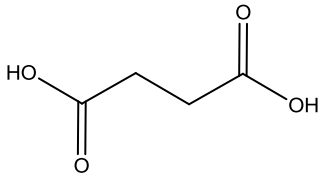
Amide and nitrile **[1/2 each]**

(ii)



P:

Q: CH_3CH_2OH

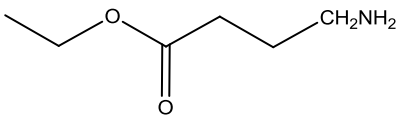


R:

S: HCO_2H **T:** CHI_3

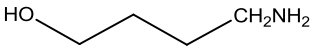
[1] each

(iii)



U:

V:



[1] each