HWA CHONG INSTITUTION
2017 C2 CHEMISTRY PRELIMINARY EXAMINATIONS
PAPER 2 MARK SCHEME

1

(a) (i)

	$H_2(g)$	+	$I_2(g)$	⇌	2HI(g)
Initial conc/ mol dm^{-3}	0.05		0.05		0
Change / mol dm^{-3}	- 0.03		- 0.03		+ 0.06
Eqm conc / mol dm^{-3}	0.02		0.02		0.06

$K_c = \dfrac{[HI]^2}{[H_2][I_2]}$ **[1]**

$K_c = \dfrac{(0.06)^2}{(0.02)^2} = 9$ **[1]**

(ii)

	$H_2(g)$	+	$I_2(g)$	⇌	2HI(g)
Initial conc/ mol dm^{-3}	0.02		0.02		0.06
Change / mol dm^{-3}	+x		+x		-2x
Eqm conc / mol dm^{-3}	0.02+x		0.02+x		0.06-2x

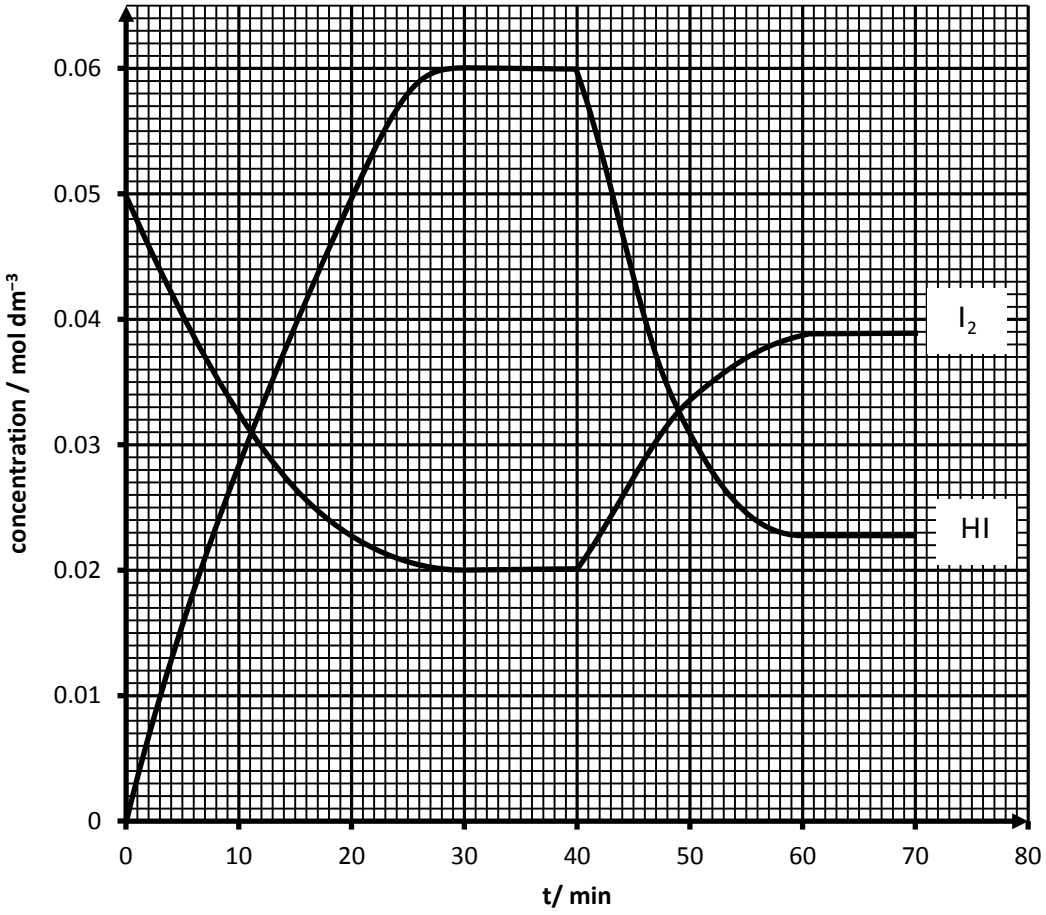
$K_c = \dfrac{(0.06-2x)^2}{(0.02+x)^2} = 0.36$

$\dfrac{(0.06-2x)}{(0.02+x)} = 0.6$

x = 0.01846 **[1]**

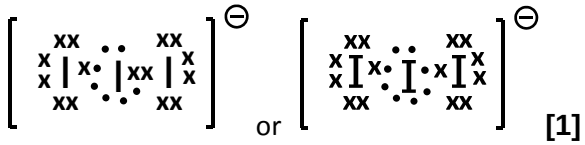
$[H_2] = [I_2] = 0.02+x =$ **<u>0.0385 mol dm^{-3}</u>**
[HI] = 0.06-2x = **<u>0.0231 mol dm^{-3}</u>** shown **[1]**

(iii)



Correct axis labels [0.5]
Appropriate scale [0.5]
Correct shape of curves [0.5]
Horizontal lines from 30 – 40 mins and 60 – 70 mins [0.5]
***Correct concentration and time values for HI at t = 0, 30 and 60 min [1]**
***Correct concentration and time values for I_2 at t = 0, 30 and 60 min [1]**
***-[0.5] for every wrong plot**

(iv) To <u>prevent the position of equilibrium from shifting</u> during the cooling process or when HI is removed when dissolved in water. **[1]**

(b)  or **[1]**

(c) Both I_2 and HI have <u>simple molecular structure</u> / consist of simple discrete molecules **[0.5]** held together by <u>dispersion forces</u>. However, I_2 has a larger number of electrons, therefore a <u>larger electron cloud than HI</u>, leading to <u>stronger</u> dispersion forces. **[1]**

So, a <u>larger amount of heat energy</u> **[0.5]** is needed to separate the molecules, leading to a higher boiling point.

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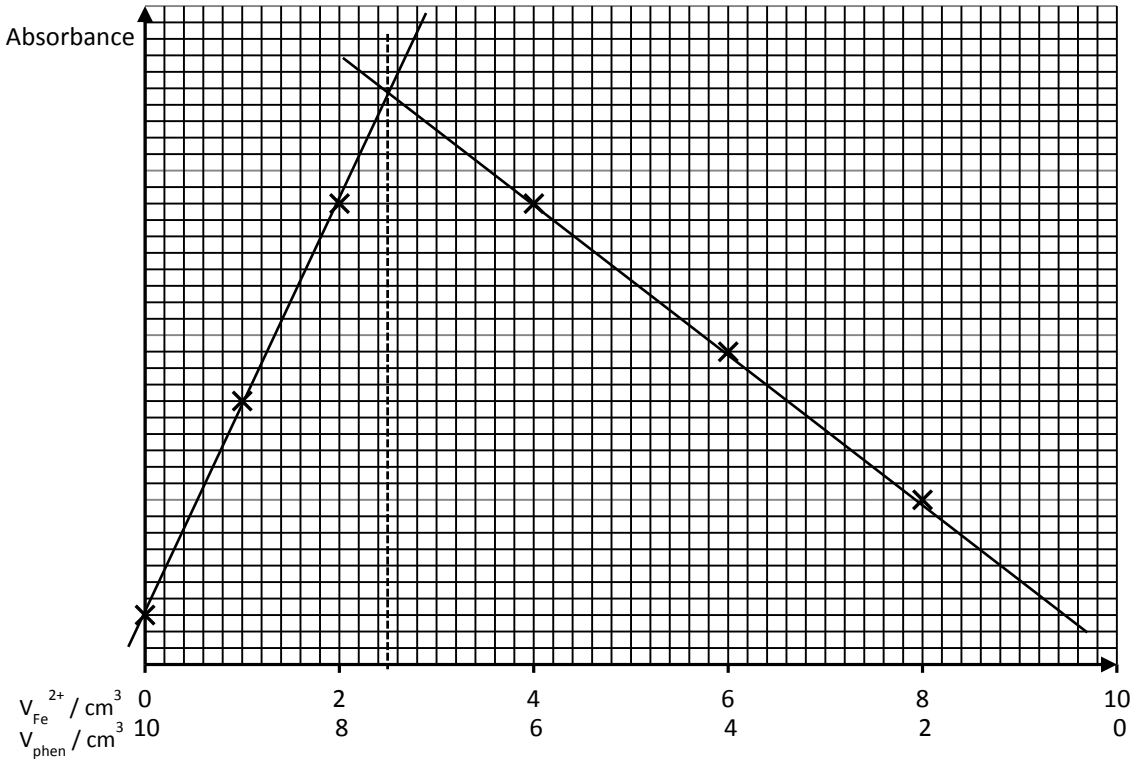
(a) (i) A ligand is an ion or molecule with <u>one or more lone pairs of electrons</u> available to be donated into the vacant <u>orbitals of transition metal</u> atom or ion.

(ii)



From the graph, V_{Fe2+}:V_{phen} = 2.5:7.5 therefore you can deduce the following reacting ratio - Fe^{2+}:phen is 1:3
Formula of the complex: **<u>$[Fe(phen)_3]^{2+}$</u>**

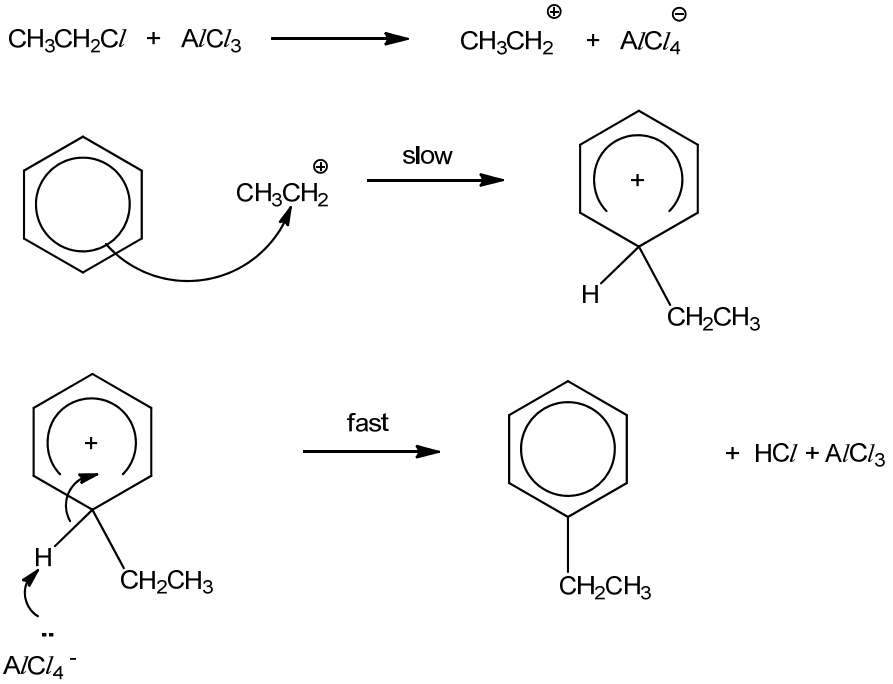
(iii)

- Fe^{2+} has an incomplete/ <u>partially filled 3d subshell</u> (insufficient to just give electronic configuration)
- In the presence of ligands (phen), the degenerate 3d orbitals of Fe^{2+} <u>split into **two** different energy levels with an energy gap ΔE</u>
- <u>ΔE</u> falls within the <u>visible region</u> of the electromagnetic spectrum
- An electron in a lower energy d-orbital can <u>absorb</u> energy from the visible spectrum and be <u>promoted</u> to a higher energy d orbital that is <u>vacant</u>
- The orange-red colour seen is the <u>complement</u> of the blue light absorbed.

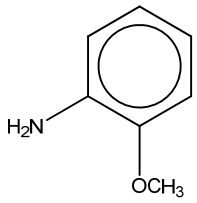
(iv) The <u>energy gap, ΔE, is of a different magnitude</u> in both complexes. Hence wavelength of light absorbed by the ferrozine complex is different from that absorbed by the phen complex and different colours are observed. (no need details on the exact colour of wavelength).

(b) (i) Reagent: CH_3CH_2Cl ; condition: $AlCl_3$, warm

(ii) Electrophilic substitution



(c) (i)



[1]

(ii) Accepted answers:

- 2,4-dinitrophenylhydrazine. Orange precipitate observed for vanillin but no precipitate for 4-VG
- Tollen's reagent with heating. Silver mirror observed for vanillin but no silver mirror for 4-VG
- Hot acidified KMnO4. Solution turns from purple to colourless for both but only 4-VG gives an effervescence that formed white ppt when passed through limewater
- Hot acidified $K_2Cr_2O_7$. Orange solution turned green for vanillin but solution remained orange for 4-VG.

3 (a) (i) hybridisation: $\underline{sp^3}$ **[1]**

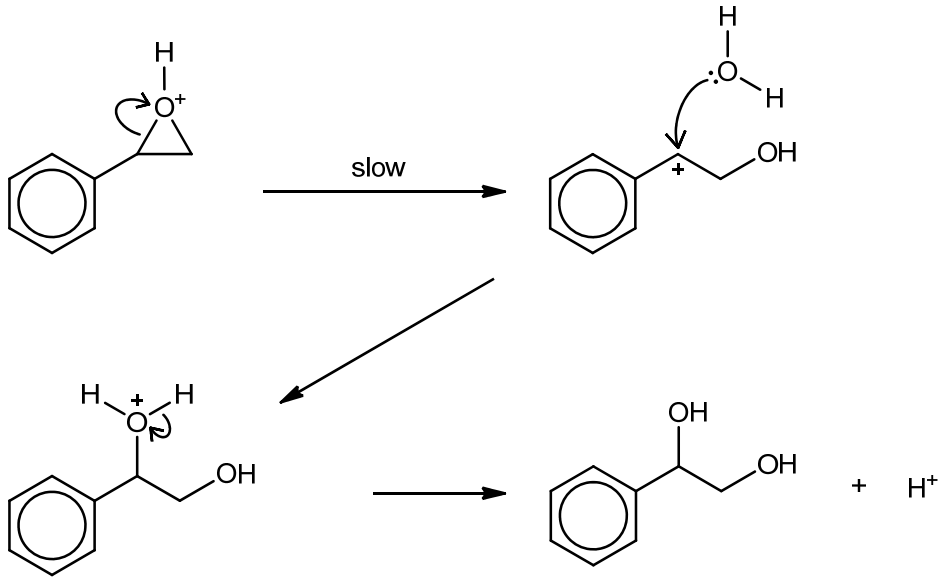
typical bond angle: $\underline{109.5°}$ **[1]**

(ii) Forcing the bond angle in the epoxide ring to 60° brings electron pairs in the covalent bonds closer and they experience <u>increased repulsion</u>, weakening the C–O bonds and making them easier to break. **[1]**

or

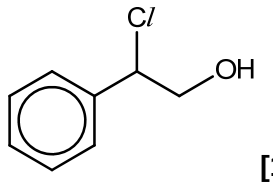
After opening the ring, the resulting product is able to attain an optimal bond angle of 109.5° around the carbon atoms, minimising electron repulsion and eliminating the ring strain.

(b) **(i)**



curly arrow from benzylic C–O$^+$ bond to O$^+$ [½], correct carbocation [½]
curly arrow from lone pair on O in H_2O to C bearing the positive charge [½], correct intermediate formed [½]
curly arrow from O$^+$–H bond to O$^+$ and H$^+$ regenerated [1]

(ii)



[1]

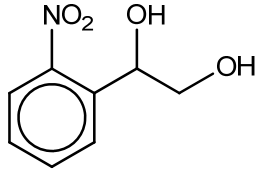
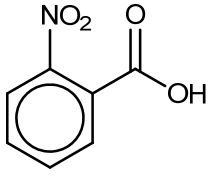
(iii) The other C–O bond was broken instead, forming a primary carbocation intermediate. $H_2{}^{18}O$ was then able to attack the primary carbocation to form isotopic isomer **A**. **[1]**

The primary carbocation formed is much more unstable than the secondary carbocation (which is particularly stable as it is resonance stabilised). The reaction mechanism is therefore much less likely to proceed via the 1° carbocation intermediate to form **A**. **[1]**

(c) step 1: conc HNO_3, conc H_2SO_4 **[½]**, maintained at 55 °C or < 55 °C **[½]**

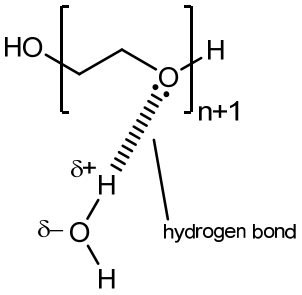
step 2: $KMnO_4$(aq), H_2SO_4(aq), heat **[1]**

step 3: CH_3CH_2OH (accept ethanol), few drops of conc H_2SO_4, heat (under reflux) **[1]**

 **B**	 **C**

[1] each

(d)



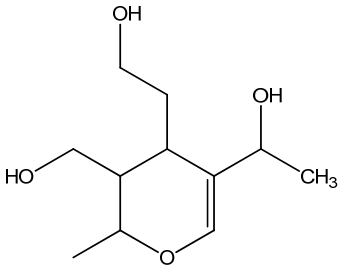
[1]

Extensive hydrogen bonding exists between PEG and water molecules. Energy released from this intermolecular hydrogen bonding with water is able to compensate for dispersion and p.d.-p.d. interactions between PEG, and intermolecular hydrogen bonding in water. **[1]**

4

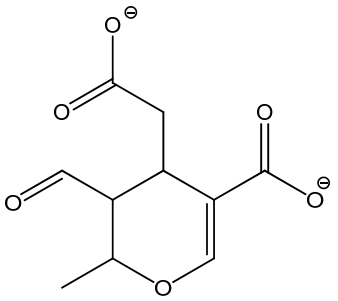
(a) Carboxylic acid, aldehyde, ketone, alkene **4 x [1]**

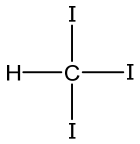
(b) **(i)**



[1]

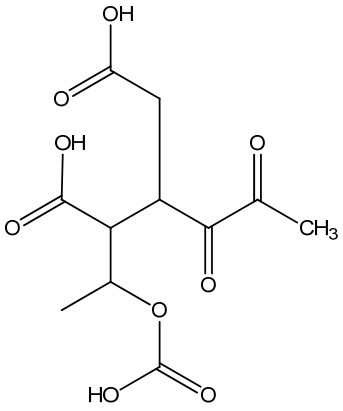
(ii)





2 x [1]

(iii)



1 mark for correct structure for oxidative cleavage of C = C bond
1 mark for correct structure for the oxidation of –CHO to –CO_2H

(c) Elenolic acid is a <u>stronger acid</u> / has <u>higher acidity</u> than compound M, which is a primary alcohol. [1]

The <u>negative charge</u> on the carboxylate ion (conjugate base of elenolic acid) is <u>delocalised</u> equally over two highly <u>electronegative</u> oxygen atoms. The negative charge is dispersed and the carboxylate ion is greatly <u>stabilised</u>. [1]

Whereas the electron-donating alkyl group <u>intensifies the negative charge</u> on the alkoxide ion (conjugate base of compound M) and the alkoxide ion is <u>destabilised</u>. [1]

5

(i) $Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e^-$ **[1]**

(ii) $Q = 3100 \times 0.700 = 2170\ C$ **[1]**

Amount of electrons transferred = $(0.714/63.5) \times 2 = 0.02249$ mol **[1]**

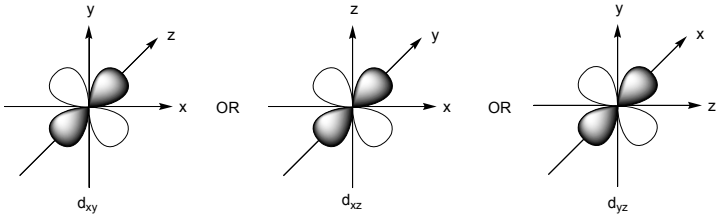
Since $Q = \eta_e \times L \times e$
$2170 = 0.02249 \times L \times 1.60 \times 10^{-19}$
$L = 6.03 \times 10^{23}\ mol^{-1}$ **[1]**

(b) (i) $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ –0.25V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ +0.34V **[1] (correct quotation)**

The reduction potential of the Cu^{2+}/Cu half cell is more positive than that of Ni^{2+}/Ni half cell and therefore Cu^{2+} will be preferentially reduced at the cathode. **[1]**

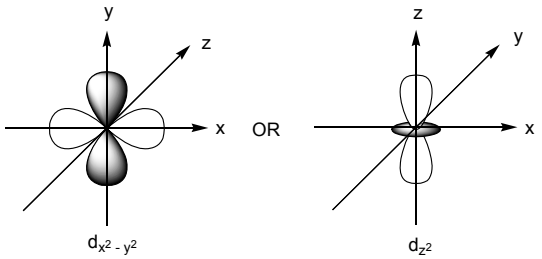
(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ **[1]**

(iii) **<u>Upper</u>**



[1] for **<u>any</u>** of the three being drawn + **<u>correct label</u>** (shading not required; ignore if drawn)

<u>Lower</u>



[1] for **<u>any</u>** of the two being drawn + **<u>correct label</u>** (shading not required; ignore if drawn)

(c) **(i)** From the graph, since the plot of k_{obs} against OH^- is a straight line that passes through the origin, m=1. **[1]**

(ii) Rate = $k[OH^-][isocyanide]$ **[1]**

When $[OH^-] = 0.74$ mol dm^{-3}, $k_{obs} = 5.6 \times 10^{-3}$ s^{-1}
rate = k_{obs} [isocyanide] = $5.6 \times 10^{-3} \times (5.0 \times 10^{-4}) = 2.8 \times 10^{-6}$ mol dm^{-3} s^{-1} **[1]**
OR
Gradient for X=C*l* graph, $k = 0.6 \times 10^{-3}/0.8 = 7.5 \times 10^{-3}$ mol dm^{-3} s^{-1}
rate = $k[OH^-][isocyanide] = 7.5 \times 10^{-3} \times 0.74 \times (5.0 \times 10^{-4}) = 2.8 \times 10^{-6}$ mol dm^{-3} s^{-1}

(iii) The OH^- nucleophile approaches the electron deficient carbon of isocyanide. The substituents NO_2 and C*l* are electron withdrawing and they enhance the electron deficiency of isocyanide, making it more susceptible to nucleophilic attack. Their rate of reaction (as reflected in the rate constant represented by the gradient) thus exceeds that when X=H (when there is no substituent). **[1]**

6

(a) A buffer solution is a solution that resists changes in pH upon addition of small amounts of acid or base. **[1]**

(b) $$pH = pK_a + \lg\frac{[SO_3^{2-}]}{[HSO_3^-]} = -\lg(1.02 \times 10^{-7}) + \lg(1/4)$$

pH = 6.39 **[1]**

(c) $HSO_3^- + OH^- \rightarrow SO_3^{2-} + H_2O$ **[1]**

(d) $K_{sp} = [Mg^{2+}][OH^-]^2$
$5.66 \times 10^{-12} = (5 \div 405 \times 2)\,[OH^-]^2$
$[OH^-] = 1.51 \times 10^{-5}$ mol dm^{-3} **[1]**

pH = 14−pOH = 14 + lg(1.51×10^{-5})
pH = 9.18 shown. **[1]**

(e) Solution B **[1]**

(f) "Tea" appears earlier because the working pH range of 3-nitrophenol indicator (6.7-8.7) is lower than the pH at which white precipitate occurs (9.18). **[1]**

(g) Phenolphthalein **[1]**