Calculator Model / No.

Name ________________________ **Class:** ____________ **Reg Number:** ______

MERIDIAN JUNIOR COLLEGE

Preliminary Examination

Higher 2

Chemistry 9647

Paper 2 Structured Questions

19 September 2013
2 hours

Additional Materials: *Data Booklet*

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Write your calculator brand and model/number in the box provided above.

Answer **all** questions in the spaces provided on the question paper.

All working must be shown clearly.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [ ] at the end of each question or part question.

You are reminded of the need for good English and clear presentation in your answers.

Examiner's Use		
Paper 1	**MCQ**	**/ 40**
Paper 2	**Q1**	**/ 12**
	Q2	**/ 9**
	Q3	**/ 15**
	Q4	**/ 12**
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	Q6	**/ 14**
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Paper 3		**/ 80**
Total		**/ 192**
% & Grade		

1 Planning (P)

You are to design an experiment to determine the enthalpy change of the reaction of magnesium with sulfuric acid as follows:

$$Mg\,(s) + H_2SO_4\,(aq) \rightarrow MgSO_4\,(aq) + H_2\,(g) \qquad \Delta H_1$$

You are provided with the following information and a list of apparatus and reagents. You may also use other apparatus normally found in a school laboratory.

Reagents and apparatus:

- 1.0 mol dm^{-3} H_2SO_4
- Mg turnings
- A thermometer with 0.2 °C division
- A 200 cm^3 styrofoam cup

Assume that 4.18 J is required to raise the temperature of 1 cm^3 of any solution by 1 °C.

(a) **(i)** The enthalpy change of reaction between magnesium and sulfuric acid is determined to be approximately –140 kJ mol^{-1}. A student attempted to plan the experiment and suggested the use of 100 cm^3 of sulfuric acid with 0.1 g of Mg turnings but was told by his teacher that the quantity of Mg used was inappropriate.

Explain with the aid of suitable calculations why the quantity of Mg suggested was inappropriate.

[2]

(ii) Hence, write a detailed plan to verify the enthalpy change of reaction between magnesium and sulfuric acid, ΔH_1.

Your plan should include the following:

- Justification of the mass of Mg turnings to be used
- Tabulation of raw data
- Brief description of how the data can be used to determine the enthalpy change of reaction

[6]

[Turn over

(b) The standard enthalpy change of formation of magnesium oxide, ΔH_f cannot be determined directly by experiment and is determined via an indirect approach using Hess' Law.

As such, in order to determine ΔH_f, two other experiments were conducted and the enthalpy change of each of the two reactions is found to be as follows:

$MgO\ (s) + H_2SO_4\ (aq) \rightarrow MgSO_4\ (aq) + H_2O\ (l)$ $\Delta H_2 = +176\ kJ\ mol^{-1}$

$H_2\ (g) + \frac{1}{2}O_2\ (g) \rightarrow H_2O\ (l)$ $\Delta H_3 = -286\ kJ\ mol^{-1}$

(i) Define the *standard enthalpy change of formation of magnesium oxide*.

(ii) Construct an energy cycle to determine the standard enthalpy change of formation of magnesium oxide, using the approximate value of ΔH_1 ($-140\ kJ\ mol^{-1}$) in **(a)**, and the above values of ΔH_2 and ΔH_3.

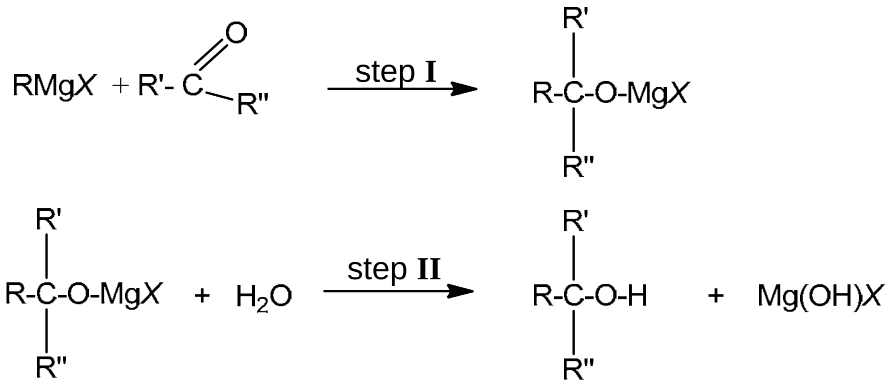
[4]

[Total : 12]

2 Grignard reagents are very useful in organic synthesis reactions. This question concerns the preparation and use of Grignard reagents. A Grignard reagent has the formula RMg*X* where *X* is a halogen, and R is an alkyl or aryl group.

$$RX + Mg \longrightarrow \underset{\text{Grignard reagent}}{RMgX}$$

Grignard reagents readily react with carbonyl compounds to form their corresponding alcohols as outlined in the general equations below.



(a) State the type of reaction for steps **I** and **II** respectively.

[1]

Step **I:** …………………………………………

Step **II:** …………………………………………

(b) Grignard reagents are formed readily by iodoalkanes. Using the above general reaction scheme, the Grignard reagent, CH_3CH_2MgI is first generated from iodoethane. This is subsequently reacted with pentan–2–one, converting it into a tertiary alcohol.

Draw the displayed formula of the final organic product formed in step **II**.

[1]

The experimental procedure below details the conversion of pentan–2–one to the alcohol product, which involves the initial preparation of a Grignard reagent.

The Grignard reagent is highly reactive and has to be carefully prepared in an anhydrous environment.

Procedure

1 1.50 g of magnesium turnings is added to a pear-shaped flask with an equimolar quantity of iodoethane and 20 cm^3 of diethylether.

2 A crystal of iodine is added to the mixture from **step 1** to activate the magnesium, and this mixture is refluxed.

3 The mixture is allowed to cool and 6.0 cm^3 of pentan–2–one is added dropwise. The mixture is then gently heated under reflux.

4 Next, the mixture is cooled using an ice bath, and then 25 cm^3 of 4 mol dm^{-3} hydrochloric acid is slowly added.

5 The mixture from **step 4** is added to a separating funnel. The aqueous layer is separated and shaken successively with two 10 cm^3 portions of diethylether, retaining the diethylether extracts and combining them with the original diethylether layer.

6 The combined diethylether layer is washed successively with 20 cm^3 of
(i) water,
(ii) saturated sodium hydrogencarbonate solution,
(iii) 1 mol dm^{-3} aqueous sodium thiosulfate,
(iv) saturated sodium chloride solution.

7 The diethylether layer is allowed to stand over anhydrous magnesium sulfate.

substance	formula	molar mass / g mol^{-1}	density / g cm^{-3}	solubility in water	boiling point / °C
iodoethane	C_2H_5I	156	1.93	slightly soluble	72
diethylether	$C_2H_5OC_2H_5$	74	0.713	slightly soluble	35
magnesium turnings	Mg	24.3	1.74	insoluble	1110
pentan-2-one	$C_5H_{10}O$	86	0.814	slightly soluble	102
product alcohol			0.823	slightly soluble	143

Table 2.1: Physical Properties of the reagents and the organic product

(c) Suggest the role of the diethylether in **step 1** of the procedure.

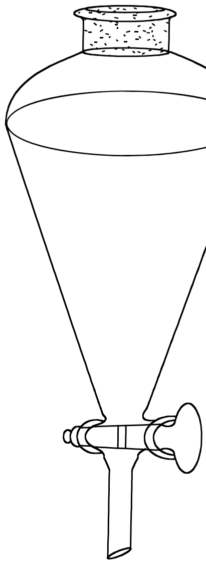
[1]

(d) **(i)** In **step 2**, the mixture is refluxed. Suggest why elevated temperatures and long periods of time are required for reactions such as this.

(ii) Show, with the use of calculation whether the Grignard reagent or pentan–2–one is in excess. Assume that the reaction between magnesium and iodoethane in **step 2** had 100 % yield.

[2]

(e) In the diagram of the separating funnel below, draw the two layers that will be observed after **step 4.** Indicate the **relative position** of the two layers.



[1]

(f) In **step 6**, the water and the three aqueous solutions used to wash the diethylether layer are intended to remove a particular impurity, either by dissolving or by chemical reaction followed by dissolving.

Suggest the impurity removed in each step.

(i) water ………………………………..

(ii) saturated sodium hydrogencarbonate ………………………………..

(iii) sodium thiosulfate ………………………………..

(iv) saturated sodium chloride ………………………………..

[2]

(g) After **step 7**, further separation and purification has to be carried out in order to collect the alcohol product. Briefly describe how you would obtain a pure sample of the alcohol product.

[1]

[Total : 9]

3 Group VII elements are often referred to as the halogens. They form silver halides and hydrogen halides which exhibit physical and chemical properties that have been used widely in both qualitative and quantitative analysis of the halides.

(a) Silver halides differ in their colours as well as solubility product values as shown in the table below.

compounds	**colour**	**solubility product at 298 K**
$AgCl$	white	2.02×10^{-10}
Ag_2CrO_4	red	3.01×10^{-12}

(i) In an experiment, when 0.1435 g of $AgCl$ (s) is shaken with 10.0 cm^3 of NH_3 (aq), the solid just dissolves.

1 Calculate the $[Cl^-]$ and $[Ag^+]$ when the $AgCl$ (s) just dissolves.

2 The K_c for the following reaction is 1.50 x 10^7 mol^{-2} dm^6.

$$Ag^+ (aq) + 2\ NH_3 (aq) \rightleftharpoons [Ag(NH_3)_2]^+ (aq)$$

You may assume that $[Ag(NH_3)_2]^+$ has the same concentration as the chloride ions when AgC*l* just dissolves in NH_3.

- Calculate the $[NH_3]$ at equilibrium.

- Hence, calculate the **minimum** concentration of 10.0 cm^3 of NH_3 which will dissolve 0.1435 g of AgC*l* (s).

(ii) When a precipitate is formed, ΔG^{θ}_{ppt} in J mol^{-1} is given by the following expression:

$$\Delta G^{\theta}_{ppt} = 2.303\, RT \lg K_{sp}$$

1 Use the data above to calculate ΔG^{θ}_{ppt} , in kJ mol^{-1}, for Ag_2CrO_4.

2 Hence, determine whether Ag_2CrO_4 is soluble in water at 298 K. Explain your answer.

[6]

(b) The probe on a pH meter has two electrodes, one is a glass electrode that responds to changes in [H^+(aq)] and the other a reference electrode that has a stable electrode potential.

The reference electrode is often a silver electrode dipped in a solution of 0.50 mol dm^{-3} KC*l* in contact with AgC*l* (s). The electrode assembly of the pH meter could be represented in **Figure 1**.

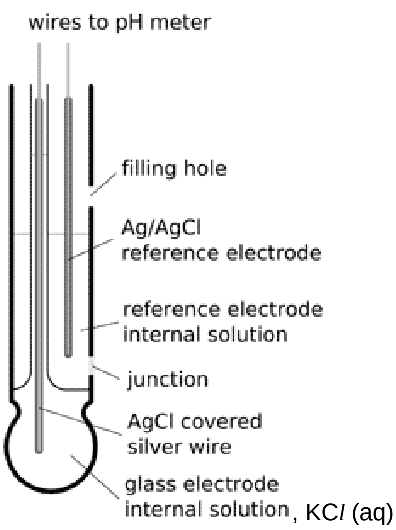


Figure 1

(i) Calculate the $[Ag^+]$ in the electrode assembly using the value of solubility product for $AgCl$ in **(a)**.

(ii) The electrode potential, E, changes from the standard value, E^θ, if the concentration of the ions is non-standard. This change is given by the Nernst equation.

$$E = E^\theta + 0.059 \lg [Ag^+]$$

Using appropriate information from the *Data Booklet*, calculate the electrode potential of the silver electrode, E at 298 K.

(iii) Suggest why a 0.50 mol dm^{-3} solution of KCl is used rather than pure water.

[3]

(c) The gaseous hydrogen halides HC*l*, HBr and HI, may be prepared by reacting the corresponding sodium salt with concentrated phosphoric (V) acid, H_3PO_4.

When sodium halide Na*X* was used, a sample of gaseous H*X* was collected in a gas jar. A hot glass rod was placed in the sample of H*X* and orange fumes was observed immediately. When aqueous NaOH was added, the orange colour disappeared.

(i) Suggest the identity of Na*X*.

(ii) Explain why concentrated phosphoric (V) acid rather than concentrated sulfuric acid is used to prepare samples of H*X* from the corresponding sodium salt.

(iii) With the aid of an ionic equation, suggest the type of reaction between NaOH (aq) and the orange fumes.

Type of reaction: …………………………………………………..

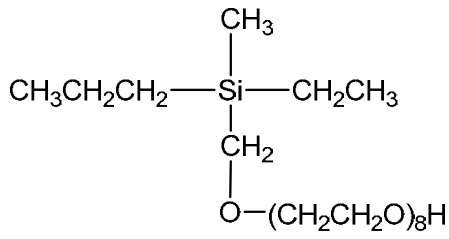
Ionic equation: …………………………………………………..

(iv) The hydrogen halides can be thermally decomposed under suitable conditions. By quoting appropriate data from the *Data Booklet*, explain the trend in the thermal stability of the hydrogen halides.

[6]
[Total : 15]

4 *Limonene*, which has the characteristic smell of oranges, is an organic compound that can be used in an array of applications ranging from food manufacturing to cleaning industries.

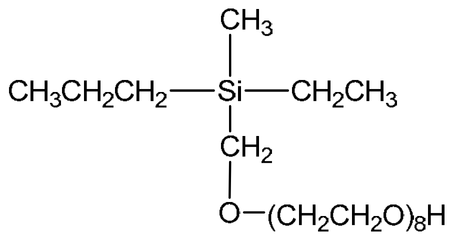
(a) Besides *limonene*, the following compound is another commonly used cleaning agent in the chemical industry.



This cleaning agent is an example of a typical oil spill dispersant, used to combat oil spills.

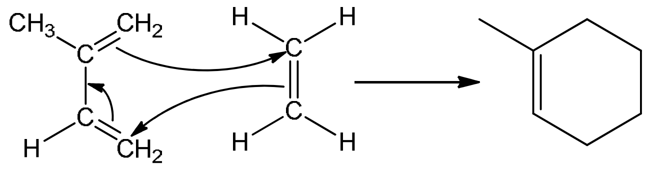
(i) By reference to the type of intermolecular forces, explain why this molecule is able to function as an oil spill dispersant.

(ii) On the diagram below, illustrate and label the interaction between a molecule of this cleaning agent and **one** water molecule.



[2]

(b) *Limonene* can be obtained via a series of organic reactions involving the *Diels–Alder* reaction. The *Diels–Alder* reaction is a cycloaddition mechanism involving a diene and a dienophile as shown below:

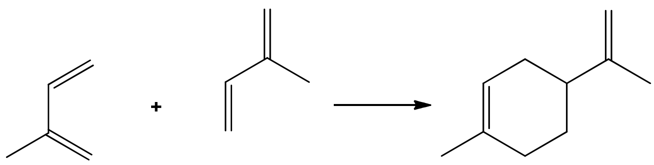


diene **dienophile**

The dienophile acts as the electrophile in the *Diels–Alder* reaction.

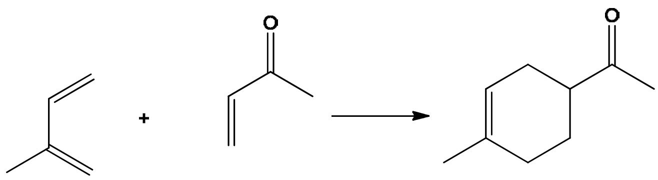
Isoprene, a diene can be used to synthesise *Limonene* and compound **A** using the cycloaddition mechanism.

Reaction **I**:



isoprene ***limonene***

Reaction **II**:

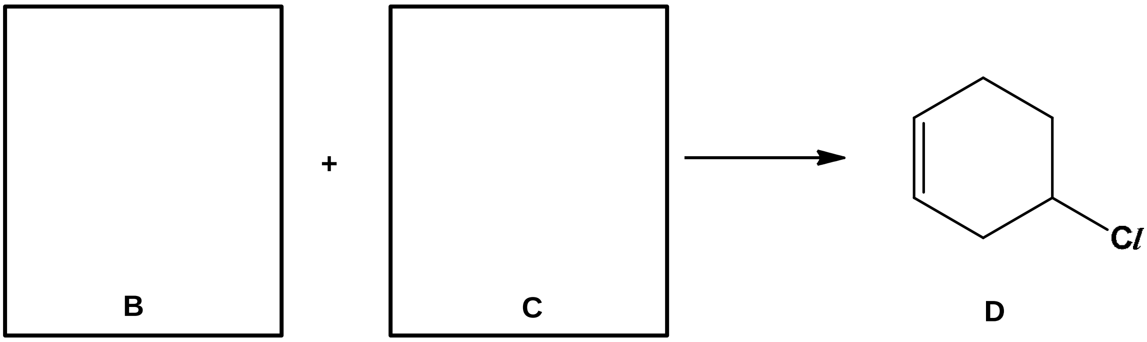


isoprene **compound A**

(i) With reference to the cycloaddition mechanism, explain qualitatively why the rate of reaction **II** is faster than that for reaction **I**.

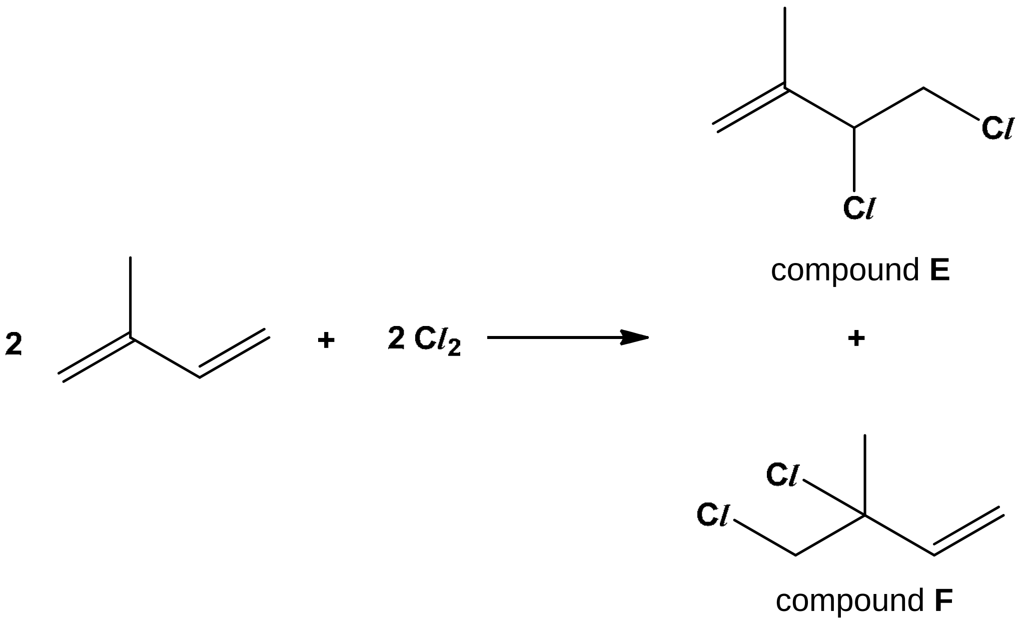
(ii) Compound **D** may also be synthesised from the *Diels–Alder* reaction.

Suggest the structural formula of reactants **B** and **C** from which compound **D** may be synthesised.



[3]

(c) When *isoprene* is reacted with chlorine gas, the following products may be formed in various proportions.



To determine the rate equation for the reaction between *isoprene* and chlorine gas, a student conducted a series of experiments and obtained the following data:

expt	**concentration / mol dm^{-3}**		**initial rate / mol dm^{-3} s^{-1}**
	CH_2=C(CH_3)CH=CH_2	**Cl_2**	
1	0.04	0.128	1.77×10^{-3}
2	0.08	0.064	1.76×10^{-3}

(i) The order of reaction with respect to chlorine is found to be 1.

Using data from the table above, determine the order of reaction with respect to CH_2=C(CH_3)CH=CH_2, showing your working clearly.

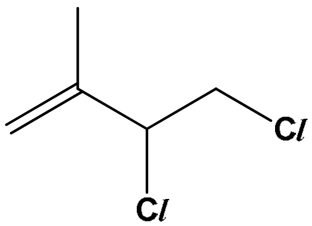
(ii) Hence, construct the rate equation for the reaction.

(iii) State which product, **E** or **F** will be formed in a greater proportion.

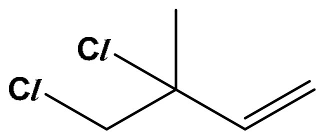
(iv) Using your answers to **(c)(ii)** and **(c)(iii)**, describe a mechanism that is consistent with the rate equation. Indicate which step is the rate-determining step.

[5]

(d) Suggest how compound **E** could be distinguished from compound **F** by a **two-step** chemical test.



compound **E**

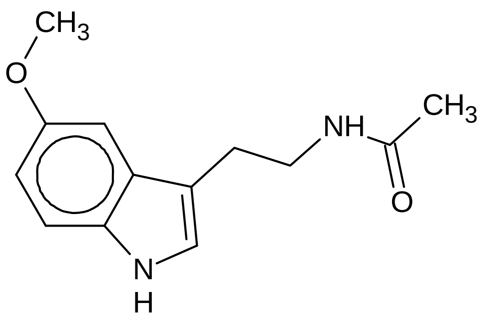


compound **F**

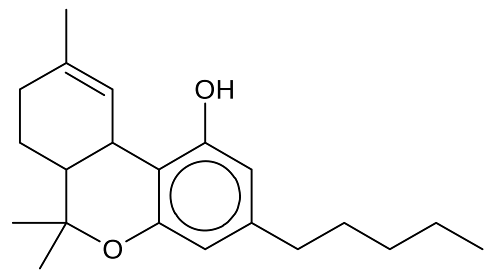
[2]

[Total : 12]

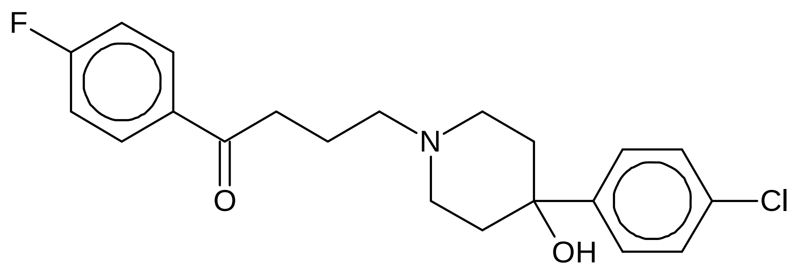
5 *Melatonin* is a naturally occurring hormone found in animals, *THC* is a drug obtained from the cannabis plant, and *haloperiodol* is an antipsychotic drug.



melatonin



THC



haloperiodol

(a) All three organic molecules share similar reactions with some reagents only.

(i) State one reagent that will react with both *melatonin* and *haloperiodol* and **not** with *THC*.

(ii) State one reagent and the required condition that will react with both *melatonin* and *THC* but **not** with *haloperiodol*.

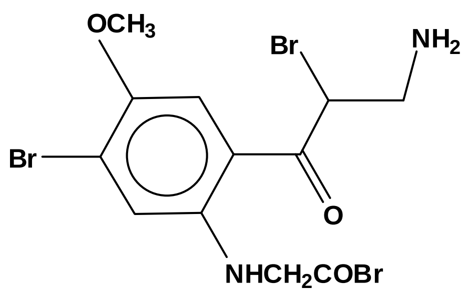
(iii) State one reagent, other than MnO_4^- ions, and the conditions required that will react with all three compounds.

[3]

(b) *Melatonin* can be made through the reaction between two organic compounds in the laboratory. Suggest the structural formulae of these two compounds.

[2]

(c) *Melatonin* can undergo a series of reactions to obtain compound **X**.



Compound **X**

Explain the different reactivities of the three bromine atoms in compound **X.**

[3]

(d) Describe a chemical test that would allow you to distinguish between *THC* and *melatonin.* The distinguishing may rely on a preliminary breaking-up of the compounds, and subsequent testing of the reaction products.

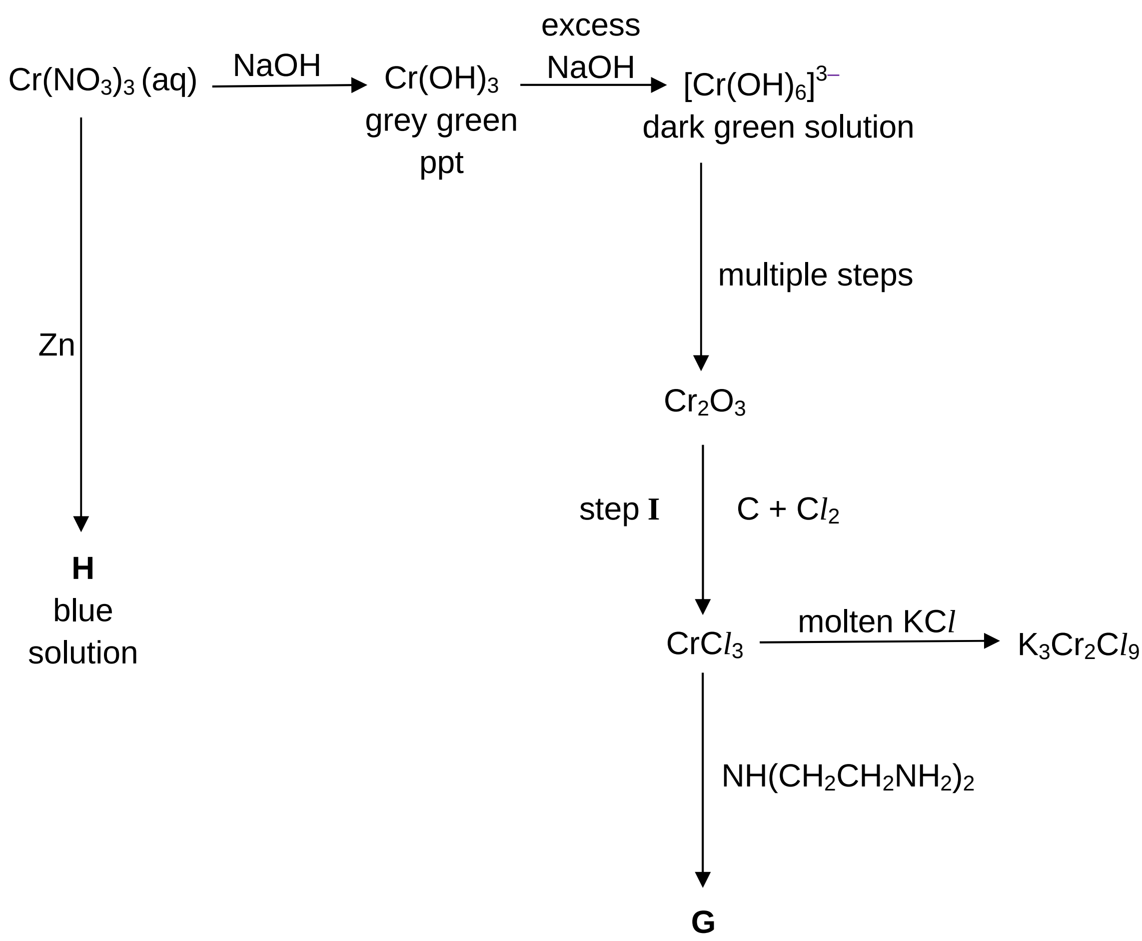
You must identify *melatonin* positively. State only the observations for the positive test.

[2]

[Total: 10]

6 Chromium is a transition metal which exists as a grey, lustrous metal. It exists in more than one oxidation state and forms compounds with many colours.

Aqueous chromium (III) nitrate undergoes the following reactions.



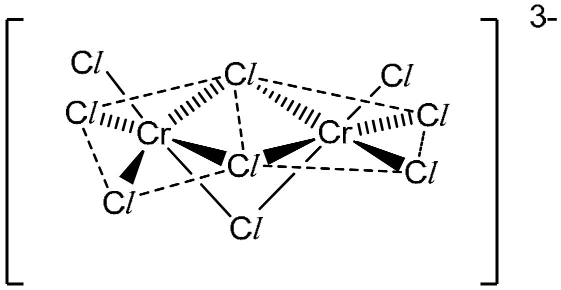
(a) Account for the observation when aqueous sodium hydroxide was added to a solution of $Cr(NO_3)_3$, until in excess. Write balanced equations for the reactions which occur.

[2]

(b) Suggest a balanced equation for step **I** involving the formation of chromium (III) chloride from chromium (III) oxide, given that a poisonous gas was given off in the process.

[1]

(c) Molten potassium chloride reacts with chromium (III) chloride to form a $K_3Cr_2Cl_9$ where the two chromium ions are linked via three chloride bridges.



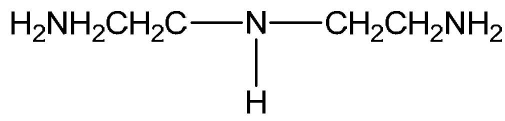
Suggest the coordination number of chromium in the complex.

[1]

(d) Suggest the formula of the complex ion present in **H**.

[1]

(e) Chromium (III) chloride reacts with diethylenetriamine, $NH(CH_2CH_2NH_2)_2$, to form **G**. It was experimentally deduced that three moles of $AgNO_3$ is required to react completely with one mole of **G**.



diethylenetriamine

(i) What type of reaction occurs when $CrCl_3$ is converted to **G**?

(ii) Draw the structure of **G**.

[2]

(f) Chromium (III) nitrate dissolves in water to form a purple solution.

Suggest an explanation for chromium (III) nitrate being coloured.

[3]

(g) *In a 'high spin' state, the electrons occupy all the d-orbitals singly, before pairing up in the lower energy d-orbitals. In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing, before the higher energy d-orbitals are used.*

A simple mathematical relationship between the number of unpaired electrons and the magnetic moment is given below.

$$\mu = \sqrt{n(n+2)}$$

where μ is the magnetic moment and n is the number of unpaired electrons.

The value of magnetic moment, μ, is 4.90 for Cr^{2+} in $[Cr(H_2O)_6]^{2+}$.

Calculate the value of n and hence predict the spin state of Cr^{2+} in $[Cr(H_2O)_6]^{2+}$. Hence or otherwise, show the electronic distribution of Cr^{2+} ion in this spin state.

[2]

(h) The standard electrode potential of the $[Cr(H_2O)_6]^{3+}$/ $[Cr(H_2O)_6]^{2+}$ system is given below.

$[Cr(H_2O)_6]^{3+}$ (aq) + e^- $\rightleftharpoons$ $[Cr(H_2O)_6]^{2+}$ (aq) **----- (1)** $E^\ominus$ = -0.41 V

$[Cr(CN)_6]^{3-}$ (aq) + e^- $\rightleftharpoons$ $[Cr(CN)_6]^{4-}$ (aq) **----- (2)** $E^\ominus$ = ?

The presence of cyanide ions will stabilise chromium (III) ion in $[Cr(CN)_6]^{3-}$, hence lowering the oxidising ability of the chromium (III) ion.

(i) Other than commenting on the stability of $[Cr(CN)_6]^{3-}$, explain the observation above.

(ii) Suggest a possible standard electrode potential value for equation **(2)**.

[2]

[Total : 14]

End of Paper 2