Answer ALL questions on the spaces provided.

1 Planning (P)

A student was given 50 cm^3 of three acidic solutions labelled **X**, **Y** and **Z**. She was asked to provide the identities of them by conducting a simple experiment.

The identities of the three solutions are

1 mol dm^{-3} ethanoic acid, CH_3COOH
1 mol dm^{-3} hydrochloric acid, HCl
2 mol dm^{-3} hydrochloric acid, HCl

Her teacher advised her to measure the temperature change of the reactions and calculate the enthalpy change of neutralisation of an acid and base reaction. The student is also provided with 200 cm^3 of 1 mol dm^{-3} sodium hydroxide, $NaOH$.

The student let the volume ratio of each of the three solutions to sodium hydroxide be 1:1. She tested the experiment and realised that with this volume ratio, she is unable to differentiate the different concentrations of hydrochloric acid.

(a) Construct balanced equations for the reactions between the given acids and base.[1]

$HCl + NaOH \rightarrow NaCl + H_2O$ [½ m]
$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ [½ m]

(b) The following table shows the volumes used by the student.
Explain, with the aid of calculation, why the student's experiments will **not** aid the differentiation of the different concentrations of hydrochloric acid.

Experiment	**Volume of 1 mol dm^{-3} NaOH / cm^3**	**Volume of 1 mol dm^{-3} HCl / cm^3**	**Volume of 2 mol dm^{-3} HCl / cm^3**
1	50	50	
2	50		50

No. of moles of 1 mol dm^{-3} NaOH = $1 \times \frac{50}{1000}$ = 0.05 moles

No. of moles of 1 mol dm^{-3} HCl = $1 \times \frac{50}{1000}$ = 0.05 moles

No. of moles of 2 mol dm^{-3} HCl = $2 \times \frac{50}{1000}$ = 0.10 moles

NaOH is the limiting reagent [½ m]

No. of moles of water formed (for the acids) = 0.05 moles

Thus, the amount of water produced is the same throughout Thus, the heat evolved / temperature change measured will be the same for the different concentrations of HCl, unable to differentiate the different concentration of HCl.

Note: The enthalpy change of neutralisation of different [HCl] will be the same.

[2]

(c) Write a plan which will allow an identification of the three solutions to be made. You may use the reagents and apparatus normally found in a school or college laboratory. However, you are **not** provided with an indicator.

In your plan you should give essential details, including quantities, of the identification procedure.

To insert lines…………………………………………………………………………[6]

Procedure

1.By using a $50cm^3/100cm^3$ measuring cylinder, place $50cm^3$ of NaOH, into the dry polystyrene cup provided supported with a glass beaker.

2. Measure and note the initial temperature of NaOH solution using a 1.0 °C interval thermometer.

3.By using a second $50cm^3/100cm^3$ measuring cylinder (otherwise must mention washing & drying of the previous m.cyliner), measure 25 cm^3 of acidic solution X.

4.Note the initial temperature of solution X.
(both initial temp taken to find the average initial temp)
5.Add solution X to the cup in step 1.

6.Stir gently with a thermometer and note the highest temperature reached

7. Repeat the experiment (steps 1 to 6) with solutions Y and Z, using different measuring cylinders or mentioned in procedure measuring cylinder must be dry.

Record all your readings (temperature) in an appropriate table. or a sample table is drawn.

(d) Explain how you can make use of your experimental data to identify the three solutions.

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…………………………………………………………………………………………[2]

Feasibility of the identification depends on volume used in the experiment.

Must use results obtained (either ΔH_{neu} calculated or ΔT) .

When **V_{NaOH} should be greater than $V_{HCl:}$**

-using enthalpy change of neutralisation calculated:
Due to partial dissociation of CH_3COOH, some heat is absorbed to dissociate the weak acid. Thus, the ΔH_{neu} is less exothermic/smaller Δ T than HCl of same concentration.

In this experiment, more no. of moles of water produced with 2.0 mol dm^{-3} HCl used is than when 1.0 mol dm^{-3} HCl used. Thus, the one with a larger/twice the Δ T is the one using solution 2.0 mol dm^{-3} HCl.
(Although different concentration of HCl used in the experiment, they will have same ΔH_{neu} calculated.)

(e) Discuss one possible source of error in conducting your experiment and suggest improvement to produce a more reliable result.

....

....

....[1]

- Heat loss to the surrounding is not taken into account, the enthalpy change of neutralisation is less exothermic than expected. Use a lid to cover the cup to reduce heat loss.
- (dependent on thermometer used) There is a percentage error in the enthalpy change calculated as the 1°C interval thermometer is used. Use a thermometer with higher precision (0.2°C interval) to reduce the percentage error.
- Slow response of thermometer. Use a data logger with temperature sensor instead.

[Total: 12]

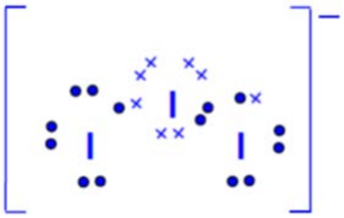
2 **(a)** Iodine is not very soluble in water but in the presence of iodide ions, it can dissolve to form a tri-iodide complex as follows:

$$I_2 + I^- \rightarrow I_3^-$$

(i) Draw a dot and cross diagram for the tri-iodide ion and hence state its shape and bond angle.

Bond angle of 180°.

Thus the complex is **linear** in shape.



(ii) Explain why fluorine does not form the corresponding F_3^- ion.

Fluorine, being in Period 2, is not able to expand it outermost shell to accommodate 10 electrons.

[3]

(b) IF_7 is a colourless gas prepared by the direct combination of iodine and fluorine. The I–F bond energy can be obtained from thermochemical data.
Standard enthalpy change of formation of $IF_7(g) = -944\ \text{kJ mol}^{-1}$
Standard enthalpy change of atomisation of iodine = $+107\ \text{kJ mol}^{-1}$

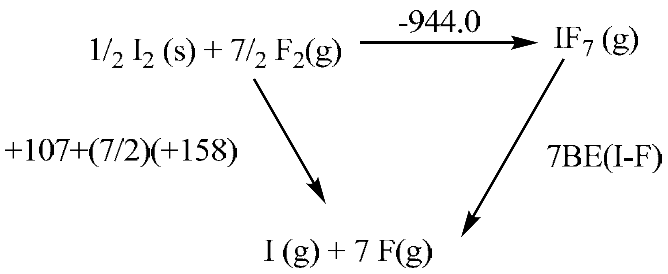
(i) Define what is meant by the *standard enthalpy change of formation* of IF_7.

It is the enthalpy change when 1 mole of IF_7 is formed from its constituent elements, iodine and fluorine in their standard states under standard conditions of 1 atm and 298 K.

(ii) Draw an energy cycle diagram to determine the I-F bond energy. Incorporate values from the data above and any other relevant data from the *Data Booklet* into the diagram.

$$7BE(\text{I-F}) -944.0 = +107+ \frac{7}{2}(+158)$$

$BE(\text{I-F}) = +229\ \text{kJ mol}^{-1}$



(iii) Explain why the I–F bond energy is not the mean of the I–I and F–F bond values.

Fluorine is more electronegative than iodine. The covalent bond between the atoms is polarised, giving rise to a stronger bond.

[6]

(c) The typical daily food requirement of a person can be considered to be 1.2 kg of carbohydrate. The person obtains energy by oxidation of the carbohydrate, which can be represented by the formula $(CH_2O)_n$.

(i) Construct an equation for the complete oxidation(combustion) of the carbohydrate $(CH_2O)_n$.

$(CH_2O)_n + nO_2 \rightarrow nCO_2 + nH_2O$

(ii) The empirical relative formula mass of the carbohydrate is 30. Use your equation in **c(i)** to calculate the number of moles of oxygen required by the person each day.

Moles of carbohydrate = 1200/30n = 40/n mol

Moles of oxygen = n x 40/n = 40 mol

(iii) Calculate the volume of oxygen at room temperature and pressure for a human with a lifetime of 70 years.

Moles of oxygen in 70 years = 40 x 70 x 365 = 1.02×10^6 mol

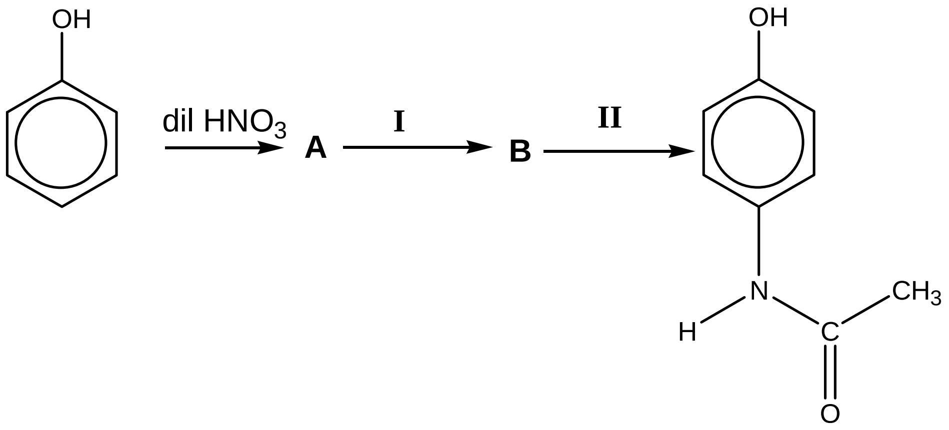
Volume at rtp = $1.02 \times 10^6 \times 24 = 2.45 \times 10^7$ dm^3

[3]

[Total:12]

3 **(a)** Panadol is the trade name for paracetamol or acetaminophen which is an over the counter analgesic (pain reliever) and antipyretic (fever reducer).

It can be synthesised in the lab from phenol via a series of steps.



paracetamol

(i) State the reagents and conditions for step I and step II.

Step I:

Reagent(s): ……….………………………………………………………………………..

Condition(s): ………………………………………………………………………………..

Step II:

Reagent(s): ……………………………………………………………………………………….

Condition(s): ……………………………………………………………………………………..

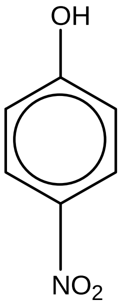
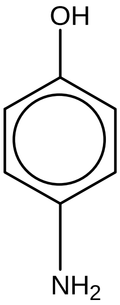
Step 1 : Sn, concentrated HCl; heat with reflux

Then NaOH (aq); room temperature

Step 2: CH_3COCl, r.t.

(ii) Draw the structures of compound **A** and **B** in the boxes below.

A:	**B**:

A:	**B**:
 [1]	 [1]

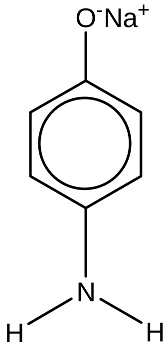
Paracetamol can be easily hydrolysed by aqueous NaOH. In the spaces below, write the formulae of the two products.

(iii)

C:	**D**:

Ans

C:	**D**:
	$CH_3COO^-Na^+$

[6]

(b) One of the causes of fever is bacterial infection. Alcohol (ethanol) solutions are used as disinfectants on the skin as it can penetrate the bacterial cell wall and *denature* the proteins inside the cell.

(i) What do you understand by the term *denaturation* of proteins?

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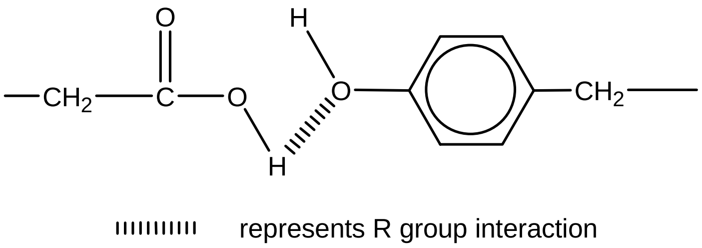
Denaturation of proteins refer to the disruption of the shape of the protein molecule without altering its primary structure but resulting in the loss of biological activity.

(ii) The part of the protein molecule which is affected by the ethanol added is as follows:



Suggest what R group interaction was disrupted by ethanol.

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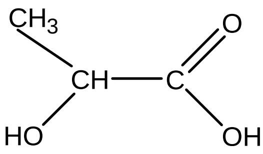
Ethanol disrupts the intermolecular hydrogen bonds

(iii) Another application of denaturation is found in the making of cheese. Casein is the predominant protein found in milk. When Lactobacillus bacterium is added to milk, lactic acid (2-hydroxypropanoic acid) is produced.



2-hydroxypropanoic acid

Besides hydrogen bonding, suggest and write an equation to explain what R group interaction is disrupted in this case.

Explanation ……………………………………………………………………………

……………………………………………………………………………

Equation ……………………………………………………………………………

Lactic acid produced disrupts the <u>ionic bonds</u> in the protein

$-COO^- + H^+ \rightarrow -COOH$

[4]

(c) The following table compares the pKa values of ethanol, 2-hydroxypropanoic acid with that of ethanoic acid.

compound	**formula**	**pKa**
Ethanol	CH_3CH_2OH	15.9
2-hydroxypropanoic acid	$CH_3CHOHCOOOH$	3.86
Ethanoic acid	CH_3COOH	4.76

(i) Suggest a reason why pK_a value of ethanoic acid is so much less than ethanol.

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Comparing the pK_a values, <u>ethanoic acid is more acidic]</u> than alcohol because

$$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+$$

For the ethoxide ion, $CH_3CH_2O^-$, the <u>electron donating ethyl group</u> <u>intensifies the negative charge on the oxygen atom of the anion (ethoxide</u>

ion).Thus, the anion is not stable, hence less acidic than ethanoic acid.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

For the ethanoate ion, there is a delocalisation of the negative charge over the two oxygen atoms. . This disperses the negative charge and stabilises the anion. Thus CH_3COO^- is more stable than $CH_3CH_2O^-$.

(ii) Suggest a reason why 2-hydroxypropanoic acid is more acidic that ethanoic acid.

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[3]

The higher acidity is due to the stabilisation of the carboxylate ion by intramolecular hydrogen bonding with the hydroxy group.

(d) The degree of dissociation (ionisation) of ethylamine ($CH_3CH_2NH_2$) in 0.010 moldm^{-3} aqueous solution is 0.17.

(i) Calculate the hydroxide ion concentration of this solution.

Ans:
[OH-] = concentration x degree of dissociation = cα
= 0.010 x 0.17 = 0.0017 = 1.7 x 10^{-3}

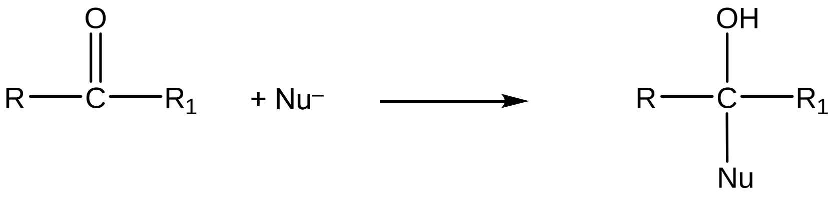
(ii) Calculate a value for the base dissociation constant, Kb, for ethylamine ($CH_3CH_2NH_2$), stating the units.

$$K_b = \frac{[OH^-][CH_3CH_2NH_3^+]}{[CH_3CH_2NH_2]} = \frac{(1.7x10^{-3})^2}{0.01} = 2.89 \times 10^{-4} \text{ mol dm}^{-3}$$

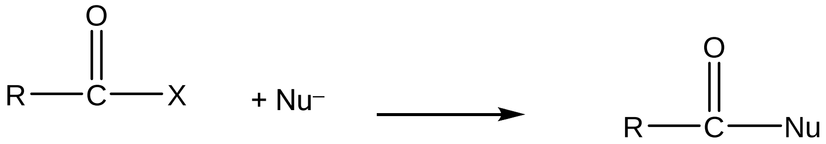
[2]

[Total: 15]

4 **(a)** Nucleophiles are electron-rich species that can donate electrons and attack regions of low electron density.



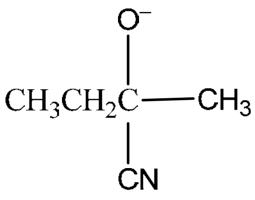
Reaction 1



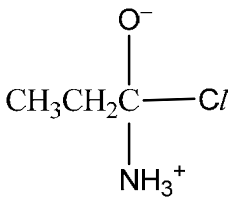
Reaction 2

where X: C*l*, Br, I

The intermediates, **X** and **Y**, shown below are formed by nucleophilic attack on the above two different compounds containing a carbonyl group of low electron density.



X



Y

(i) State the nucleophile to form intermediate **X** and **Y** respectively.

Nucleophile for intermediate **X**: ……………………………………….

Nucleophile for intermediate **Y**: ………………………………………..

[2]

Nucleophile for intermediate **X**:: **CN^-**

Nucleophile for intermediate **Y**:: **NH_3**

(ii) Identify the organic starting material to form intermediate **X**.

[1]

Butan-2-one or $CH_3CH_2COCH_3$

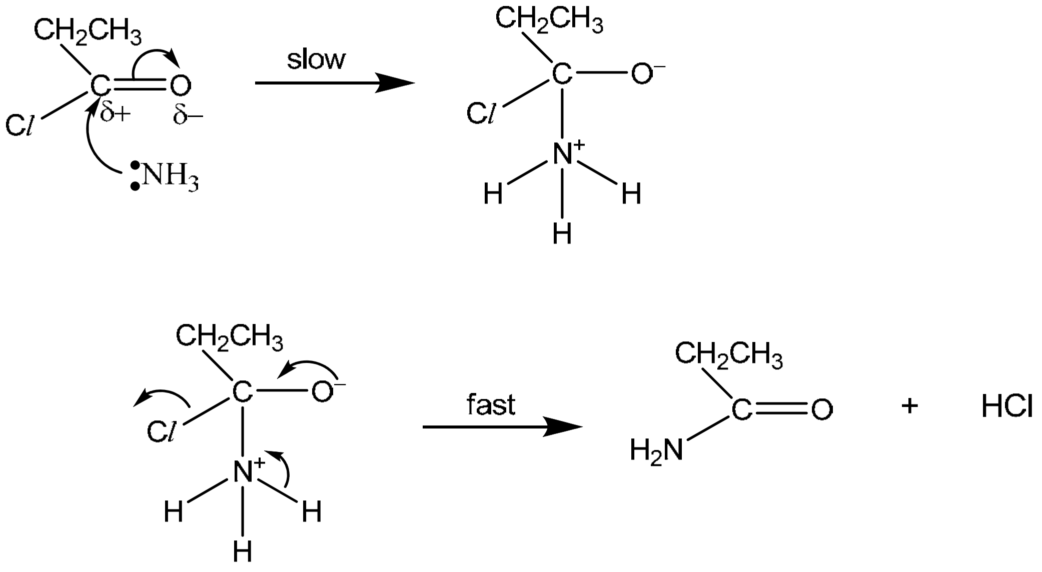
(iii) State the type of reaction that gives intermediate **Y**.

……………………………………………………………………………………….[1]

Nucleophilic addition

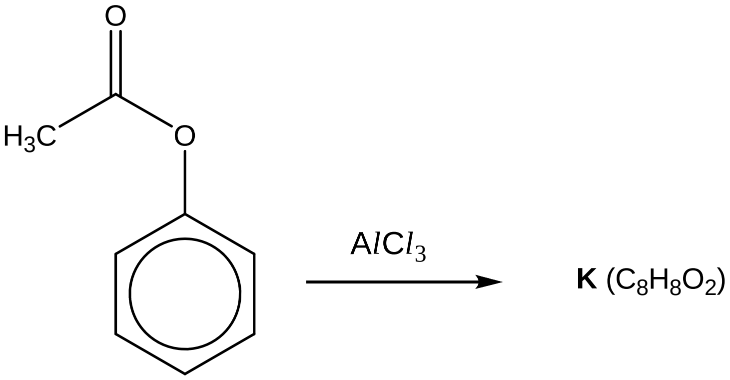
(iv) Describe a mechanism for the complete reaction in which **Y** is an intermediate.

[3]



(b) In a reaction discovered just over 100 years ago by the German chemist Karl Fries, compound **G** is converted into compound **K** when it is heated with $AlCl_3$.

Compound **K** is a structural isomer of **G**.



Compound **G**

Compound **K** is a 1,4-disubstituted benzene derivative. It is insoluble in water, but dissolves in NaOH(aq). It gives a white precipitate with Br_2(aq), and a yellow precipitate with alkaline aqueous iodine.

(i) Use the information given above to **name** the functional groups in compound **K**.

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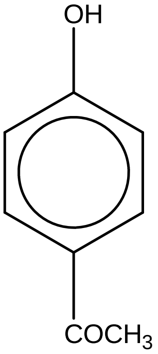
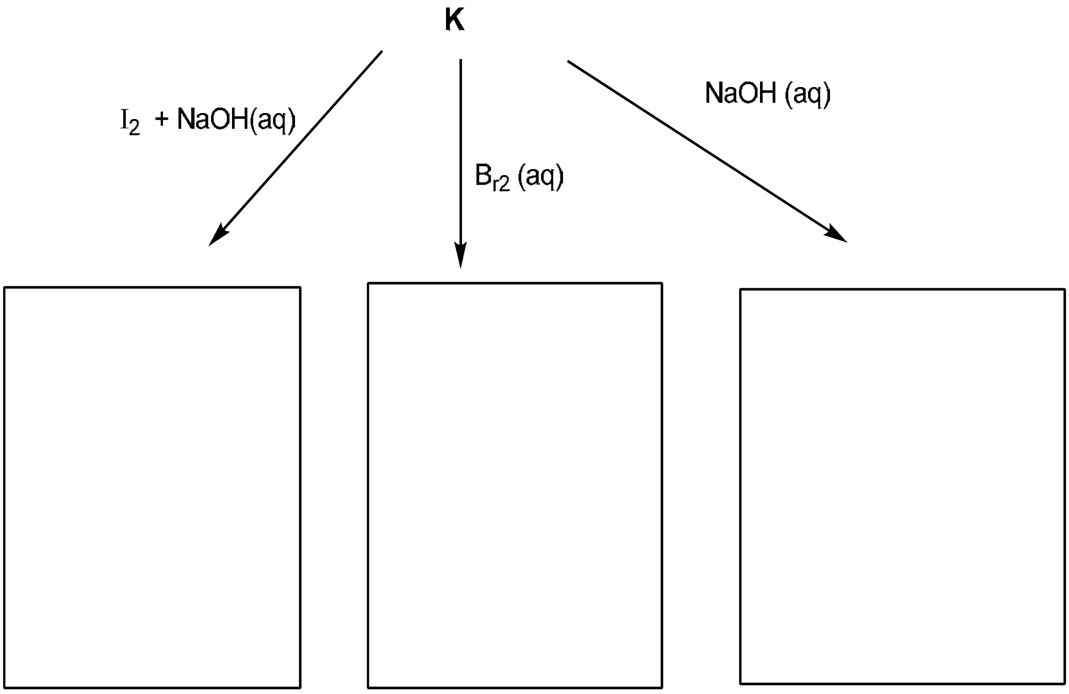
Phenol & ketone

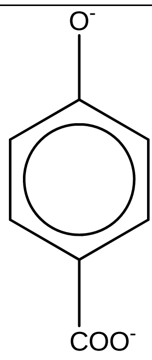
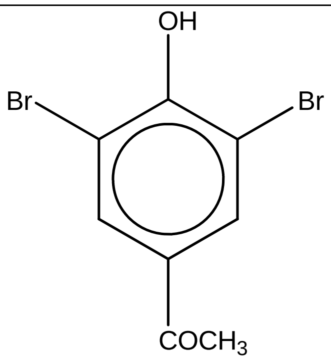
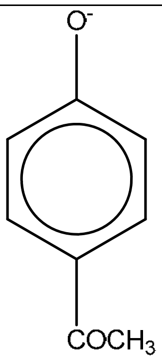
(ii) Suggest the structural formula of **K**.



(iii) Suggest structures for the aromatic products of the following reactions.



[5]

With I_2 + NaOH:	With Br_2(aq)	With NaOH(aq)
		

[Total: 12]

5 **(a)** An element M forms an oxide which is a powerful oxidising agent.
An acidified solution of the oxide of M, MO_x (x = 1, 2 or 3) will oxidise Mn^{2+}(aq) to MnO_4^-(aq), itself reduced to the element M.
When 10.0 cm^3 of 0.5 mol dm^{-3} of MO_x was reacted with 0.40 $moldm^{-3}$ Mn^{2+}(aq) in

the presence of H^+(aq), 15.0cm^3 of Mn^{2+}(aq) was needed for complete reaction.

(i) Calculate the number of moles of electrons donated by Mn^{2+}.

$Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e$

Mol of $Mn^{2+} = \frac{15}{1000} \times 0.40 = 6.00 \times 10^{-3}$ mol

Mol of e donated by $Mn^{2+} = 5 \times 6.00\ 10^{-3} = 0.03$ mol = mol of e accepted by MO_x

(ii) Calculate the mole ratio of MO_x and electrons accepted by MO_x.

Mol of $MO_x = \frac{10}{1000} \times 0.5 = 5.00 \times 10^{-3}$ mol

MO_x : mol of e accepted by MO_x

$5 \times 10^{-3}: 0.03$

1: 6

(iii) Determine the original oxidation number of M and the value of x.

$MO_x + 6e \rightarrow M$

Original oxidation number of M = + 6

x = 3

(iv) Construct an equation for the reaction between MO_x(aq) and acidified Mn^{2+}(aq).

[O]: $Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e$

[R]: $MO_3 + 6e + 6H^+ \rightarrow M + 3H_2O$

Overall: $6Mn^{2+} + 9H_2O + 5MO_3 \rightarrow 6MnO_4^- + 18H^+ + 5M$

(b) Water, H_2O, covers 70.9% of the Earth's surface and is vital for all known forms of life. About 0.005% of water molecules consist of an oxygen atom bonded to two atoms of the hydrogen isotope, deuterium, ${}^2_1D$.

Deuterium oxide, D_2O, is known as 'heavy water' and is used for research in chemical reactions because deuterium atoms react less quickly than normal hydrogen atoms, ${}^1_1H$.
Like H_2O, pure D_2O is weakly ionised.

$$2D_2O \rightleftharpoons D_3O^+ + OD^-$$

For D_2O, we can use the term K_D instead of K_W and pD instead of pH.

(i) Explain what is meant by *dynamic equilibrium*.

Dynamic equilibrium is a system in which the forward and the backward reactions are taking place at the same rate and thus the concentrations of reactants and products remain constant.

(ii) For pure D_2O, $K_D = 1.35 \times 10^{-15}$. Calculate the values of the following.

I. $[D_3O^+]$
II. pD

(I) $[D_3O^+] = (1.35 \times 10^{-15})^{1/2} = 3.67 \times 10^{-8}$ mol dm^{-3}

(II) pD = $-\lg(3.67 \times 10^{-8}) = 7.43$

(iii) For this system, K_D increases when temperature increases. Suggest and explain whether the ionic dissociation of 'heavy water' is an exothermic or endothermic process.

As temperature increases, position of equilibrium shifts to the right since K_D increases. By LCP, increase in temperature favours endothermic reaction by absorbing additional heat. Thus ionic dissociation of 'heavy water' is endothermic.

[5]

(iv) When pure H_2O and pure D_2O are mixed, exchange of H and D atoms takes place and the following equilibrium is established.

$$D_2O(l) + H_2O(l) \rightleftharpoons 2HDO(l)$$

A mixture of 30 g of D_2O and 27g of H_2O was placed in a vessel at 298 K. At equilibrium, it was found that the degree of dissociation of D_2O is 0.49. Calculate the K_c for this system.

[2]

Mol of D_2O = $\frac{30}{20}$ = 1.5 mol

Mol of H_2O = $\frac{27}{18}$ = 1.5 mol

	$D_2O(l)$	$+ H_2O(l)$ $\rightleftharpoons$	$2HDO(l)$
$n_{initial}$ / mol	1.5	1.5	0
change / mol	-1.5×0.49 $= -0.735$	-0.735	$+1.47$
n_{final} / mol	0.765	0.765	1.47

$$K_c = \frac{[HDO]^2}{[H_2O][D_2O]} = \frac{(\frac{1.47}{V})^2}{(\frac{0.765}{V})^2} = 3.69$$

[Total: 11]

6 Many copper minerals are found in hydrothermal deposits where they were formed by crystallization from very hot solutions which were trapped underground at high pressures. One such copper mineral is chalcopyrite, $CuFeS_2$.

Copper is extracted from the ore chalcopyrite ($CuFeS_2$) in a three-stage process. In the first stage of this extraction, the chalcopyrite is heated with silicon dioxide and oxygen.

(a) Balance the following equation for this first stage in which copper sulfide is formed.

$$……CuFeS_2 + ……SiO_2 + ……O_2 \longrightarrow Cu_2S + ……FeSiO_3 + ……SO_2$$

[1]

$$\mathbf{2CuFeS_2 + 2SiO_2 + 4O_2 \longrightarrow Cu_2S + 2FeSiO_3 + 3SO_2}$$

(b) Write the electronic configuration for Cu^+ in Cu_2S:

Cu^+ ………………………………………………………

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

[1]

(c) When water is added to white anhydrous $CuSO_4$, the solid dissolves to give a blue solution. On addition of concentrated NH_4Cl (aq), the solution changes to a yellow-green due to formation of copper containing species **D**. Concentrating the solution produces green crystals **E** of an ammonium salt with empirical formula $CuN_2H_8Cl_4$.

(i) Suggest the formulae of cation present in **E**.

Cation present in **E** ....

NH_4^+

(ii) Suggest the formulae of anion present in **D**

Identify of **D**……………………………………………

$CuCl_4^{2-}$

(iii) Suggest a balanced equation for the formation of **D** from aqueous $CuSO_4$.

…………………………………………………………………………………………………

$Cu(H_2O)_6^{2+}$ (aq) + $4Cl^-$ (aq) → $CuCl_4^{2-} + 6H_2O$

When excess of NH_3 (aq) is added to species **D**, the yellow green solution turns to a deep blue solution.

(iii) Use this information and the information above to suggest the strength of NH_3, H_2O and Cl^- ligands in decreasing order.

………………… > ………………… > …………………

…NH_3……>…Cl^-……>……H_2O…

[4]

(d) When a dilute aqueous solution containing a bidendate ligand, ethanedioate ion ($C_2O_4^{2-}$) is added to a solution containing aqueous copper(II) ions, a ligand exchange reaction occurs. In this reaction, four water molecules in the hydrated copper ion are replaced and a new complex **F** is formed.

(i) Explain what is meant by a bidendate ligand.

Ligands which contains two groups that have a lone pair of electrons each which can be donated to the central metal ion, forming two dative bonds.

(ii) Identity of **F** ………………………………………………………………………….
$[Cu(C_2O_4)_2(H_2O)_2]^{2-}$

In the complex **F** formed, the two water molecules are opposite each other. Draw a diagram to show how the ethanedioate ions are bonded to a copper ion and give a value for one of the O-Cu-O bond angles. You are not required to show the water molecules.

(iii)

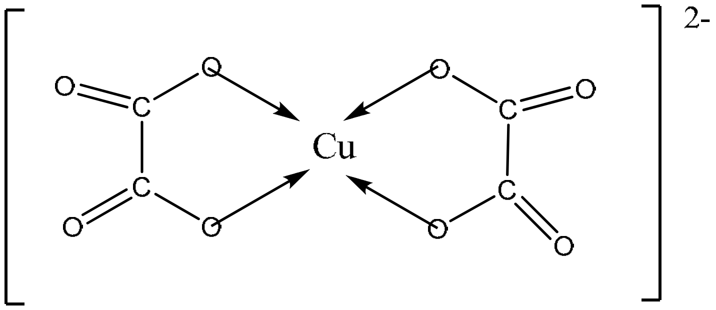


Diagram of Complex F

(iv) O-Cu-O bond angle: ………………………………………………………………
90^o

[4]