SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9746/03

Preliminary Examination
Paper 3 Free Response
MARK SCHEME

20th August 2009
2 hours

CONFIDENTIAL DOCUMENT

Teachers to keep this document under lock and key until 20 August 2009 12pm.

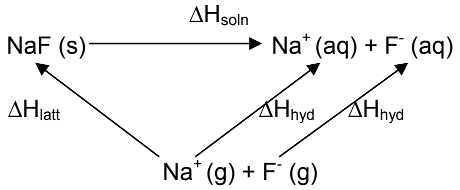
This document consists of **19** printed pages and **1** blank page

1 **(a)** A student dissolved 8.4 g of sodium fluoride in 250 g of water. Given the following data, calculate the initial temperature of water if the final temperature of the solution is 20.0 °C.

Assume that the specific heat capacity of sodium fluoride solution is 4.2 J g^{-1} K^{-1}.

Lattice energy of NaF	–918 kJ mol^{-1}
Enthalpy change of hydration of F^-	–457 kJ mol^{-1}
Enthalpy change of hydration of Na^+	–390 kJ mol^{-1}

[3]



$\Delta H_{soln\ (NaF)}$ = $-\Delta H_{latt\ (NaF)} + \Delta H_{hyd\ (Na^+)} + \Delta H_{hyd\ (F^-)}$

½ m = -(-918) + (-457) + (-390) ***{give method marks, if answer is wrong}***

½ m = **+71.0 kJ mol^{-1}** (since ΔH_{soln} > 0, temp of surroundings decreases)

½m **Amt of NaF** dissolved = 8.4 / (23+19) = **0.2000 mol**

Q = ΔH_{soln} x Amt of NaF

= 71 x 0.2000

½m = **14.2 kJ** ***{give method marks, if answer is wrong}***

Q = mcΔT

½m 14.2 x 1000 = 250 x 4.2 x (T_i - 20) Note: since $temp_{surr}$ decreases, $T_i > T_f$

{give method marks, if answer is wrong}

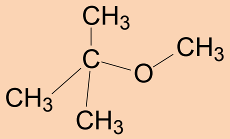
14200 = 1050 (T_i – 20)

14200 = 1050T_i - 21000

½m 1050T_i = 35200

T_i = 33.5°C

(b) In the manufacture of fuel for industries, liquid MTBE is added as a solvent to petroleum to reduce pollution.



Methyl t-butyl ether (MTBE)

(i) What is meant by the term *standard enthalpy change of formation* of MTBE? Support your answer with the aid of an appropriate equation with state symbols.

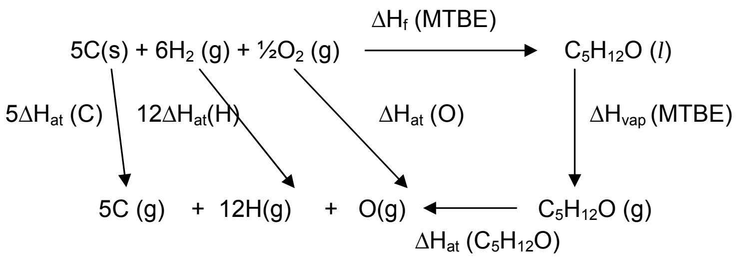
1m Standard enthalpy change of formation of MTBE is the **energy evolve/change** when **1 mole** of MTBE is formed from its **elements** under standard conditions.

1m **$5C(s) + 6H_2\ (g) + \frac{1}{2}O_2\ (g) \rightarrow C_5H_{12}O\ (l)$** ***{½ for state symbol, ½ for equations}***

MTBE

(ii) Use the following data and by means of an appropriate energy cycle, prove that the bond energy for the C–H bond in MTBE is +418 kJ mol^{-1}.

Enthalpy change of atomisation of C(s)	+715 kJ mol^{-1}
Enthalpy change of formation of MTBE	–383 kJ mol^{-1}
Enthalpy change of vapourisation of MTBE	+30.4 kJ mol^{-1}
Bond Energy of H-H	+436 kJ mol^{-1}
Bond Energy of O=O	+496 kJ mol^{-1}
Bond Energy of C-O	+360 kJ mol^{-1}
Bond Energy of C-C	+350 kJ mol^{-1}



2m **correct energy cycle** ***{one mistake minus ½m}***

By Hess' Law,

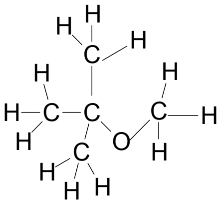
ΔH_f (MTBE) = $5\Delta H_{at}$ (C) + $12\Delta H_{at}$ (H) + ΔH_{at} (O) – ΔH_{at} ($C_5H_{12}O$)- ΔH_{vap} (MTBE)

-383 = 5(715) + 12 [½ BE(H-H)] + ½BE(O=O) - ΔH_{at} ($C_5H_{12}O$) – 30.4

-383 = 3575 + 12(½ x 436) + ½ (496) -30.4 - ΔH_{at} ($C_5H_{12}O$)

-383 = 3575 + 2616 + 248 – 30.4 - ΔH_{at} ($C_5H_{12}O$)

1m **ΔH_{at} ($C_5H_{12}O$) = + 6791.6 kJ mol^{-1}**



Displayed formula of MTBE

Bond energy of $C_5H_{12}O$ involves breaking a total of: 2(C-O), 3(C-C) and 12(C-H) bonds.

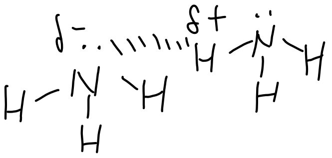
1m

6791.6 = 2BE(C-O) + 3BE(C-C) + 12BE(C-H)
6791.6 = (2 x 360) + (3 x 350) + 12BE(C-H)
6791.6 = 1770 + 12BE(C-H)
12 BE(C-H) = 5021.6
BE(C-H) = +418 kJ mol^{-1}

{Italics give full method marks}

		(iii) Suggest a reason for the difference in the C–H bond energy in **(b)(ii)** from the value given in the *Data Booklet*. **[7]**
	1m	The bond energy values from the Data Booklet are **average values** and would differ from experimental values.
	(c)	Magnesium chloride, $MgCl_2$, is an important coagulant used in the preparation of soy products. The lattice energy of magnesium chloride is given to be –2490 kJ mol^{-1}. **(i)** How would you expect the numerical magnitude of the lattice energy of barium chloride, $BaCl_2(s)$ to compare with that of $MgCl_2(s)$? Hence predict a likely value for the lattice energy of barium chloride.
	½m ½m 1m ½m	ΔH_{latt} is proportional to $\frac{q^+q^-}{r^+ + r^-}$, Ionic radius: **$Mg^{2+} < Ba^{2+}$** $\lvert\Delta H_{latt}\rvert$: **$MgCl_2 > BaCl_2$** or Numerical value of lattice energy of $BaCl_2$ will be **smaller**. or Lattice energy of **$BaCl_2$** will be less exothermic. Accept any **value smaller than 2490 kJ mol^{-1}**.
		The enthalpy change of reaction, for the reaction below is given to be -391 kJ mol^{-1}. $2MgCl\,(s) \rightarrow MgCl_2(s) + Mg\,(s)$ **(ii)** Comment on the stability of $MgCl\,(s)$ relative to that of $MgCl_2(s)$. **[4]**
	 ½m 1m	Since $\Delta H_{reaction}$ is exothermic, **Energy of products** is **lower** than that of reactants. $MgCl_2(s)$ is energetically **more stable** than $MgCl\,(s)$. (accept proper energy profile diagram)
	(d)	Part of the research on Supramolecular Chemistry focuses on Host-Guest Chemistry, in which cationic transition metal complexes are involved in second-sphere coordination which is provided by ligands with an organised set of donors. For example, a transition metal rhodium complex that contains hydrogen bond donor groups (ammonia or water ligands) in its primary coordination sphere can be considered as a guest capable of binding to a hydrogen bond acceptor host via second sphere coordination. **(i)** State the bonding formed between rhodium and ammonia.
	1m	**dative / coordinate/covalent** bond
		(ii) Describe the chemical structure and bonding in solid rhodium.
	½m ½m	Rh has a **giant metallic** structure with **strong electrostatic forces of attraction** between **cations** and **sea of delocalised electrons**.

Deleted: ¶

		(iii) Show with aid of a diagram the intermolecular bonding in ammonia.
	½m ½m	**Partial charge** **Others** 
		(iv) Predict and account for the boiling point of ammonia relative to water.
	½m ½m ½m ½m	Both NH_3 and H_2O have **simple molecular structures** with **intermolecular hydrogen bonds**. *For the identification of hydrogen bonds, either mentioned here or in part (iv).* **Number / Extent** of hydrogen bonds: **$NH_3 < H_2O$** **Energy** required: **$NH_3 < H_2O$** **Boiling point**: **$NH_3 < H_2O$**
		(v) Predict and account for the solubility of ammonia in water. **[6]**
	½m ½m	NH_3 is **soluble** in water as **favourable hydrogen bonds between** NH_3 and water / **solute-solvent interaction** can be formed. *{Do not accept the $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ as the extent of dissociation is too small}*

[Total: 20]

2 **(a)** The table below gives some data on some oxides of elements in Period 3 of the Periodic Table.

oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_2
Boiling point / K	1548	3873	3253	2503	448	263

(i) Explain, in terms of chemical bonding and structure, why the boiling point of MgO is higher than P_4O_6.

MgO
- ½m has a **giant ionic lattice** structure
- ½m **large amount of energy** is needed to
- 1m **overcome the strong ionic bonds**
  OR electrostatic forces of attraction between **oppositely charged ions**.
- has a high boiling point

P_4O_6
- ½m has a **simple molecular** structure
- ½m **small amount of energy** is needed to
- 1m **overcome the weak intermolecular Van der Waals' forces of attraction**
- has a low boiling point

(ii) Write an equation for the reaction of Al_2O_3 with dilute hydrochloric acid.

1m $\mathbf{Al_2O_3 (s) + 6HCl (aq) \rightarrow 2AlCl_3(aq) + 3H_2O (l)}$ *{no need state symbol}*
{½ m species, ½ m for coefficient}

(iii) Write an equation for the reaction of SO_2 and Al_2O_3 separately with dilute sodium hydroxide.

1m $\mathbf{SO_2 (g) + 2NaOH (aq) \rightarrow Na_2SO_3 (aq) + H_2O (l)}$ *{no need state symbol}*
{½ m species, ½ m for coefficient}
$\mathbf{Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4] (aq)}$ *{no need state symbol}*
1m *{½ m species, ½ m for coefficient}*

(iv) Comment on the role of Al_2O_3 in reactions **(a)(ii)** and **(iii)** above. **[8]**

1m Al_2O_3 behaves as an **amphoteric** oxide or
Al_2O_3 is able to **react with both acid and base**

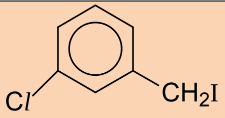
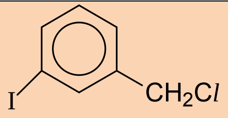
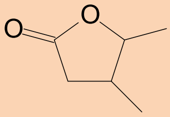
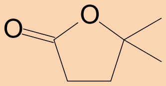
(b) **(i)** Write a balanced equation for the action of heat on magnesium nitrate.

1m $\mathbf{Mg(NO_3)_2(s) \rightarrow MgO(s) + 2NO_2 (g) + \frac{1}{2} O_2 (g)}$ *{no need state symbol}*
{½ m species, ½ m for coefficient}

(ii) Magnesium nitrate decomposes at a lower temperature than strontium nitrate. Explain why the two nitrates decompose at different temperatures. Predict if barium nitrate would decompose at a higher or lower temperature compared to strontium nitrate. **[4]**

Down the group,
- Ionic radius of cation: $Mg^{2+} < Sr^{2+}$.
- ½m **Charge density** of cation: $\mathbf{Mg^{2+} > Sr^{2+}}$ / **decreases**
- 1m **Polarising power** of cation: $\mathbf{Mg^{2+} > Sr^{2+}}$ / **decreases**
  or
  Polarising effect on NO_3^- anion: $\mathbf{Mg^{2+} > Sr^{2+}}$ / **decreases**
- ½m $Mg(NO_3)_2$ is **less stable** than $Sr(NO_3)_2$, hence it decomposes at a lower temperature

1m Thermal stability of Group II nitrates increases down the group; hence barium nitrate would decompose at a **higher** temperature compared to strontium nitrate.

	(c)	For each of the following pairs of structural isomers, describe **one** chemical test which would enable you to distinguish them. You should state the reagents and conditions for each test, and describe the observations.
		(i) $CH_2(NH_2)COCl$ and $CH_2ClCONH_2$
		Test:
	½m	Add **<u>water</u>** to each compound
	½m	at **<u>rtp</u>**
		Observation:
	½m	$CH_2(NH_2)COCl$ will form **<u>white fumes</u>** of HCl
	½m	$CH_2ClCONH_2$ will **<u>not form</u>** white fumes
		OR
	1m	Test: Add NaOH (aq) and heat, test any gas evolved with moist red litmus. (can use blue litmus as well)
	½m	Observation:
	½m	$CH_2(NH_2)COCl$: Gas will be evolved, **<u>moist red litmus remain unchanged</u>**.
		$CH_2ClCONH_2$:Gas evolved turns **<u>moist red litmus blue</u>**.
		(ii)  and 
		Test:
	½m	**<u>heat</u>** each compound
	½m	with **<u>NaOH(aq)</u>**.
	½m	Acidify with **<u>dil. HNO_3</u>** (to neutralise the excess NaOH to prevent ppt of AgOH from forming.)
	½m	before adding **<u>$AgNO_3$(aq)</u>**
		OR
	2m	**<u>heat</u>** each compound with **<u>ethanolic silver ethanoate</u>**
		Observation:
	½m	Chlorobenzene derivative will form a **<u>yellow ppt</u>** of AgI
	½m	Iodobenzene derivative will form a **<u>white ppt</u>** of AgCl
		(iii)  and  **[8]**
		Test:
	½m	**<u>heat</u>** each compound
	½m	with **<u>H_2SO_4(aq)</u>** **(NaOH or H^+)**
	½m	then add **<u>$KMnO_4$(aq) / $K_2Cr_2O_7$(aq)</u>** with H_2SO_4(aq)
	½m	**<u>heat</u>**
		.

Observation:

½m Left ester will **decolourise** $KMnO_4(aq)$ / turn $K_2Cr_2O_7(aq)$ from **orange to green**

½m Right ester will **remain purple** / **remain orange**

OR

Alternative Test:

1m **heat** each compound with **$H_2SO_4(aq)$** (accept HCl)

1m then add **alkaline aqueous iodine, warm**

Observation:

½m Left ester: **pale yellow ppt observed** or **brown iodine solution decolourised**

½m Right ester: **no pale yellow ppt observed orbrown solution remain unchanged**.

[Total: 20]

3 **(a)** **(i)** In Singapore, chlorine is added to the drinking water. Explain briefly the importance of the addition of chlorine to drinking water.

1m Chlorine is used in water purification to **kill bacteria** or **disinfect water** due to its strong and effective oxidising property.

(ii) Explain, with the aid of an equation why the addition of a base at room temperature will result in the elimination of chlorine smell from drinking water. State the type of reaction that chlorine undergo. **[3]**

1m $\mathbf{2OH^-\,(aq) + Cl_2\,(aq) \rightarrow Cl^-\,(aq) + ClO^-\,(aq) + H_2O\,(l)}$

OR

$\mathbf{2\,NaOH\,(aq) + Cl_2\,(aq) \rightarrow NaCl\,(aq) + NaClO\,(aq) + H_2O\,(l)}$

{no need state symbol}

{½ m species, ½ m for coefficient}

1m Presence of base will result in the **disproportionation** of chlorine, hence eliminating the smell. *(if state redox award ½ mark)*

(b) The oxyacids of chlorine are:

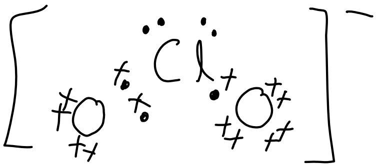
Chemical formula	$HOCl$	$HOClO$	$HOClO_2$	$HOClO_3$
Chemical Name	chloric (I) acid	chloric (III) acid	chloric (V) acid	chloric (VII) acid
K_a	$10^{-7.50}$	$10^{-1.96}$	10^{1}	10^{10}

(i) Describe and explain how an increase in oxygen content of the acids affects K_a.

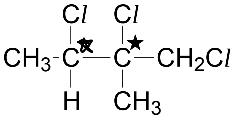
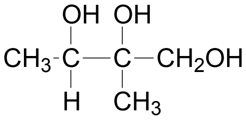
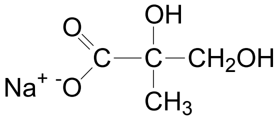
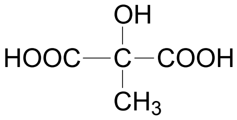
1m The **more oxygen atoms** that are bonded to the chlorine atom, **the greater the electron-withdrawing effect** (or the more the **electron will be pulled away)** from the O–H bond, thus **weakening the bond**.

Hence, **lesser** amount on **energy** is thus required to break the **O–H bond** and to dissociate H^+.

Therefore, $HOClO_3$ is the most acidic and have the largest K_a value.

		(ii) Draw the dot-and-cross diagram of ClO_2^-. Suggest the shape and state bond angle of the ion. **[4]**
	1m 1m 1m	 **bent** **104.5° or 104° or 105°** *(ecf for bond angle only)*
(c)		**(i)** A sample of sodium hypochlorite, NaOC*l*, was dissolved in 100 cm^3 of 0.123 mol dm^{-3} HOC*l* solution forming a buffer of pH 6.20. Determine the ratio of the concentration of OCl^- to HOC*l* in the solution. **[1]**
	½ m ½ m	$pH = pKa + \lg \frac{[OCl^-]}{[HOCl]}$ $6.20 = 7.50 + \lg \frac{[OCl^-]}{[HOCl]}$ $\lg \frac{[OCl^-]}{[HOCl]} = -1.30$ $\frac{[OCl^-]}{[HOCl]} = 0.0501$
		(ii) The buffer is then used to absorb HC*l* gas. By using the above ratio or otherwise, calculate the amount of gaseous HC*l* (in mol) that is required to be added to the buffer solution until it reaches pH 6. **[4]**
	1m ½ m	$\frac{[OCl^-]}{[HOCl]} = 0.0501$ $[OCl^-] = 0.0501[HOCl]$ $= 0.0501 \times 0.123$ $= 0.006162$ mol dm^{-3} On addition of HCl, let x be the concentration of H^+ $[HOCl]_{new} = 0.123 + x$ $[OCl^-]_{new} = 0.006162 - x$ $6.00 = 7.50 + \lg \frac{[OCl^-]}{[HOCl]}$ $6.00 = 7.50 + \lg \frac{0.006162 - x}{0.123 + x}$

		$-1.50 = \lg \frac{0.006162 - x}{0.123 + x}$
	½ m	$0.03162 = \frac{0.006162 - x}{0.123 + x}$
		$0.03162(0.123) + 0.03162x = 0.006162 - x$
		$1.03162x = 0.00227$
	1m	$x = 0.00220$ mol dm^{-3}
	1m	amount of HCl= $0.00220 \times \frac{100}{1000}$ = 0.000220 mol
	(d)	In the production of CH_3Cl using methane and chlorine under certain conditions, it has been noticed that a small quantity of chloroform, $CHCl_3$, has been produced. Using CH_3Cl as the starting material, name and describe the mechanism of this reaction that would result the production of chloroform.
	½ m	**Free Radical Substitution**
		Initiation
	½m	$Cl - Cl \xrightarrow{\text{Ultraviolet light}} 2\,Cl\bullet$ [Slow step]
		Propagation
	½m	$CH_3Cl + Cl\bullet \longrightarrow CH_2Cl\bullet + HCl$ $CH_2Cl\bullet + Cl_2 \longrightarrow CH_2Cl_2 + Cl\bullet$
		Chain reaction continues
	½m	$CH_2Cl_2 + Cl\bullet \rightarrow CHCl_2\bullet + HCl$ $CHCl_2\bullet + Cl_2 \rightarrow CHCl_3 + Cl\bullet$
		Termination
	½m	$Cl\bullet + Cl\bullet \longrightarrow Cl_2$ $CHCl_2\bullet + CHCl_2\bullet \longrightarrow CHCl_2CHCl_2$ $CHCl_2\bullet + Cl\bullet \longrightarrow CHCl_3$
	½ m	**For mentioning of initiation, propagation and termination.**

	(e)	**A**, $C_5H_9Cl_3$, is an optically active compound which reacts with hot aqueous sodium hydroxide to form **B**, $C_5H_{12}O_3$. **B** reacts with warm alkaline aqueous iodine to give a yellow precipitate **C** as well as **D**, $C_4H_7O_4Na$. When **D** undergoes vigorous oxidation in acidic medium, **E**, $C_4H_6O_5$, is produced. **E** gives a negative test with 2,4-dinitrophenylhydrazine. Suggest the structural formulae of **A – E**, indicating clearly on **A** the chiral carbon. **[5]**
	5 x 1m	 $CH_3CHClCCl(CH_3)CH_2Cl$ **A**  $CH_3CH(OH)C(OH)(CH_3)CH_2OH$ **B** **CHI_3** **C**  **D**  $HOOCC(OH)(CH_3)COOH$ **E**

[Total: 20]

4 The use of the *Data Booklet* is required for this question

(a) **(i)** Given the following half cells:

H_2O (*l*) / H_2 (g)
PbO_2 (s) / Pb^{2+}(aq)
MnO_4^- (aq) / MnO_2 (s)

Suggest the half cell which, when combined with the Cu^{2+}(aq) /Cu (s) half cell, will generate the highest E^θ_{cell}. State the anode and the cathode of the electrochemical cell, indicating the direction of electron flow in the external circuit.

Cu^{2+}(aq) /Cu (s) (+0.34 V)

H_2O (*l*) / H_2 (g) (-0.83 V)
PbO_2 (s) / Pb^{2+}(aq) (+1.47 V)
MnO_4^- (aq) / MnO_2 (s) (+1.67 V)
From $E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxd}$
Combination which will result in highest voltage is when
Cu^{2+}/Cu half cell undergo oxidation and when MnO_4^-/ MnO_2 undergo reduction

1 m For choosing MnO_4^-/MnO_2
½ m Anode: Cu^{2+}/Cu
Cathode: MnO_4^-/MnO_2
1m E^θ_{cell} = + 1.67 - 0.34 = +**1.33 V**
(ecf ½ m if chose wrong half cell)

½ m **Electron flow from** Cu^{2+}/Cu half cell to MnO_4/MnO_2 half cell

(ii) The set up from **a(i)** was then used as the battery in the electrolysis of a solution of copper (II) sulphate with inert platinum electrodes. An ammeter showed a reading of 0.45 A in the external circuit of a cell. 0.30 g of copper metal was deposited at the cathode after 30 minutes. Determine the actual current used in the electrolysis process. Hence, determine the percentage error (if any) of the ammeter reading.

At the cathode, $Cu^{2+} + 2e \rightarrow Cu$

½m Amount of copper deposited = $\frac{0.30}{63.5} = 4.724 \times 10^{-3}$ mol

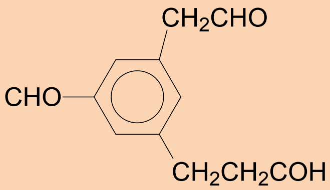
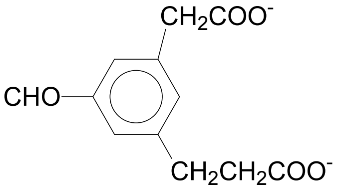
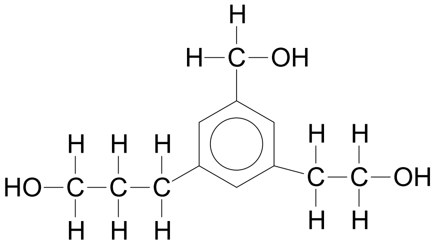
Amt of copper deposited = $\frac{Q}{2F}$

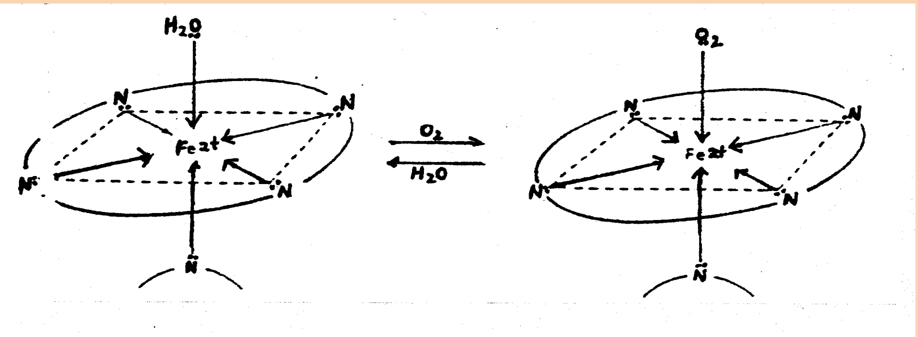
½m Q = $4.724 \times 10^{-3} \times 2 \times 96500 = 911.732$ C
(Allow ECF)

½m $I = \frac{Q}{t} = \frac{911.732}{30 \times 60} = 0.506\text{A}$
(Allow ECF)

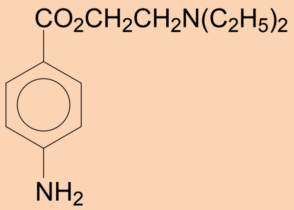
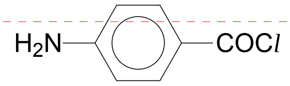
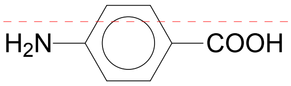
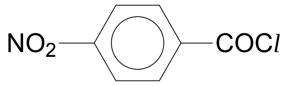
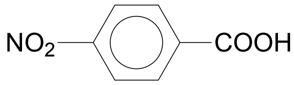
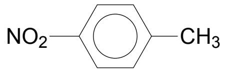
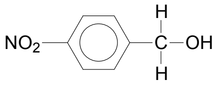
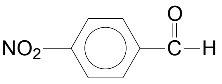
½m % error = $\frac{0.506 - 0.450}{0.506} \times 100\% = 11.1\%$

		(iii) A student carried out a reaction involving potassium dichromate (VI) with an unknown half cell which consists of transition metal ions. The Gibbs Free Energy of the reaction was known to be –324 kJ mol^{-1} and the procedure involved transfer of 6 mol of electrons from the unknown solution to potassium dichromate (VI). Using the expression of $\Delta G = -nFE^{\theta}_{cell}$, where n is the number of electrons transferred, F is the Faraday constant and E^{θ}_{cell} is the overall cell potential, determine the E^{θ}_{cell} value and hence deduce the identity of the unknown half cell. **[8]**
		Using $\Delta G = -nFE^{\theta}_{cell}$ $-324 \times 10^3 = -6\ (96500)\ E^{\theta}_{cell}$
	1m	**$E^{\theta}_{cell} = +0.5595$ V** Since procedure involved transfer of 6 mol of electrons from potassium dichromate (VI) to the unknown solution, Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$ (+1.33) $E_{red} = +1.33$ V Using $E^{\theta}_{cell} = E^{\theta}_{red} - E^{\theta}_{oxd}$ $0.5595 = +1.33 - E^{\theta}_{oxd}$
	1m	$E^{\theta}_{oxd} = -(0.5595 - 1.33) = +0.77$ V
	1m	The E^{θ}_{oxd} tally with the **Fe^{3+}/Fe^{2+} half cell**
	(b)	**(i)** Copper is a transition element and can exist in variable oxidation states. Suggest why transition elements have the tendency to have variable oxidation states.
	1m	Transition metals possess variable oxidation states **due to the small energy difference between the 3d and 4s electrons.** Thus different number of 3d and 4s electrons may be lost to form stable ions or compounds of different oxidation states.
		(ii) When dilute ammonia is gradually added to a solution containing copper (II) ions, a pale blue precipitate is formed, which re-dissolves on adding excess dilute ammonia. Explain the above observations, writing equations where appropriate.
	½m	$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$ $Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2\ (s)$ ----- (1)
		When $NH_3(aq)$ is added gradually, $[OH^-]$ will increase
	1m	▪ Ionic product of $Cu(OH)_2$ > K_{sp} of $Cu(OH)_2$
	½m	▪ **Pale blue ppt, $Cu(OH)_2$** is formed
	½m	$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ -----(2) deep blue
		When excess NH_3 is added,
	½m	▪ **NH_3 ligands** replaces the **H_2O** ligands, forming a **more stable deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$** complex with $Cu^{2+}(aq)$.
	½m	▪ **$[Cu^{2+}]$ decreases** as it is being used to form the complex, equilibrium position in **(1)** shifts **left to increase $[Cu^{2+}]$**
	½m	▪ **Pale blue ppt dissolves.**

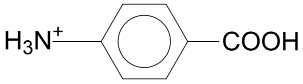
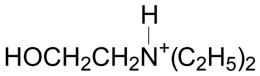
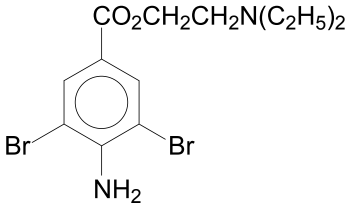
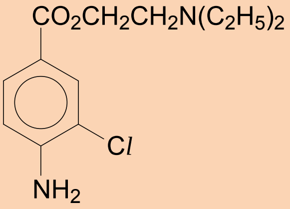
		(iii) Explain why copper (II) ions solution is coloured. **[7]**
	1m 1m	The **d orbitals of Cu^{2+} (aq) are split into two different energy level** due to presence of **H_2O ligands**. The **d electron** undergoes **d-d transition** and is **promoted to a higher energy d orbital.** During the process, red wavelength of light energy from the visible region of the electromagnetic spectrum is absorbed and **blue wavelength is transmitted** which appears as the **colour observed**.
(c)		**(i)** Fehling's solution, which is a solution of alkaline aqueous copper (II) complex, is commonly used to test for the presence of a functional group. Determine the organic product formed when compound **F** reacts with Fehling's solution.  Compound **F**
	½ m ½ m	
		(ii) Compound **F** was allowed to react with hydrogen in the presence of nickel catalyst. Explain why nickel is able to catalyse the reaction and draw the product formed in this reaction. **[3]**
	½m ½m 1m	**Nickel has partially filled 3d orbitals** which allow the reactants molecules to be **adsorbed** onto the catalyst surface. This adsorption **lowers the activation energy** and allowing reaction to occur. 

	(d)	Haem can be represented schematically as shown below. Briefly explain how the haemoglobin carry oxygen and why carbon monoxide are toxic to the human body.  **[2]**
	  ½m **½m** **½m** **½m**	▪ In haemoglobin molecule, Fe(II) ion is octahedrally bonded to five nitrogen atoms and a water molecule. ▪ H_2O ligand may be replaced by an **oxygen (O_2) ligand** in a **reversible** reaction allowing the haemoglobin to **carry oxygen from one part of body to another**. ▪ **Stronger ligands like CO (or CN^-)** bond **irreversibly** with haemoglobin and this **prevents the haemoglobin from carrying oxygen.**

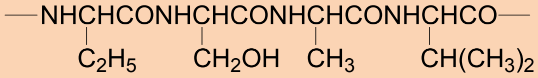
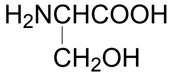
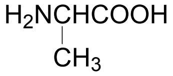
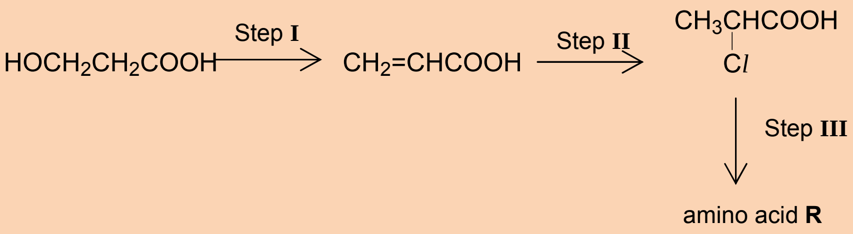
[Total: 20]

5	**(a)**	When an organic compound **G**, is heated with acidified potassium manganate (VII), the purple colour is decolourised and compound **H** is obtained. When phosphorus pentachloride is added to **H**, white fumes is observed and compound **J** is formed. **J** is heated with tin in concentrated hydrochloric acid, followed by aqueous sodium hydroxide to form compound **K**. **K** reacts with $(C_2H_5)_2NCH_2CH_2OH$ to form procaine which has the following structure:  Procaine Identify compounds **G**, **H**, **J** and **K** and explain the reactions involved. **[7]**
	½m	• **G** undergoes **oxidation** with acidified $KMnO_4$.
	½m	• **H** undergoes **nucleophilic substitution** with PCl_5. o **H** is an alcohol or carboxylic acid o **J** is a halogenoalkane or acyl chloride
	½m	• **J** undergoes **reduction** with tin in concentrated hydrochloric acid.
	½m	o **J** contains **nitrobenzene**
	½m	o **K** contains **phenylamine**
	½m	• **K** reacts with $(C_2H_5)_2NCH_2CH_2OH$ through **esterification/nucleophilic substitution/acylation**
	½m	o **J** must contain **acyl chloride**
	½m	o **H** is a **carboxylic acid**
	1m	**K** is  or 
	1m	**J** is 
	1m	**H** is 
	1m	**G** is  or  or  *(7 out of 8 marks)*

Deleted: ¶
¶

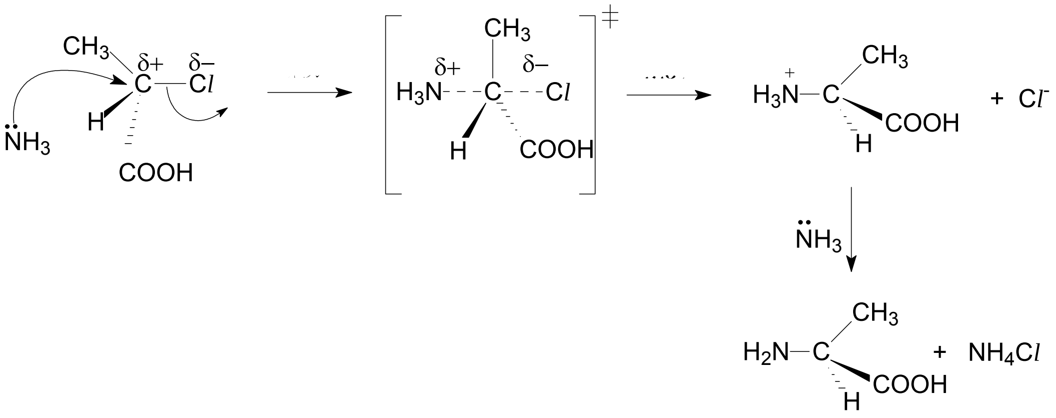
	(b)	Draw the structure of the compound(s) formed when procaine reacts with: **(i)** Hot, dilute hydrochloric acid
	1m	
	1m	 $HOCH_2CH_2\overset{H}{N}^+(C_2H_5)_2$
		(ii) aqueous bromine **[3]**
	1m	
	(c)	Compound **M** has the following structure:  State and explain whether procaine or compound **M** is more basic. **[2]**
	½m	▪ **Procaine is more basic**
	½m	▪ **Electron-withdrawing group** C*l* in **M**
	½m	**reduces the availability of the lone pair on N** atom
	½m	to accept a proton **via a dative bond**
		OR
	½m	▪ **Electron-withdrawing group** C*l* in **M**
	½m	**intensifies the positive charge** on the conjugate acid ion
	½m	hence **destabilising it**

Deleted: ¶
¶

	(d)	The diagram below shows the structure, at pH 7, of a fragment from a protein which contains 4 amino acids **P**, **Q**, **R** and **S** in the following sequence:  $-\mathrm{NH}\underset{\underset{\mathrm{C_2H_5}}{\vert}}{\mathrm{C}}\mathrm{HCONH}\underset{\underset{\mathrm{CH_2OH}}{\vert}}{\mathrm{C}}\mathrm{HCONH}\underset{\underset{\mathrm{CH_3}}{\vert}}{\mathrm{C}}\mathrm{HCONH}\underset{\underset{\mathrm{CH(CH_3)_2}}{\vert}}{\mathrm{C}}\mathrm{HCO}-$ **(i)** Draw the structures of the amino acids, **Q** and **R**, when this protein is hydrolysed.
	½m	**Q:**  $\mathrm{H_2N}\underset{\underset{\mathrm{CH_2OH}}{\vert}}{\mathrm{C}}\mathrm{HCOOH}$
	½m	**R:**  $\mathrm{H_2N}\underset{\underset{\mathrm{CH_3}}{\vert}}{\mathrm{C}}\mathrm{HCOOH}$
		(ii) State the interactions in amino acids **Q** and **R** that could be involved in the maintenance of the tertiary structure of proteins. **[2]**
	½m	**Q:** Hydrogen bond
	½m	**R:** Van der Waals forces of attraction
	(e)	Amino acid **R** can be obtained via the following route:  **(i)** Name the types of reactions and the reagent and conditions needed for Step **I**, **II** and **III.**
	½m	Step 1: **Elimination**
	½m	**excess concentrated sulphuric acid**, heat at **170°C** OR **Passing alcohol vapour over alumina catalyst at 350°C** OR **Phosphoric acid**, heat at **200°C**
	½m	Step 2: **Electrophilic Addition**
	½m	**HC*l***, r.tp
	½m	Step 3: **Nucleophilic substitution**
	½m	**Alcoholic/ concentrated NH_3, heat in a sealed tube/ heat under high pressure**

(ii) Outline the mechanism involved in Step **3**.

[6]



Arrows + lone pair of electrons - ½**m** each
Partial charge – ½**m**
Transition state – ½**m**
Amine salt – ½**m**
Final pdts – ½**m**

[Total: 20]

-END OF MARK SCHEME-

BLANK PAGE