ACJC H2 Prelim 2012 Paper 2 Answers

1 Planning (P)

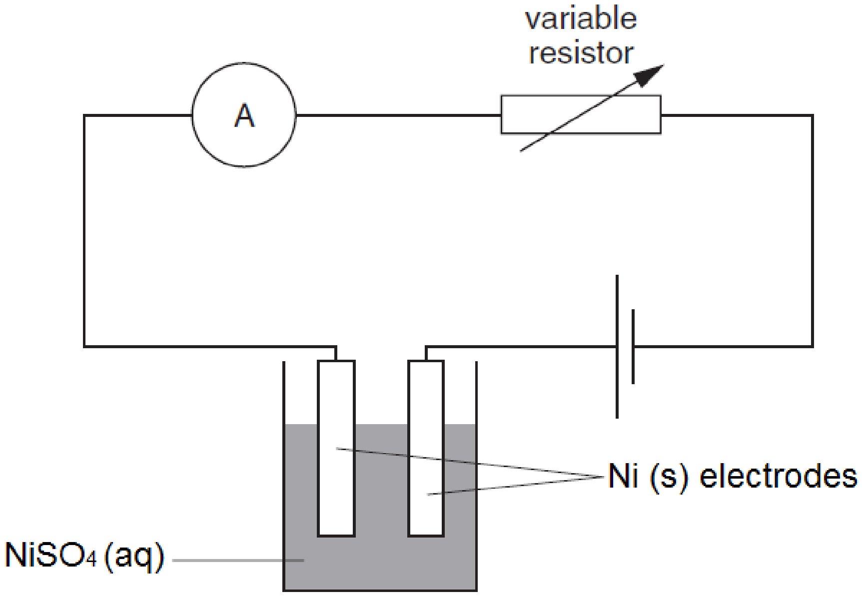
A student is interested to determine the Faraday constant. He proposed that the value of the Faraday constant can be determined experimentally using the electrolysis of aqueous nickel (II) sulfate.

The student did some research and made the following notes.

General information

- Reaction at the cathode: Ni^{2+} (aq) + 2e → Ni (s)
- Reaction at the anode: Ni (s) → Ni^{2+} (aq) + 2e
- 1 mol of Ni (s) is deposited at the cathode by 2 mol of electrons.
- The Faraday constant is the charge in coulombs, C, carries by 1 mol of electrons.
- The Faraday constant = 96500 C mol^{-1}

Experimental setup



The experimental setup for the electrolysis of nickel (II) sulfate solution is shown above. The student will electrolyse some nickel (II) sulfate solution using nickel electrodes. Before the nickel cathode is placed into the electrolyte, it will be cleaned and weighed.

The current that passes through the electrolyte will be kept constant at 0.3 A for 40 min by adjusting a variable resistor in the experiment. At the end of 40 min, the nickel cathode will be weighed.

The experiment will be repeated for another 7 times at 40 min intervals.

(a) Based on the information given under experimental setup, give a full description of the procedures you would use in **Step A (Start of experiment)** in the space provided. **Step B (Rinsing and reweighing of cathode)** is provided.

[2]

Experimental method

Step A (Start of experiment)

1. **The cathode is cleaned and weighed before being placed in the nickel (II) sulfate solution.**
2. **The circuit is switched on and the current is maintained at 0.3 A by adjusting the variable resistor.**
3. **The current is maintained at 0.3 A for exactly 40 mins and the circuit is switched off.**

Step B (Rinsing and reweighing of cathode)

1. The cathode is removed from the solution and carefully washed with distilled water to remove any nickel (II) sulfate solution.
2. Distilled water is removed from the cathode by rinsing it with propanone in which the water dissolves.
3. The cathode is finally dried by allowing the propanone to evaporate from the surface.
4. The cathode is reweighed and placed back to the solution.
5. A constant current of 0.3 A is passed for a further 40 mins when the rinsing, drying and weighing are repeated.

This procedure (Step A and B) is repeated for a further 6 times.

(b) The student performed the experiment using the experimental setup and method above.

The results of his experiment are recorded below.

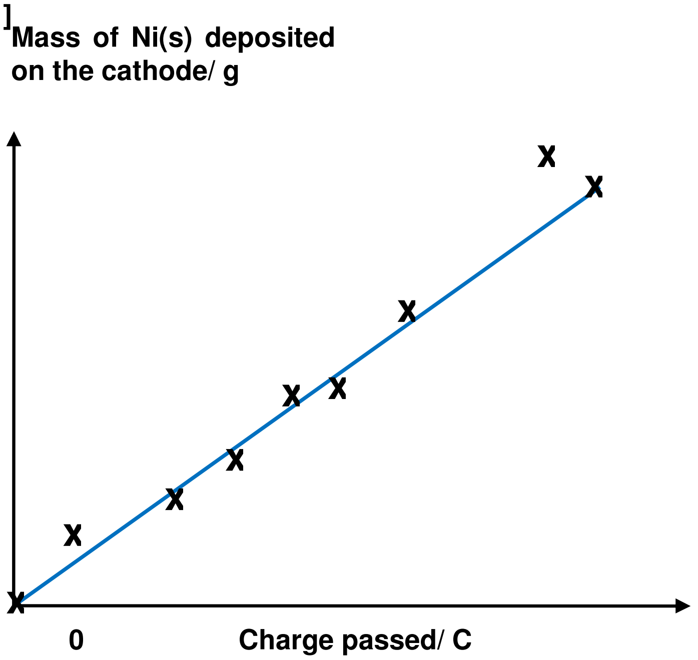
Time/ min	Mass of cathode/ g	Charge passed/ C	Mass of Ni (s) deposited on the cathode/ g
0	115.74	0	0
40	115.97	720	0.23
80	116.22	1440	0.48
120	116.46	2160	0.72
160	116.70	**2880**	**0.96**
200	116.94	3600	1.20
240	117.19	4320	1.45
280	118.01	5040	2.27
320	117.67	5760	1.93

Calculate and record the charge passed and the mass of nickel deposited on the cathode at **160 min** in the space given above.

[1]

(c) The student plotted the data on the graph of mass of Ni (s) deposited on the cathode against charge passed.

Draw a best-fit line on the graph below. **[1]**



(d) With reference to part **(b)** and part **(c)**, state the anomalous point. Based on the procedures for the experiment, explain for the anomaly. **[2]**

(5040C, 2.27g)

There could be some residual liquid on the cathode when it is weighed.

(e) The weighing balance used by the student weighed to 2 decimal places. With reference to the results of the experiment, explain why it is not appropriate to use a weighing balance accurate to 2 decimal places. **[1]**

As the mass of Ni (s) deposited is very small, the % error of the calculated value is large.

(f) The student calculated the value of the gradient in part **(c)**.

Gradient of the line = 3.05×10^{-4} g C^{-1}

Using the information provided, calculate a numerical value of the Faraday constant. **[2]**

Ni^{2+} (aq) + 2e → Ni (s)

Mass of Ni (s) deposited = 3.05×10^{-4} (charge passed)
Mass of Ni (s) deposited by 1 mol of electron = 0.5 x 58.7 = 29.35g

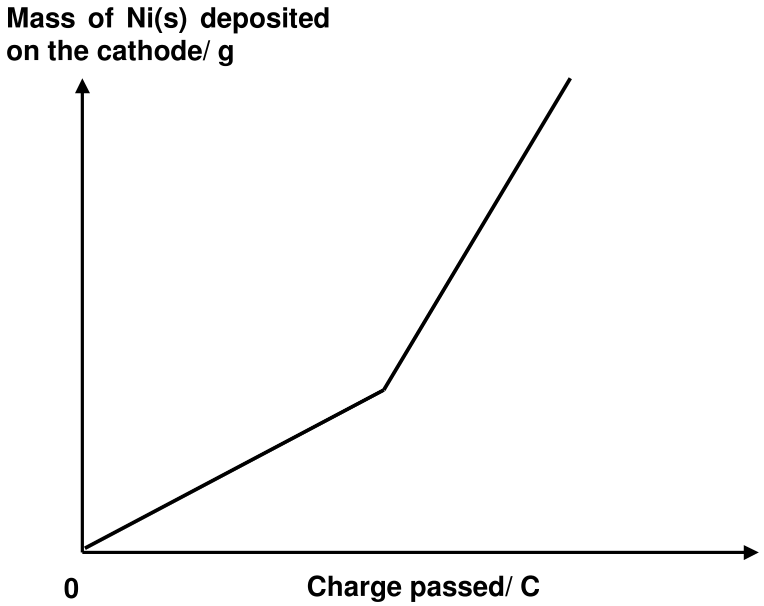
Charge passed to deposit 29.35 g of Ni (s) = 29.35/3.05 x 10^{-4} = 96230 C

Faraday constant = 96230 C mol^{-1}

(g) What other measurements could be made during the course of the experiment to provide alternative data to confirm the determined value of the Faraday constant? **[1]**

The loss in mass of the Ni anode can also be measured and recorded to confirm the determined value of the Faraday constant.

(h) The same experiment was performed by another student. The plotted mass of nickel deposited against charge passed was obtained below.



Suggest an explanation for the shape of this graph. Hence, comment on the accuracy of the value of the Faraday constant obtained by this student. **[2]**

The $NiSO_4$ solution is impure. It could be acidified $NiSO_4$ solution. Thus, the evolution of H_2 (g) could compete with the deposition of Ni (s) as H^+ and Ni^{2+} could be simultaneously discharged.

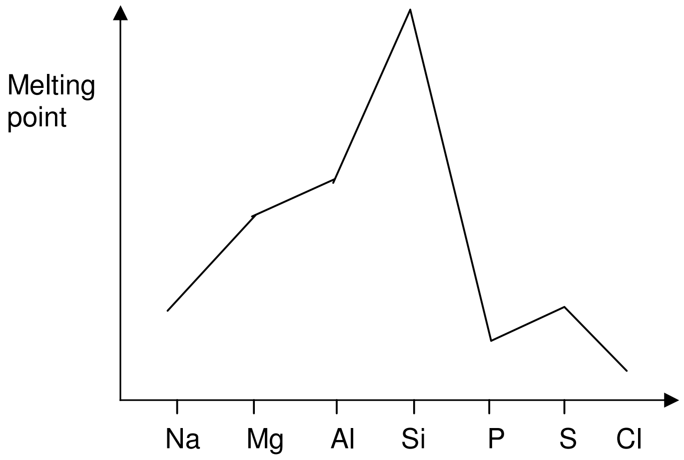
[Note: E° (H^+/H_2) = 0.00V and E° (Ni^{2+}/Ni) = -0.25V). Simultaneous reduction of H^+ and Ni^{2+} can occur although E° (H^+/H_2) is more positive than E° (Ni^{2+}/Ni)]. Given the amount of charges pass through the circuit, less Ni(s) is deposited initially. The gradient becomes steeper when all the H^+ are completed reduced and only Ni^{2+} is being discharged.

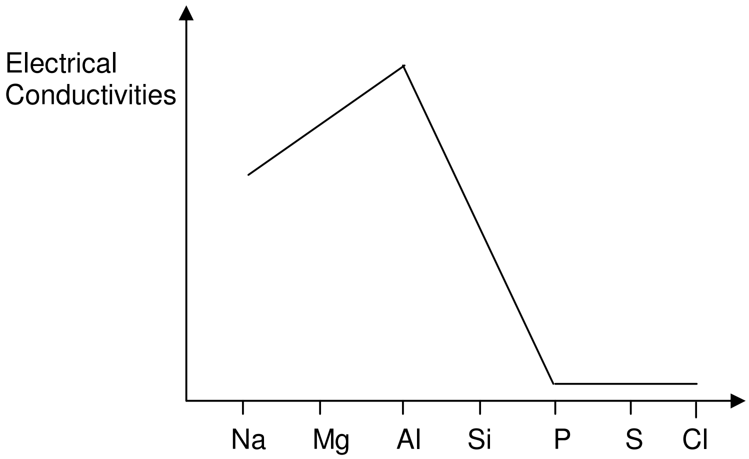
The F constant is accurate if the student use the steeper gradient in his calculation. OR The F constant is not accurate if the student use the gentle gradient in his calculation.

[Total: 12 marks]

2 Period 3 elements vary in their melting points and electrical conductivities.

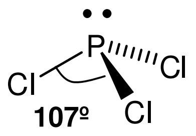
(a) **(i)** On the axes below, sketch these trends for the stated elements.



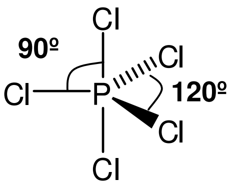


[4]

(ii) Phosphorus reacts with chlorine to form mixtures of PCl_3 and PCl_5 which are commonly used in organic reaction synthesis. Draw and name the shapes of PCl_3 and PCl_5, and state clearly the bond angles. **[4]**



Trigonal pyramidal



Trigonal bipyramidal

(b) The second ionisation energies of Period 3 elements from sodium to phosphorus are given in the table below.

Element	Second Ionisation Energy / kJ mol^{-1}
Sodium	4560
Magnesium	1450
Aluminium	1820
Silicon	1580
Phosphorus	1900

(i) Explain why the second ionisation energy of sodium is the highest.

The removal of the second electron from sodium is from inner quantum shell which experience greater nuclear attraction whereas the rest are removing from valence shell, thus it has the highest second ionization energy.

(ii) Explain why the second ionisation energy of silicon is lower than that of aluminium.

The removal of second electron from silicon is from 3p orbital which is further away from the nucleus compared to that from 3s orbital of aluminium.

(iii) Generally, second ionisation energy of an element is more endothermic than its first ionization energy. Explain why this is so. Include the equations for the first and second ionisation energy of an element in your answer. You may use element 'X' to write the equations.

$$X(g) \rightarrow X^{+}(g) + e$$
$$X^{+}(g) \rightarrow X^{2+}(g) + e$$

After the first electron is removed from a neutral element, a unipositively charged ion is formed. The second electron will be removed from this positively charge ion. Due to electrostatic attraction, it is more difficult to pull an electron away from a positively charge ion than a neutral atom hence second electron needs more energy to be removed.

[4]

[Total: 12 marks]

3 **(a)** Aluminium reacts with various non-metals to form simple compounds.

(i) Aluminium reacts with phosphorus to form aluminium phosphide, AlP which is used as a rodenticide.

Aluminium phosphide is hydrolysed by water to generate the highly toxic gas phosphine, PH_3. NH_3 is a polar molecule with a dipole moment of 1.47 D while PH_3 has a dipole moment of 0.58 D. Predict whether PH_3 is acidic, neutral or basic.

Neutral

Solutions of aluminium chloride and lithium hydride in ethoxyethane are mixed together and the resultant white precipitate filtered off. The filtrate is carefully evaporated to dryness and white crystals, compound **A**, are obtained. They contain:

Li,18.2%; *Al*,71.2%; H,10.6% by mass

(ii) Suggest the identity of compound **A** and write a balanced equation for the formation of compound **A**.

	Li	**A*l***	**H**
mass	**18.2**	**71.2**	**10.6**
n	**18.2/6.9** **=2.64**	**71.2/27** **=2.64**	**10.6/1** **=10.6**
Simplest ratio	**1**	**1**	**4**

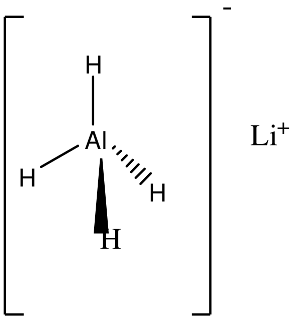
Compound A is $LiAlH_4$

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$$

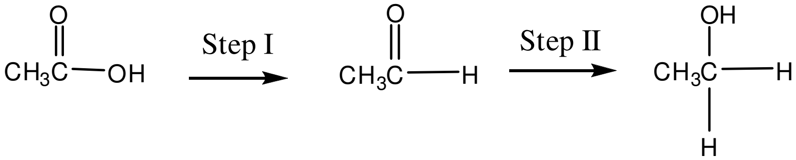
(iii) Compound **A** reacts violently with water, producing hydrogen gas and a white precipitate. Write a balanced equation for the reaction of **A** with water.

$$LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$$

(iv) Draw the structural formula of compound **A**, clearly illustrating its shape and bondings.



(v) Compound **A** is one of the most useful reducing agents in organic chemistry. It serves generally as a source of H^-, the hydride ion. Reduction of ethanoic acid to ethanol by compound **A** occurs in two steps as shown:

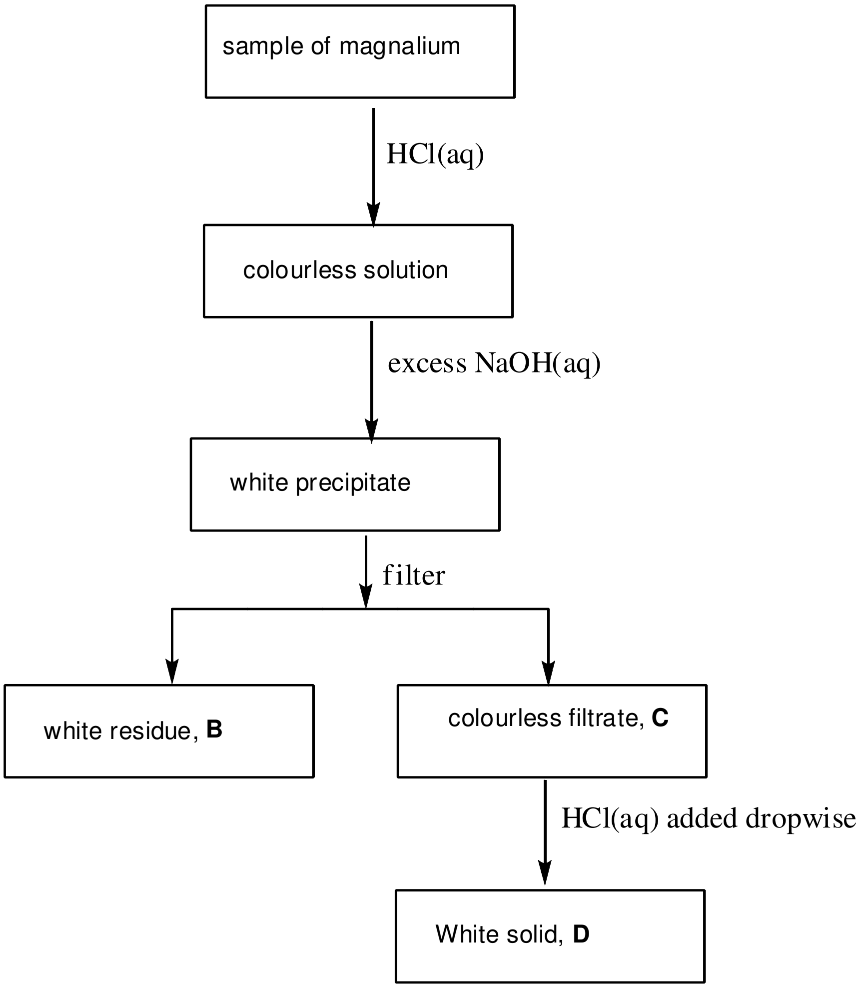


In step II, the aldehyde is rapidly reduced further to the primary alcohol and cannot be isolated. State the types of reaction mechanism that occur in Step I and Step II.

	Type of reaction mechanism
Step I	**Nucleophilic substitution**
Step II	**Nucleophilic addition**

[7]

(b) Magnalium is an alloy of aluminium and magnesium which is used in boat-building. The diagram below shows some reactions of magnalium.



(i) Identify **B**,**C** and **D**

B----$Mg(OH)_2$
C----$Al(OH)_4^-$
D----$Al(OH)_3$

(ii) When 1.75 g sample of magnalium is used in the above reactions, it is found that 0.18 g of compound **B** is obtained. Determine the percentage by mass of magnesium and aluminium in the magnalium sample.

No of moles of $Mg(OH)_2$ = 0.18/58.3 =0.00309

Mass of Mg = 0.00309 x 24.3 = 0.0751 g

% by mass of Mg = (0.0751/1.75) x 100 =4.29%

% by mass of Al= 100-4.29 =95.71% (or 95.7%)

[5]

(c) Across Period 3, the types of oxides vary from basic oxide to amphoteric oxide to acidic oxide.
In Group IV, the most typical oxides of tin and lead are SnO, SnO_2, PbO and PbO_2.

The following two generalisations can be made about the oxides of the elements in group IV.

- As the metallic character of the elements increases down the Group, the oxides become more basic.
- The oxides of the elements in their higher oxidation states are more acidic than the oxides of the elements in their lower oxidation states.

Use these generalisations to suggest which of the above oxides of tin or lead is most likely to react with each of the following reagents.

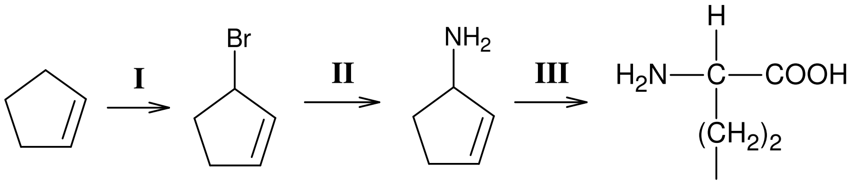
(i)	With NaOH(aq)	Formula of oxide: **SnO_2**
(ii)	With HCl(aq)	Formula of oxide: **PbO**

[2]

[Total: 14 marks]

4 **(a)** Fibrinogen is produced by the liver and it is used for blood coagulation. This protein is converted by thrombin into fibrin, which is cross-linked for a blood clot to be formed. One of the amino acids in fibrinogen is glutamic acid.

Glutamic acid can be synthesized from cyclopentene (Mr of 68) by the following route.



cyclopentene **K** **L** **glutamic acid**

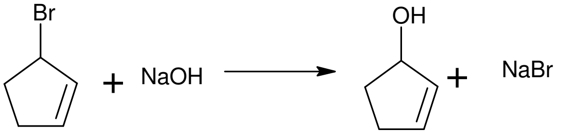
(i) Suggest the reagents and conditions for steps I, II and III. **[3]**

Step I: Br_2, UV light
Step II: NH_3 (alc), heat in sealed tube
Step III: $KMnO_4/H^+$ heat under reflux.

(iii) Suggest a simple chemical test by which compounds **K** and **L** could be distinguished from each other. Write any appropriate equation. **[3]**

R/C: Heat with NaOH (aq), cool, then add dil HNO_3. Followed by $AgNO_3$.

Sample that produces a cream ppt is K, sample that does not is L.

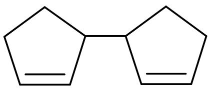


$Ag^+ + Br^- \longrightarrow AgBr$

(iii) State the name of the reaction in step I. **[2]**

The reaction in step I also produces small quantities of compound **M** which has a Mr of 134. Draw the structure of **M**.

Free radical substitution



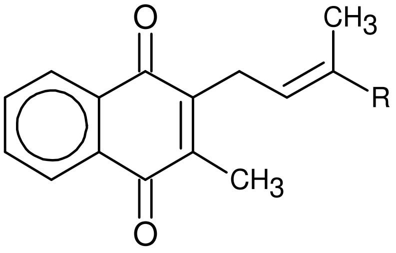
(iv) State two reasons to explain why the yield of step **I** may be small. **[2]**

Electrophilic addition across the alkene functional group serves as a competing reaction.

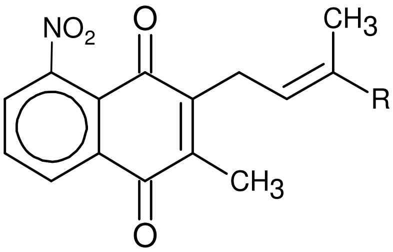
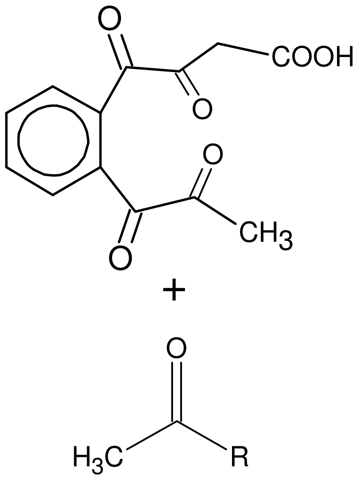
There is more than one H atom on the cyclopentene that can be substituted/ the number of byproducts produced.

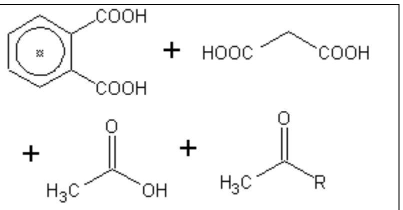
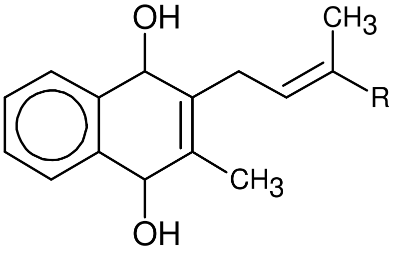
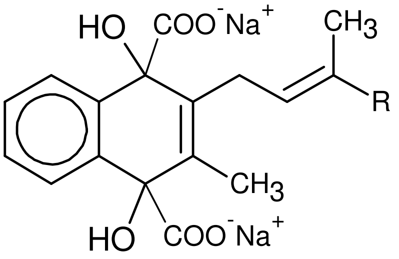
(b) Vitamin K is a fat-soluble vitamin that is essential to allow blood clotting to occur. There are three basic forms of vitamin K and they are, K1, K2 and K3. All the three basic forms contain two rings fused together. **[5]**

The following is the structure of Vitamin K1.



R is an alkyl group and it contains 16 carbons. You can assume that R remains inert for the reactions below.
Draw the structures of organic compounds formed when vitamin K1 reacts with each of the following reagents:

(i) conc. H_2SO_4, conc. HNO_3, heat	(ii) $KMnO_4/H^+$ heat
	 **OR**

	
(iii) $LiAlH_4$, in dry ether. 	(iv) HCN with traces of NaCN. Followed by heating with aqueous sodium hydroxide. 

[Total: 15 marks]

5 **(a)** Hydrogen is made from methane via a process known as steam reforming.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g) \quad \Delta H = +206\text{ kJ mol}^{-1}$$

The value of the equilibrium constant, K_p, for this reaction is 1.80×10^{-7} at 600 K.

(i) Gaseous CH_4, H_2O and CO are introduced into an evacuated container at 600 K and their initial partial pressures (before reaction) are 1.40 atm, 2.30 atm and 1.60 atm respectively.

Determine the partial pressure of $H_2(g)$ when equilibrium is reached. (You may assume that the extent of the forward reaction is small.) **[3]**

	$CH_4(g)$	**$+ H_2O(g) \rightleftharpoons$**	**$CO(g)$**	**$+ 3H_2(g)$**
Initial /atm	**1.40**	**2.30**	**1.60**	**0**
Change/atm	**-x**	**-x**	**+x**	**+3x**
Eqm	**1.40 - x**	**2.30 – x**	**1.60 + x**	**3x**

$$K_p = \frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})}$$

$$1.80 \times 10^{-7} = \frac{(1.60 + x)(3x)^3}{(1.40 - x)(2.30 - x)}$$

Assuming x is small,

$$\mathbf{1.80 \times 10^{-7}} = \frac{(1.60)(3x)^3}{(1.40)(2.30)}$$

Solving for x,

$x = 2.38 \times 10^{-3}$

Partial pressure of H_2 at equilibrium = $3 \times 2.38 \times 10^{-3}$
= $\underline{7.14 \times 10^{-3}\text{ atm}}$

(ii) Should the temperature of the reaction be raised or lowered to increase the yield of H_2? Explain your answer.

[2]

The temperature should be <u>raised</u> to increase the yield of H_2.

When the temperature is raised, the <u>endothermic reaction is favoured</u> since it absorbs energy. The <u>position of equilibrium shifts to the right</u> in favour of the forward reaction, increasing the yield of H_2.

(b) Additional hydrogen can be recovered using the carbon monoxide produced in another reaction known as the water-gas shift reaction.

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

Given that the above reaction was conducted at 400 °C and 1 atm, calculate the volume of H_2 that can be recovered from 10 kg of CO.
(You may assume that H_2 behaves as an ideal gas)

[3]

Amount of H_2 that can be recovered = 10000/28 = 357 mol

$pV = nRT$

$$V = \frac{nRT}{p}$$

$$V = \frac{357 \times 8.31 \times (400 + 273)}{1.01 \times 10^{-5}}$$

$$= \underline{\mathbf{19.8\ m^3}}$$

[Total: 8 marks]

6 Calcium (Ca^{2+}) ions play an important role in the clotting of blood as well as other cellular processes. As such, an abnormal Ca^{2+} concentration is of concern.

To determine the Ca^{2+} concentration, 1.00 cm^3 of human blood is treated with aqueous $Na_2C_2O_4$ solution. The resulting CaC_2O_4 precipitate is filtered and then treated with H_2SO_4 to release the $C_2O_4^{2-}$ ions into solution. This solution is then titrated with acidified $KMnO_4$.

2.05 cm^3 of 4.88 x 10^{-4} mol dm^{-3} $KMnO_4$ was required to reach the end-point for a particular blood sample.

(a) Given that $C_2O_4^{2-}$ is oxidised to CO_2, write a balanced ionic equation for the reaction between MnO_4^- and $C_2O_4^{2-}$. **[1]**

$$\mathbf{2\ MnO_4^- + 5\ C_2O_4^{2-} + 16\ H^+ \longrightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O}$$

(b) Calculate the amount of Ca^{2+} present in the blood sample. **[2]**

Amount of $KMnO_4$ reacted

= 2.05/1000 x 4.88 x 10^{-4}

= 1.00 x 10^{-6} mol

Amount of Ca^{2+} present in the blood sample

= 1.00 x 10^{-6} x 5/2

= 2.50 x 10^{-6} mol

(c) Given that the normal concentration of Ca^{2+} is 90 – 110 mg / L blood, show whether the concentration of Ca^{2+} in the sample is acceptable. **[2]**

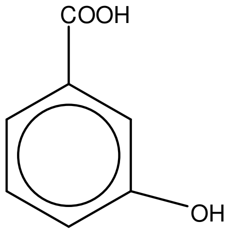
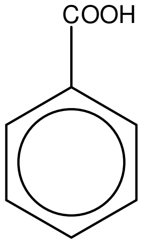
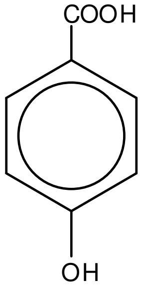
Amount of Ca^{2+} present in 1 L of blood sample
= 2.50 x10^{-6} x 1000
= 2.50 x 10^{-3} mol

Mass of Ca^{2+} present in 1 L of blood sample
= 2.50 x10^{-3} x 40.1
= 0.10035g
= 100 mg

The concentration of Ca^{2+} in the sample falls within the acceptable range.

[Total: 5 marks]

7 The acid dissociation constants, K_a, of three acids are shown as follows:

compound		K_a/ mol dm^{-3}
3-hydroxybenzoic acid		8.7 x 10^{-5}
Benzoic acid		6.3 x 10^{-5}
4-hydroxybenzoic acid		3.3 x 10^{-5}

(a) **(i)** Explain the trend of decreasing K_a values of the three acids.

In 3-hydroxybenzoic acid, the negative charge of the carboxylate anion is stabilized by the electron-withdrawing inductive effect of OH group, making it more acidic.

For 4-hydroxybenzoic acid, the negative charge on the anion is destabilized by the electron-donating resonance effect of the OH that acts over the π electron system of the ring. Hence it is less acidic than benzoic acid

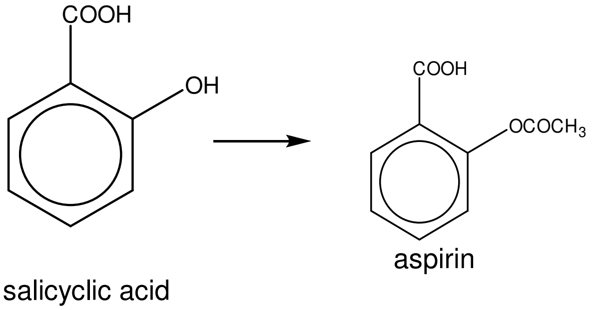
(ii) Calculate the pH of 0.0180 mol dm^{-3} solution of benzoic acid?

[[H$^+$] =√(6.3 x 10^{-5})(0.0180) = 1.06 x 10^{-3} mol dm^{-3}

pH= -lg{H$^+$] = -lg(1.06 x 10^{-3}) = 2.97

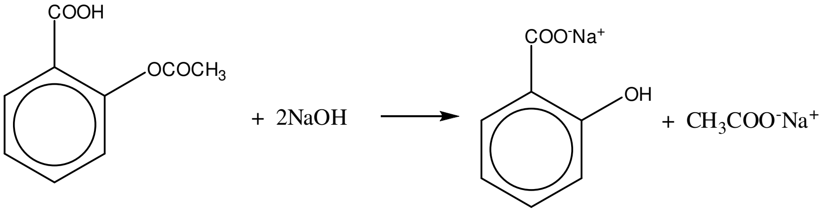
[3]

(b) **(i)** State the reagent and condition required to convert salicyclic acid to Aspirin.



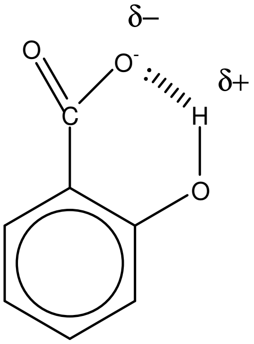
NaOH(aq), CH_3COCl, room temperature

(ii) The purity of the Aspirin obtained is often estimated by hydrolysis with an excess of aqueous sodium hydroxide. The equation for the hydrolysis is



The amount of excess sodium hydroxide is found by titration with hydrochloric acid.

Although phenol reacts with sodium hydroxide, the hydrolysis equation indicates that the hydroxyl group in salicyclic acid does not. With the aid of a diagram, suggest a reason for this behavior.



Intramolecular hydrogen bond stabilizes the anion.

(iii) When 0.10 mol of aspirin was treated with 0.30 mol of aqueous sodium hydroxide, the excess sodium hydroxide reacts with 0.15 mol of hydrochloric acid. Calculate the percentage purity of the aspirin prepared.

No. of moles of excess NaOH =0.15

No. of moles of NaOH reacted with aspirin = 0.30-0.15 = 0.15

No of moles of aspirin = 0.15/2 = 0.0750

%purity = (0.075/0.10) x 100 = 75.0%

[3]

[Total: 6 marks]