NJC **SH2 Prelim 2013 H2 Chemistry Paper 2**

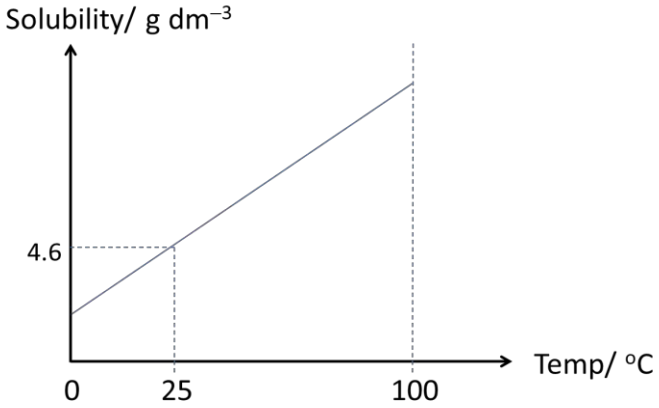
SH2 H2 Prelim H2 2013 Answers

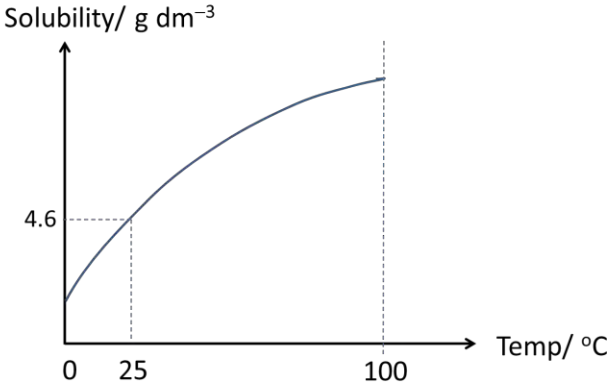
Paper 2

1(a) **(i)** $Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^-\,(aq)$ $\Delta H_{sol} > 0$

As temperature is increased, **solubility of calcium iodate(V) increases**.
When temperature is increased, equilibrium shifts right to **favour the forward endothermic reaction** to partially absorb the extra heat.
Hence more $Ca(IO_3)_2$ dissolved in water.

(ii)





[1]

1(b) **(i)** $2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$

Titrate the iodine produced with thiosulfate solution.

(ii) **Preliminary calculation**

Volume of $Ca(IO_3)_2$ used for reaction = 25.0 cm^3 (pipette capacity)

No. of moles of IO_3^- in the 25.0 cm^3 solution $= \frac{4.6}{390.1} \times 2 \times \frac{25}{1000}$

$= 5.896 \times 10^{-4}$ mol

IO_3^-	:	I_2	:	$S_2O_3^{2-}$
1	:	3	:	6

No. of moles of $S_2O_3^{2-}$ required for titration = $6 \times 5.896 \times 10^{-4}$
= 3.538×10^{-3} mol
Vol. of $S_2O_3^{2-}$ required for titration = $3.538\ cm^3$

Volume is too small and will results in high experimental error. Therefore, concentration of FA3 is too high and dilution is required.

Volume of H^+ required for titration = $3.538\ cm^3$
(no. of moles of H^+ required is same as $S_2O_3^{2-}$ and their concentrations are the same)

Volume of I^- required for titration will be less than volume of H^+ required. Since the I^- and H^+ can be in excess, 5 cm^3 each of FA2 and FA4 are used.

Dilution
Desired amount of $S_2O_3^{2-}$ from the burette = 25 cm^3

Dilution factor = $\frac{25}{3.538}$

Volume of FA 3 to be diluted in a 250 cm^3 volumetric flask = $250 \div \frac{25}{3.538}$
= $35.38\ cm^3$

1. Using a burette, transfer 35.40cm^3 of FA3 into a clean 250 cm^3 volumetric flask.
2. Top up to the mark with deionized water, stopper, invert and shake to ensure homogeneous solution.
3. Label this solution FA5.

Procedure

1. Filter the suspension, FA1, into a clean and dry conical flask using a dry filter paper and funnel.
2. Pipette 25.0 cm^3 of the filtrate into a 250 cm^3 conical flask.
3. Using 2 separate 10 cm^3 measuring cylinders, add 5 cm^3 each of FA2 and FA4 into the same conical flask and swirl to ensure mixing.
4. Titrate the contents of the conical flask against FA5 from a burette till a colour change from brown to pale yellow is observed.
5. Add 3 drops of starch indicator and continue titration till the blue-black colour is discharged.
6. Record the volume of FA5 required for titration.
7. Repeat steps 2 to 6 till consistent titration results of within 0.10 cm^3 are obtained.

1(c) experimental data, x = volume of $S_2O_3^{2-}$ required for titration (dm^3)

$n(S_2O_3^{2-})$ required for titration = (x) × concentration of $S_2O_3^{2-}$
= a

$[IO_3^-]$ = $\frac{a}{6(25\times10^{-3})}$ = b mol dm^{-3}

$[Ca^{2+}]$ = ½ b mol dm^{-3}

Ksp = $[Ca^{2+}]\,[IO_3^-]^2$
= (½ b) (b^2)
= ½ b^3

2(a) Rxn A : Nucleophilic addition
Rxn B: Hydrolysis

(b)(i) No naked flame around / heating should be done with electric isomantle as chemicals are flammable.
Perform experiment in fume cupboard as chemicals are toxic.

(ii) To exclude any trace of water/moisture or to ensure chemicals are dry.

(iii) $CH_3CH_2I + Mg \rightarrow CH_3CH_2MgI$

$$n_{Mg} = n_{CH_3CH_2I} = \frac{1.50}{24.3} = 0.06173\ mol$$

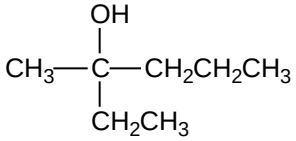
$$Vol\ of\ CH_3CH_2I = \frac{mass}{density} = \frac{0.06173 \times 156}{1.93} = 4.99\ cm^3$$

2(b)(iv) $n_{Grignard\ reagent}$ produced in step II = 0.06173 mol

$n_{pentan\text{-}2\text{-}one} = \frac{density \times vol}{molar\ mass_{pentan-2-one}} = \frac{0.814 \times 6.0}{86}$ = 0.0568 mol < $n_{Grignard\ reagent}$

Since pentan-2-one reacts with Grignard reagent in the mole ratio of 1:1, hence Grignard reagent is in excess.

(v)



(vi) CH_3CH_3 (ethane)

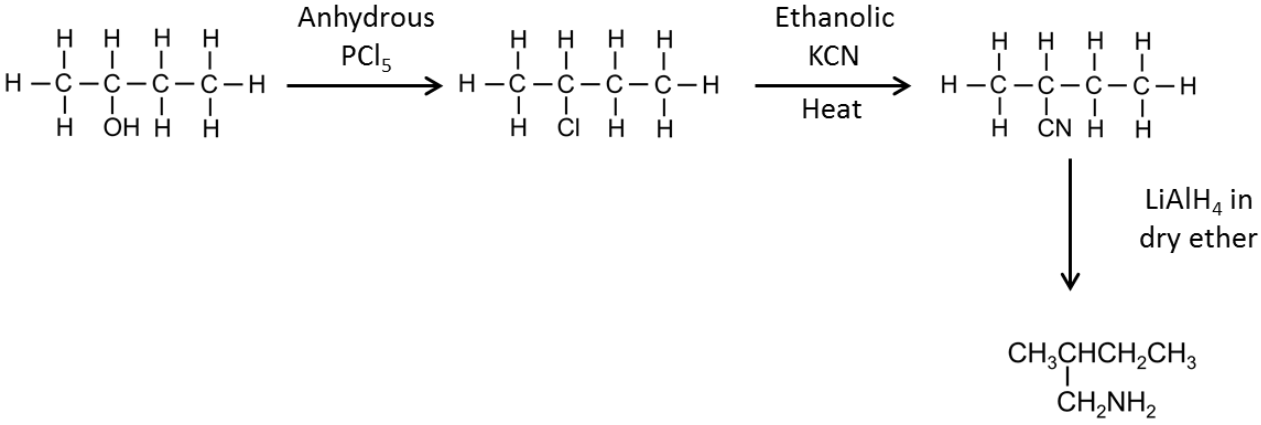
(vii) Ethoxyethane forms an *immiscilble layer above* the aqueous layer because of :

- unfavourable interaction between ethoxyethane and water or forces of attraction between water molecules are stronger than the forces of attraction between ethoxyethane and water
- ethoxyethane is less dense than water (0.713 g cm^{-3} as against 1 g cm^{-3})

2(b)(viii)

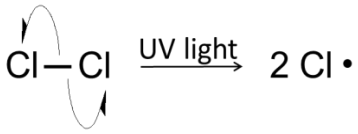
Chemicals added	Impurity removed
1 water	Mg salts like MgI_2
2 saturated sodium hydrogencarbonate	HCl
3 sodium thiosulfate	iodine
4 saturated sodium chloride	H_2O

2 (c)



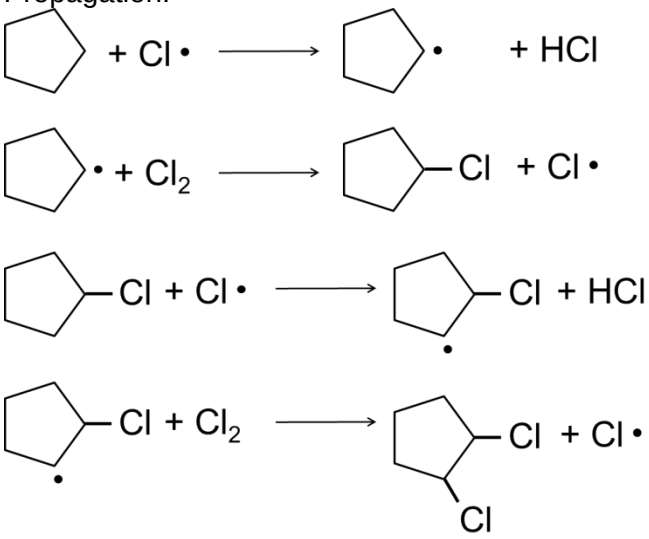
3 (a)(i) Free Radical Substitution

Initiation:



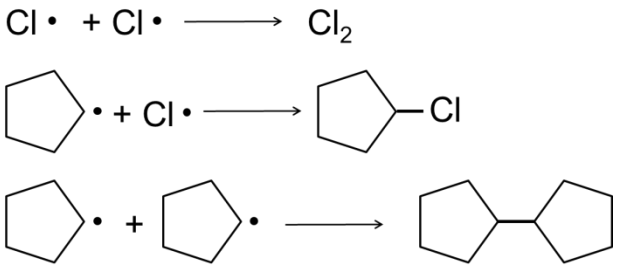
(*must use half arrows to show homolytic bond cleavage)

Propagation:



(*must show formation of $C_5H_8Cl_2$)

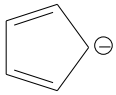
Termination:



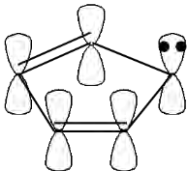
(*any two possible termination steps)

3(a)(ii) Type of reaction: Elimination
Reagents and conditions: Ethanolic KOH, heat

3(a)(iii)



The **<u>negative charge on the carbon atom is delocalised</u>** across the 5 carbon atoms in the ring due to continuous overlap of p–orbitals, thus the anion is stabilised by resonance. As the conjugate base is relatively stable, the dissociation cyclopentadiene to give H^+ is possible.



3(b)(i) Heat evolved, Q = mcΔT
= (1)(4.18)(100 – 27)
= 305.14 kJ (heat gained by water)

Since the process is only 65% efficient,

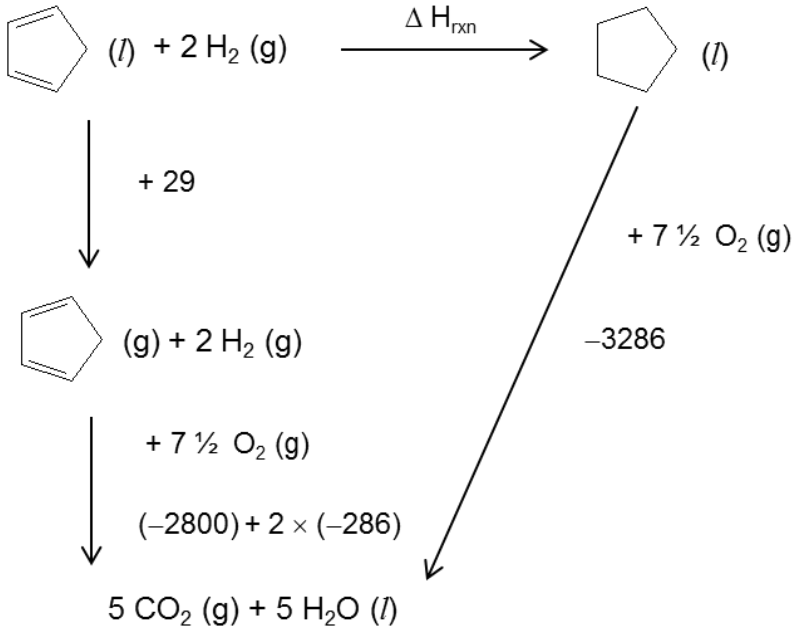
Total amount of heat released from combustion = $305.14 \times \frac{100}{65}$ = 469.4 kJ

Amount of C_5H_{10} = $\frac{10}{70}$ = 0.1429 mol

$\Delta H_c = -\frac{469.4}{0.1429} = -3286$

$= -3290$ kJ mol^{-1} (3 s.f)

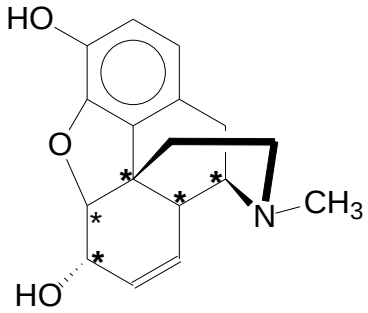
3(b)(ii)



By Hess's Law,

ΔH_{rxn} = 29 + (–2800) + 2(–286) + 3286
= –57.0 kJ mol^{-1} (3 s.f.)

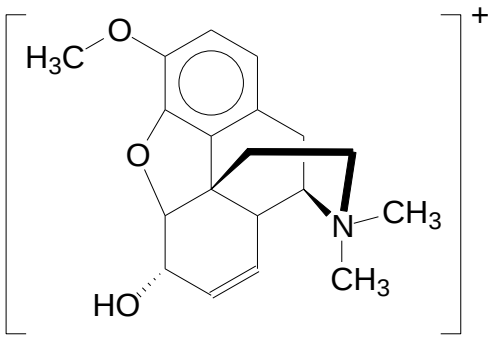
4(i)



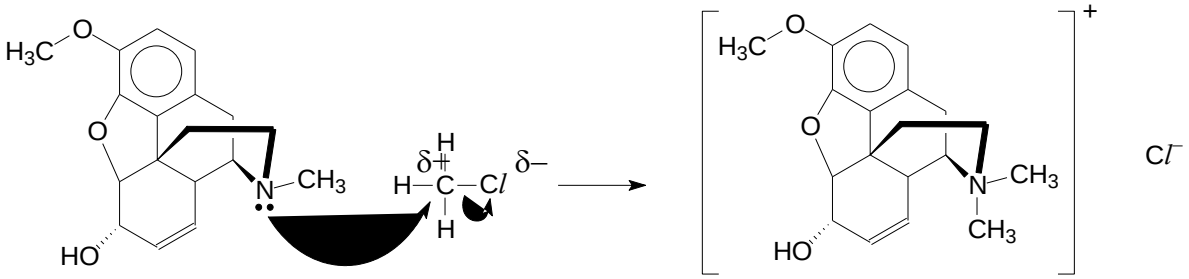
5 chiral carbon atoms

morphine 6

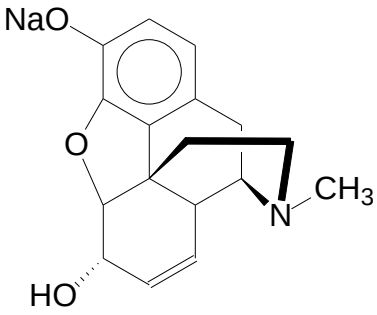
(ii)

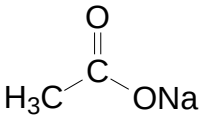


Reaction:



4(iii)





(iv) Neutral $FeCl_3(aq)$ or freshly prepared $FeCl_3(aq)$/ $FeCl_3$ solution
Morphine: Violet complex observed
Codeine: No violet complex observed or remained yellow

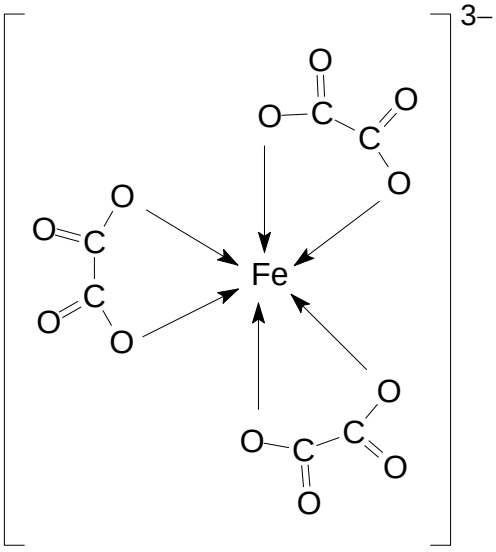
5a(i)

	K	C	Fe	O
% by mass	26.8	16.5	12.8	43.9
A_r	39.1	12	55.8	16
Divided by A_r	0.6854	1.375	0.2293	2.743
Mole ratio	3	6	1	12

Formula: $K_3[Fe(C_2O_4)_3]$ or $[Fe(C_2O_4)_3]^{3-}$

5a(ii) $[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6\ H_2O$

5a(iii)



Shape of complex ion: Octahedral

5(b) $[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6\ H_2O$ ---- (1) (from 5(a)(ii))

<u>Colour change from emerald green to yellow:</u>
$H_2C_2O_4$ formed when H_2SO_4 is added. The decrease in $[C_2O_4^{2-}]$ causes the position of equilibrium in equilibrium (1) to shift to the left. Hence, the presence of $[Fe(H_2O)_6]^{3+}$ gives rise to a yellow solution.

<u>Colour change from yellow to pale green with the liberation of CO_2 gas:</u>
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^o_{red} = +0.77$ V
$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e$ $E^o_{ox} = +0.49$ V

$2Fe^{3+} + H_2C_2O_4 \rightarrow 2Fe^{2+} + 2CO_2 + 2H^+$ $E^o_{cell} = +1.26$V (Feasible)

The $Fe^{3+}(aq)$ formed oxidises $H_2C_2O_4$ to form CO_2 while itself is reduced to $Fe^{2+}(aq)$, giving rise to a pale green solution.

6 (a)(i) Anode: $2Cl^- \rightarrow Cl_2 + 2e$
Cathode: $2H_2O + 2e \rightarrow 2OH^- + H_2$

6(a)(ii) $Cl_2 + 2\ NaOH \rightarrow NaClO + NaCl + H_2O$ (cold or rm temp) OR
$3Cl_2 + 6\ NaOH \rightarrow NaClO_3 + 5NaCl + 3H_2O$ (high temp)
Ionic equations accepted

(iii) To ensure there is no back flow of solution from cathode department to anode so that hydroxide ions formed at cathode do not flow to anode and be oxidised instead of chloride ions.
or no mixing of Cl_2 and hydroxides ions can occur.

(iv) Q= It = (240)(50×60) = 720 000 C

Amt of electrons = $\frac{720000}{96500}$ = 7.461 mol

Amt of Cl_2 = $\frac{7.461}{2}$ = 3.7305 mol

Volume of Cl_2 = 3.7305 × 22.4 = 83.6 dm^3

6(b) $2Cl^- \rightleftharpoons Cl_2 + 2e^-$ E_{ox}^{θ} = –1.36V
$2H_2O \rightleftharpoons O_2 + 4H^+ + 2e^-$ E_{ox}^{θ} = –1.23V

Initially, oxygen is liberated as $E_{ox}^{\theta}(H_2O)$ is **more positive** than E_{ox}^{θ} (Cl^-). Hence H_2O is preferentially discharged.

As time proceeds, water is used up, concentration of Cl^- increases, $E_{ox}^{\theta}(Cl^-)$ becomes more positive than $E_{ox}(H_2O)$. Hence Cl^- is discharged and Cl_2 gas is evolved.

6(c) (i) $SiCl_4 + 4H_2O \rightarrow SiO_2.2H_2O + 4HCl$ or $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$
pH = 2

6(c) (ii) N in NF_3, unlike B in BF_3, has no empty p-orbitals to accept a lone pair of electrons from water, hence unable to undergo hydrolysis.
OR
B in BF_3 has only 6 electrons, hence can accept a lone pair of electrons from water, and undergo hydrolysis. N in NF_3 has a full octet/8 electrons, hence cannot accept a lone pair of electrons from water to undergo hydrolysis.

6(d) conc. H_2SO_4 acts as an acid to donate a proton to NaCl and NaBr to give **HCl and HBr , white fumes.**
$NaCl\ (s) + H_2SO_4(l) \rightarrow NaHSO_4\ (aq) + HCl\ (g)$
$NaBr\ (s) + H_2SO_4(l) \rightarrow NaHSO_4\ (aq) + HBr\ (g)$
$2HBr\ (g) + H_2SO_4\ (aq) \rightarrow Br_2\ (g) + SO_2\ (g) + 2H_2O\ (l)$

Conc. H_2SO_4 is only strong enough an oxidising agent to oxidise HBr to **orange-brown fumes of Br_2**, but not HCl to Cl_2. Or
HBr is a stronger reducing agent than HCl. Hence HBr can reduce conc. H_2SO_4 to SO_2, but HCl cannot.