

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

Paper 3 Free Response

9647/03

21 September 2016

2 hours

Additional Materials: Writing Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

Answer any **four** questions.

- 1(a)** Copper(I) sulfate, Cu_2SO_4 , can be made from copper(I) oxide under non-aqueous conditions. On adding this salt to water, it immediately undergoes a disproportionation reaction.

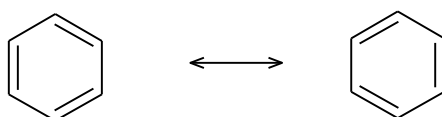
(i) Suggest, with a reason, the colour of copper(I) sulfate. [2]

(ii) Using suitable data from the *Data Booklet*, explain why the disproportionation reaction occurs, and write an equation for it. [3]

- (b)** Palladium(II) salts can form square planar complexes. Successive addition of ammonia and hydrogen chloride to an aqueous palladium(II) salt produces, under different conditions, three compounds with empirical formula $\text{PdN}_2\text{H}_6\text{Cl}_2$. Two of these, **A** and **B**, are non-ionic, with $M_r = 211$. **A** has a dipole moment, whereas **B** has none. The third compound, **C**, is ionic, having $M_r = 422$, and contains palladium in both its cation and anion.

For each **A**, **B** and **C**, deduce a structure that fits the above data, explaining your reasons fully. [6]

- (c)** Benzene ring is often represented as a structure that has a ring within the hexagon. Alternatively, chemists have also represented the structure of benzene in the following forms, known as resonance structures.

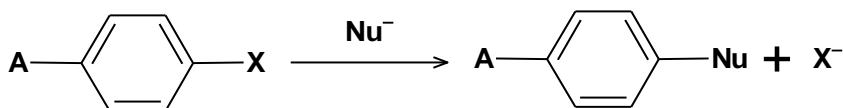


Benzene (two resonance forms)

The resonance relationship is indicated by the double headed arrow between them. The only difference between resonance forms is the placement of the pi electrons and non-bonding electrons.

Most aromatic compounds undergo electrophilic substitution. However aryl halides undergo a limited number of substitution reactions with strong nucleophiles.

An example of a reaction is as follows:

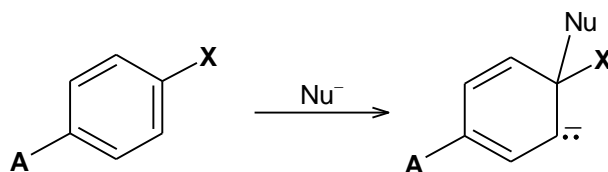


where **A** is an electron withdrawing group and **X** is a halogen

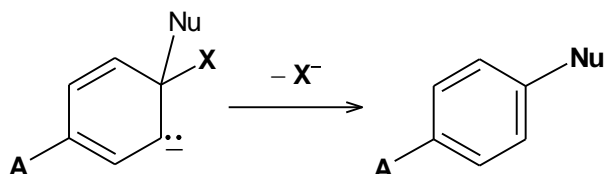
The mechanism of this reaction has two steps:

- addition of the nucleophile
- elimination of the halogen leaving group

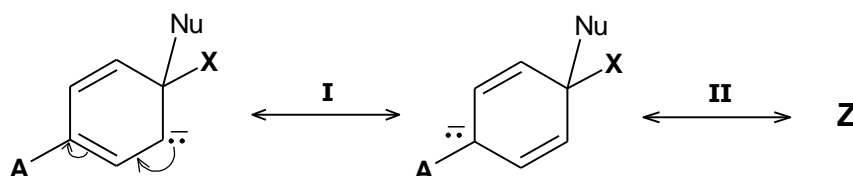
Step 1 involves the addition of the nucleophile (Nu^-). The Nu^- attacks the carbon atom bonded to a halogen, causing the pi bond to break. A resonance stabilised carbanion with a new C–Nu bond is formed. The aromatic ring is destroyed in this step.



Step 2 involves the loss of the halogen X , reforming the aromatic ring.

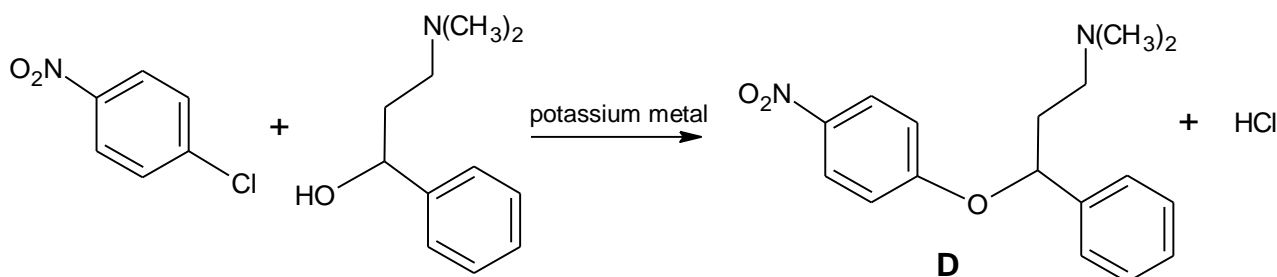


Two other resonance structures of the intermediate in **Step 1** are shown below:

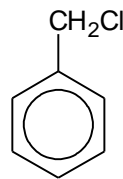
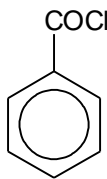
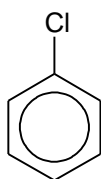


- (i) Copy the above diagram and draw the resonance structure, **Z**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons in forming **Z**. [2]

The reaction below shows the synthesis of compound, **D**.



- (ii) Suggest the role of potassium metal in the reaction. [1]
- (iii) Use the information given above to draw out the full mechanism for the reaction that forms **D**, labelling the slow and fast steps. In your answer, showing any relevant charges, lone pair of electrons and movement of electrons. [3]
- (d) Describe and explain the relative ease of hydrolysis of the following three chloro-compounds. [3]

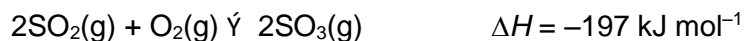


[Total: 20]

2 Sulfuric acid, H_2SO_4 , can behave as an acid, an oxidising agent or as a dehydrating agent in various reactions.

(a) Draw a diagram to illustrate the shape of pure sulfuric acid and indicate the bond angle about the sulfur atom. [2]

(b) The Contact Process is used for the manufacture of sulfuric acid. One of the reactions that takes place is the following reversible reaction:



Sulfur dioxide and oxygen in a 2:1 molar ratio at a total initial pressure of 3 atm is passed over a catalyst in a fixed volume vessel at 400 °C. When equilibrium is established, the percentage of sulfur trioxide in the mixture of gases is found to be 30%.

(i) Write an expression for the equilibrium constant, K_p , of the reaction. [1]

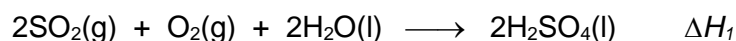
(ii) Calculate the value of K_p at 400 °C, stating its units. [3]

(iii) How would the percentage conversion of SO_2 into SO_3 be affected when the pressure is raised? Explain. [2]

(c) Dilute sulfuric acid takes part in typical acid-base reactions and it can be used to distinguish the following solids: MgO , BaO and SiO_2 .

State the observations, if any, to indicate the differences in their reaction when water is added to each solid followed by dilute sulfuric acid. [4]

(d) Sulfur dioxide is a major pollutant from sulfuric acid plants. The SO_2 emitted into the atmosphere is oxidised in the air, which then reacts with water to form sulfuric acid, hence causing acid rain:



Using the data below and data from **(b)**, construct an energy cycle to calculate

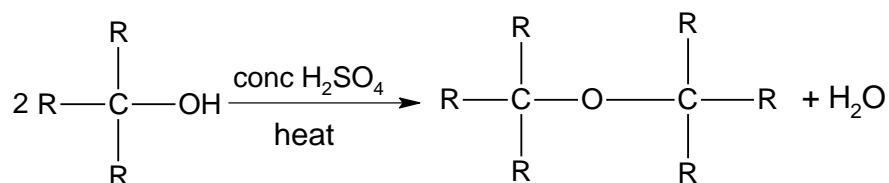
(i) the enthalpy change of formation of $\text{SO}_2(\text{g})$, and hence

(ii) the enthalpy change of reaction, ΔH_1 for the above reaction.

Enthalpy change of formation of $\text{H}_2\text{O}(\text{l})$	$= -286 \text{ kJ mol}^{-1}$
Enthalpy change of formation of $\text{H}_2\text{SO}_4(\text{l})$	$= -811 \text{ kJ mol}^{-1}$
Enthalpy change of formation of $\text{SO}_3(\text{g})$	$= -493 \text{ kJ mol}^{-1}$

[4]

- (e) Alcohols react with concentrated sulfuric acid at high temperatures to form alkenes. A common side reaction that can happen is the formation of ethers, which is also catalysed by concentrated sulfuric acid.



The mechanism occurs via 3 steps:

Step 1:

An acid base reaction in which H^+ from H_2SO_4 protonates the oxygen atom in alcohol. This step is very fast and reversible.

Step 2:

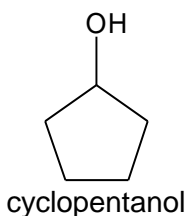
A second alcohol molecule functions as the nucleophile and attacks the product from **step 1**. The C–O bond is cleaved and a water molecule leaves the molecule. This creates

an oxonium ion $\begin{array}{c} \text{R} \\ | \\ \text{R}'-\text{O}^+-\text{H} \end{array}$ intermediate.

Step 3:

Another acid base reaction in which the proton in the oxonium ion is removed by a suitable base (in this case a water molecule) to give the ether product. This step is very fast and reversible.

- (i) Draw the ether formed when cyclopentanol undergoes the above reaction.



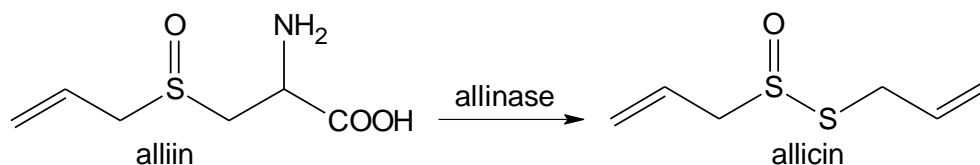
[1]

- (ii) Draw out the full mechanism for the reaction between two cyclopentanol molecules to form an ether. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [3]

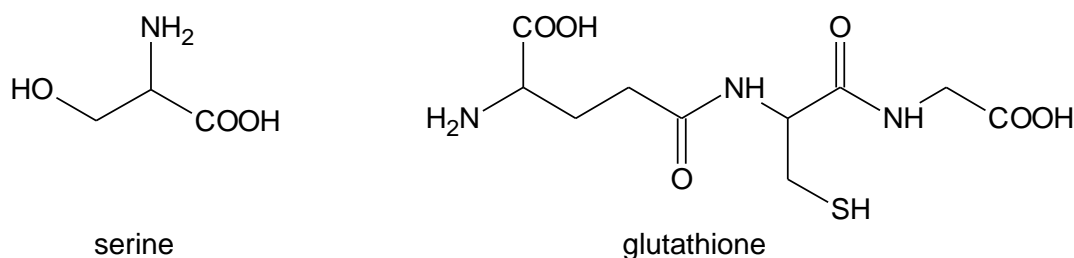
[Total: 20]

- 3 Garlic contains many amino acids, minerals and enzymes. Garlic also contains at least 33 sulfur compounds like alliin, allicin and ajoene. The sulfur compounds are responsible for both garlic's pungent odour and many of its medical effects.

(a) When raw garlic is chopped or crushed, the enzyme allinase converts alliin into allicin, which is responsible for the odour of fresh garlic.



Alliin can also be biosynthesised by using serine and glutathione.

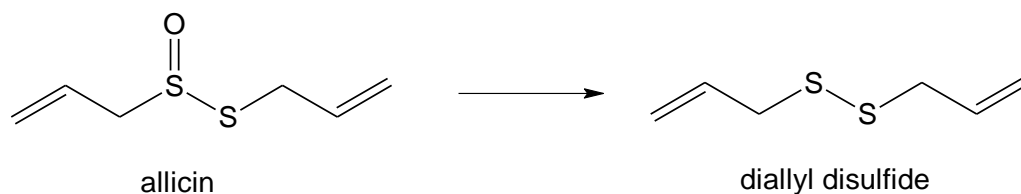


- (i) Explain why raw chopped garlic has a stronger odour than when it is cooked. [1]
- (ii) When one molecule of serine reacts with one molecule of glutathione, it is possible to form two esters with different structural formulae. Draw the structural formula of **each** of these esters. [2]
- (iii) Draw the structural formulae of the products when glutathione is hydrolysed. [3]

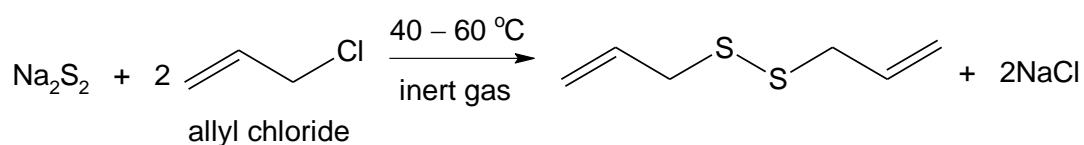
Alliin has pK_a values of 1.84 and 8.45.

- (iv) Make use of these pK_a values to suggest the major species present in solutions of alliin with the following pH values. [3]
- pH 1
 - pH 7
 - pH 11
- (v) Calculate the pH of 0.10 mol dm^{-3} solution of alliin. [1]
- (vi) With reference to the pK_a values, identify the major species formed when 10 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin. Hence, deduce whether the solution is acidic, neutral or alkaline. [2]
- (vii) Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin. Briefly describe how you have calculated the various key points on the curve. [4]

- (b) Diallyl disulfide is one of the principal components of the distilled oil of garlic. It is a yellowish liquid which is insoluble in water and has a strong garlic odour. It is produced during the decomposition of allicin.



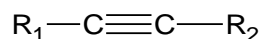
Diallyl disulfide can be produced industrially from sodium disulfide and allyl chloride at temperatures of 40 – 60 $^{\circ}\text{C}$ in an inert atmosphere.



- (i) Give the *IUPAC* name of allyl chloride. [1]
- (ii) Explain, in thermodynamic terms, suggest why diallyl disulfide is insoluble in water. [2]
- (iii) State the type of reaction when diallyl disulfide is converted back to allicin. [1]

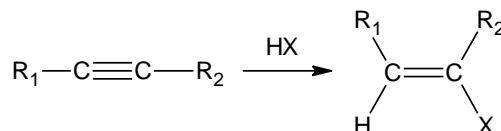
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- 4 Alkynes are organic molecules which contain carbon-carbon triple bonds and are part of the homologous series with formula of C_nH_{2n-2} i.e.

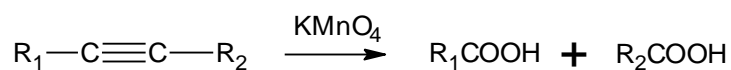


where R_1 and $R_2 = H$ or alkyl or aryl groups

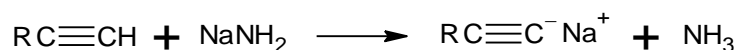
Alkynes exhibit similar chemical properties to alkenes.
e.g. addition reactions with electrophiles i.e. X_2 or HX to form alkenes



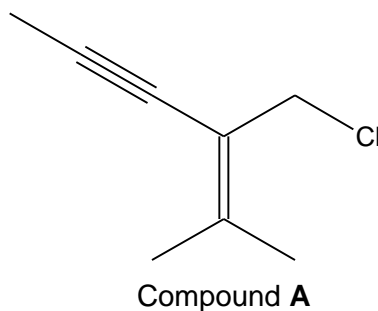
e.g. oxidation by hot concentrated $KMnO_4$ to form mixture of carboxylic acids



However, unlike alkenes, terminal alkynes are able to react with strong bases like sodium amide.



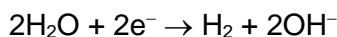
- (a) Ethyne, C_2H_2 , is heated with excess sodium bromide and concentrated sulfuric acid to produce a dihalide, $C_2H_4Br_2$. The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving the organic reagent.
- Write an equation for the first stage. [1]
 - Suggest a structure for the dihalide formed. [1]
 - When the concentrated sulfuric acid is added to the reaction mixture, cooling is necessary to prevent the formation of inorganic by-products.
Write an equation to explain the formation of these inorganic by-products. [1]
- (b) Compound **A**, is an enyne chloride (i.e. compounds that contains chloro, alkyne and alkene functional groups).



One mole of compound **A** reacts with two moles of Br_2 to produce a mixture of 4 stereoisomers. Draw structures of the stereoisomers formed. [3]

- (c) Compound **B**, which is an isomer of Compound **A** and also an enyne chloride, is treated with sodium amide, NaNH_2 followed by heating under reflux to form compound **C**, C_8H_{10} . Compound **C** reacts with hot concentrated KMnO_4 to produce butane-1,4-dioic acid only.
- (i) Explain the reaction with NaNH_2 . [1]
- (ii) Hence, explain the formation of compound **C**. [1]
- (iii) Suggest skeletal structures for compounds **B** and **C**. [2]

When a current of 1.0 A was passed through aqueous potassium maleate ($\text{KO}_2\text{CCH}=\text{CHCO}_2\text{K}$) for 15 minutes, it was found that 110 cm^3 H_2 , measured at r.t.p, was collected at the cathode. The following reaction took place.

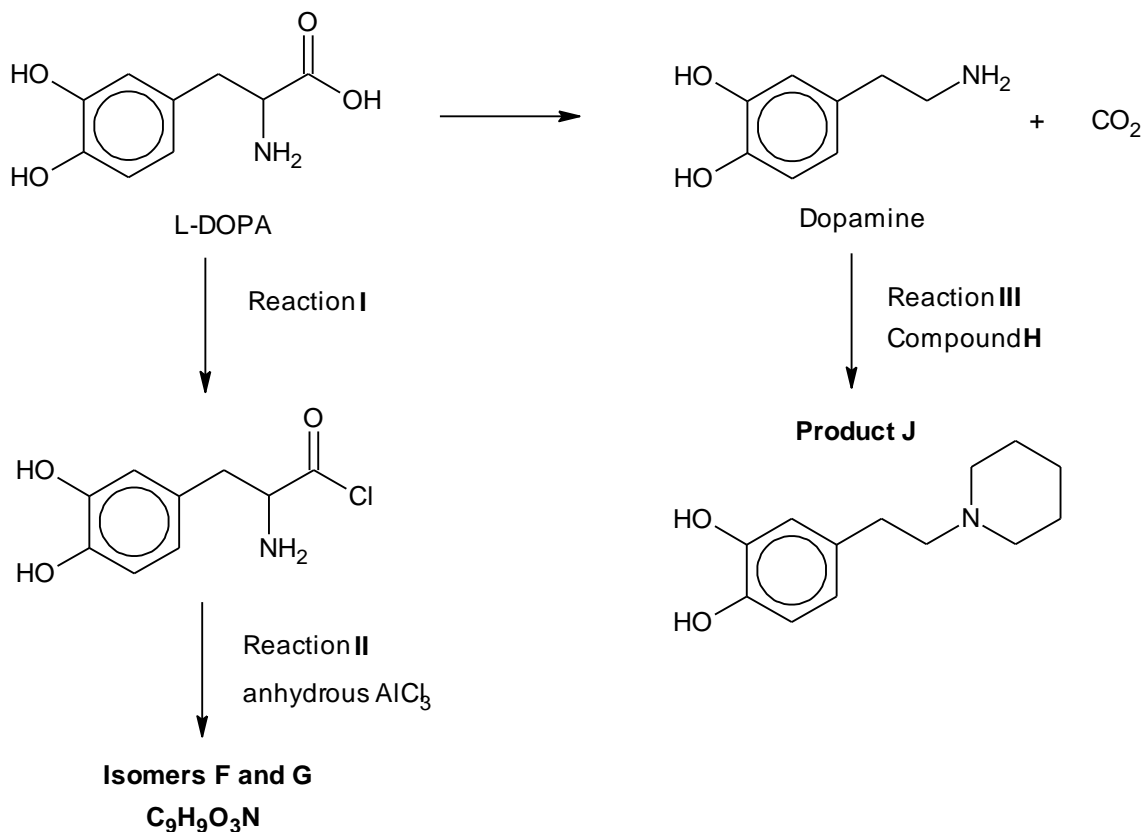


- (d) State the relationship between the Faraday constant, F and the Avogadro's constant, L . [1]
- (e) Using the data above and the *Data Booklet*, calculate a value for Avogadro's constant. [3]
- (f) Ethyne and CO_2 gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected:
- mass of NaOH before experiment = 10.501 g
 - mass of NaOH after experiment = 10.904 g
 - initial reading on syringe = 10.0 cm^3
 - final reading on syringe = 120.0 cm^3
- (i) State the oxidation state of carbon in ethyne. [1]
- (ii) With the help of an equation, explain the purpose of passing the anode gas through NaOH . [1]
- (iii) Calculate the volume of CO_2 produced, assuming r.t.p conditions. [1]
- (iv) Hence, suggest an ionic equation for the reaction that occurred at the anode. [1]
- (g) When aqueous potassium maleate was acidified, maleic acid, $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$ ($\text{p}K_1 = 1.90$ and $\text{p}K_2 = 6.07$) was liberated. Fumaric acid ($\text{p}K_1 = 3.03$ and $\text{p}K_2 = 4.44$) is a stereoisomer of maleic acid. With a suitable illustration, suggest a reason why maleic acid has a lower $\text{p}K_1$ but higher $\text{p}K_2$ than fumaric acid. [2]

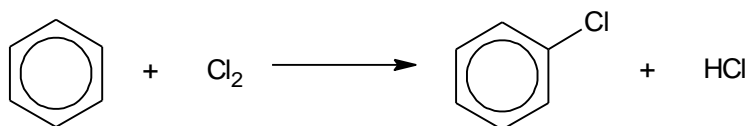
[Total: 20]

- 5(a)** Dopamine is an organic compound of the catecholamine and phenethylamine families that plays several important roles in the brain and body. Its name is derived from its chemical structure: it is an amine synthesised by removing a carboxyl group from a molecule of its precursor compound, L-DOPA.

Below is a synthetic route involving L-DOPA and dopamine:

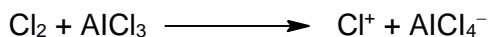


- (i) State the reagents and conditions and any observations in Reaction I. [1]
- (ii) Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.



The reaction occurs in several steps.

- The first step is the reaction between Cl_2 and AlCl_3 .



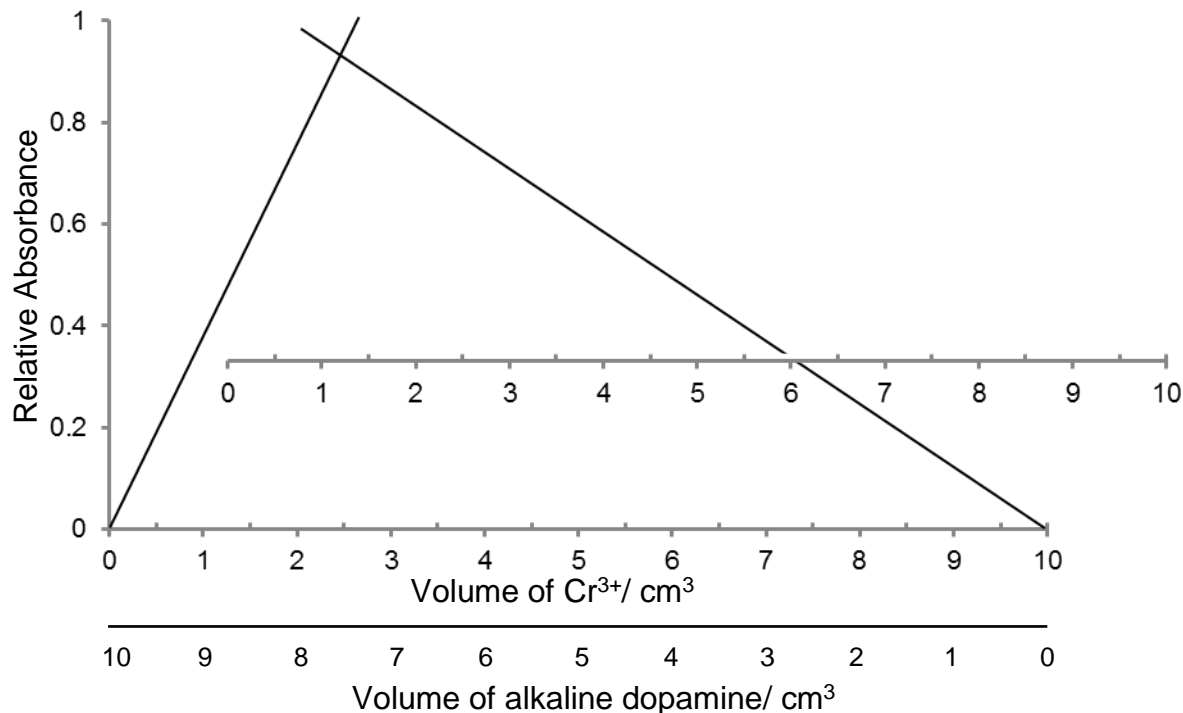
- The benzene ring is then attacked by the Cl^+ cation in the second step. AlCl_3 reacts in a similar way with acyl chlorides, producing a carbocation that can then attack a benzene ring.

Predict the structures of isomers **F** and **G** in Reaction II. [2]

- (iii) In Reaction III, dopamine was reacted with alkyl halide **H** to give the final product **J**. Draw the displayed formula of **H**. [2]

- (b) Dopamine is a bidentate ligand. When different volumes of $0.0030 \text{ mol dm}^{-3}$ of aqueous Cr(III) and $0.0020 \text{ mol dm}^{-3}$ of alkaline dopamine solution were mixed, a complex **R** is formed. Analysis of **R** shows that its formula is $[\text{Cr}(\text{C}_8\text{H}_9\text{NO}_2)_x(\text{H}_2\text{O})_y]^{z-}$, where x , y and z are integers.

To determine the stoichiometry of the complex ion formed, the colour intensities of these different mixtures were measured using a colorimeter. The following absorption spectrum was obtained.



- (i) Use the graph and the information given to determine the formula of complex **R**. Show your workings clearly. [3]
- (ii) The crystal field describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. When the d-orbitals split into high energy and low energy orbitals, the difference in energy of the two levels is denoted as Δ_o . The relationship between Δ_o and colours of complexes can be described in the equation below:

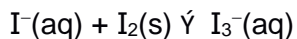
$$\Delta_o = \frac{hc}{\lambda}$$

where h is Planck's constant, c is the speed of light and λ is the wavelength of light absorbed

colour	absorbed λ / nm
violet	410
indigo	430
blue	480
blue-green	500
green	530
yellow	580
orange	610
red	680

Given that Δ_o for complex **R** is $4.125 \times 10^{-22} \text{ kJ}$ and using relevant data from the *Data Booklet*, calculate the wavelength of light. Deduce the colour of complex **R**. [2]

- (c) Iodine is not very soluble in water, it is freely soluble in KI(aq), according to the following equilibrium:



- (i) Draw a fully labelled experimental set-up for a voltaic cell made up of a $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ half-cell and a I_2/I^{-} half-cell under standard conditions. Indicate clearly the anode and cathode and show the flow of electrons. [3]
- (ii) By using appropriate values from the *Data Booklet*, predict what, if anything, will happen when a small amount of acidified vanadium(II) chloride is added to the I_2/I^{-} half-cell. [3]
- (d) Explain the following statements.
- (i) BrF_3 is a covalent compound which exhibits electrical conductivity in liquid state at room temperature. With the aid of an equation, suggest an explanation for its electrical conductivity. [2]
- (ii) SiCl_4 reacts violently in water but CCl_4 has no reaction with water. [1]
- (iii) Compounds NeF_2 and NeF_4 do not exist but XeF_2 and XeF_4 exist. [1]

[Total: 20]