



# Catholic Junior College

## JC2 Preliminary Examination

### Higher 2

CANDIDATE  
NAME

CLASS

2T

INDEX  
NUMBER

## CHEMISTRY

9729/03

Paper 3 Free Response

15 September 2025

2 hours

Candidates answer on the Question Paper.  
Additional Materials: 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.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.  
If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

#### Section A

Answer **all** questions.

#### Section B

Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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.

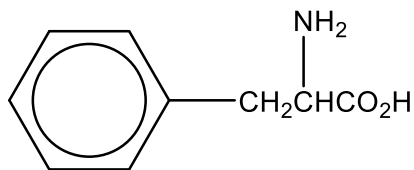
For Examiner's Use		
Section A	Q1	/21
	Q2	/20
	Q3	/19
Section B	Q4	/20
	OR	
	Q5	/20
TOTAL	80	

This document consists of **32** printed pages.

## Section A

Answer **all** the questions in this section.

- 1 (a) Phenylalanine is an essential  $\alpha$ -amino acid with the formula  $C_9H_{11}NO_2$ . It cannot be synthesised by the human body and need to be obtained through diet.



phenylalanine

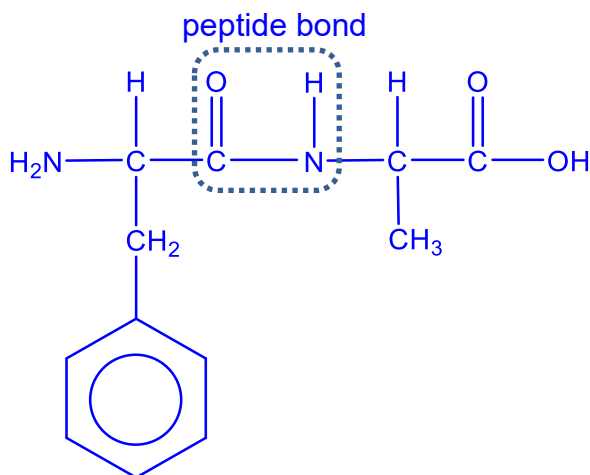
Phenylalanine can react with alanine,  $CH_3CH(NH_2)CO_2H$ , to form a mixture of dipeptides.

- (i) Name the type of reaction when phenylalanine reacts with alanine. [1]
- (ii) State the number of possible different constitutional isomers that can be formed in this reaction. [1]
- (iii) Draw the structures of the constitutional isomers with the molecular formula  $C_{12}H_{16}N_2O_3$  that are formed in this reaction. The peptide bond formed in each constitutional isomer should be shown displayed. [2]

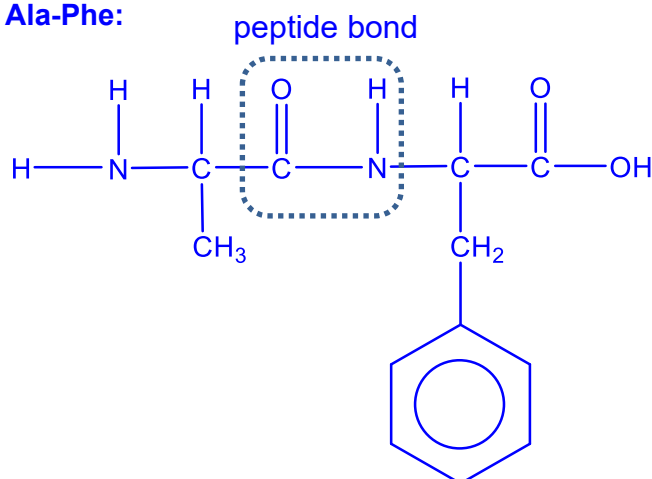
(a)(i) **condensation**

(a)(ii) **2 constitutional isomers**

(a) (iii) **Phe-Ala:**



Ala-Phe:



- (b) Table 1.1 shows the  $pK_a$  values of the different functional groups present in phenylalanine and alanine. Both amino acids exist mainly as zwitterions at pH 7.0.

(i) State what is meant by the term zwitterion. [1]

Table 1.1

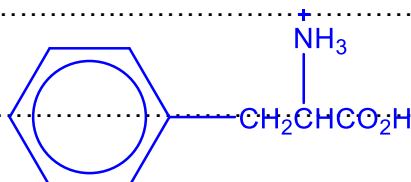
amino acid	$pK_a$ of $\alpha$ -carboxyl group	$pK_a$ of $\alpha$ -amino group
phenylalanine	1.83	9.13
alanine	2.34	9.87

(ii) Draw the predominant species of phenylalanine at pH 1.0. [1]

(iii) Suggest a pH at which the predominant species of alanine has a net negative charge. [1]

(b)(i) Zwitterion is a dipolar ion and has no net charge.

(b)(ii) Phenylalanine at pH 1.0



(b)(iii) pH 10.0

- (c) The position of substitution in the electrophilic substitution of mono-substituted arenes depends on the nature of the group already attached to the ring. This selectivity can be explained based on the stability of the intermediate formed in the first step. Fig. 1.1 shows three isomers **P**, **Q**, **R**, with the same molecular formula,  $C_9H_{11}NO_2$ , as phenylalanine that can be formed from an appropriate starting alkylbenzene.

Use this information to predict which isomer in Fig. 1.1 will be formed the least and which isomer will be formed the most. Explain your reasoning. [3]

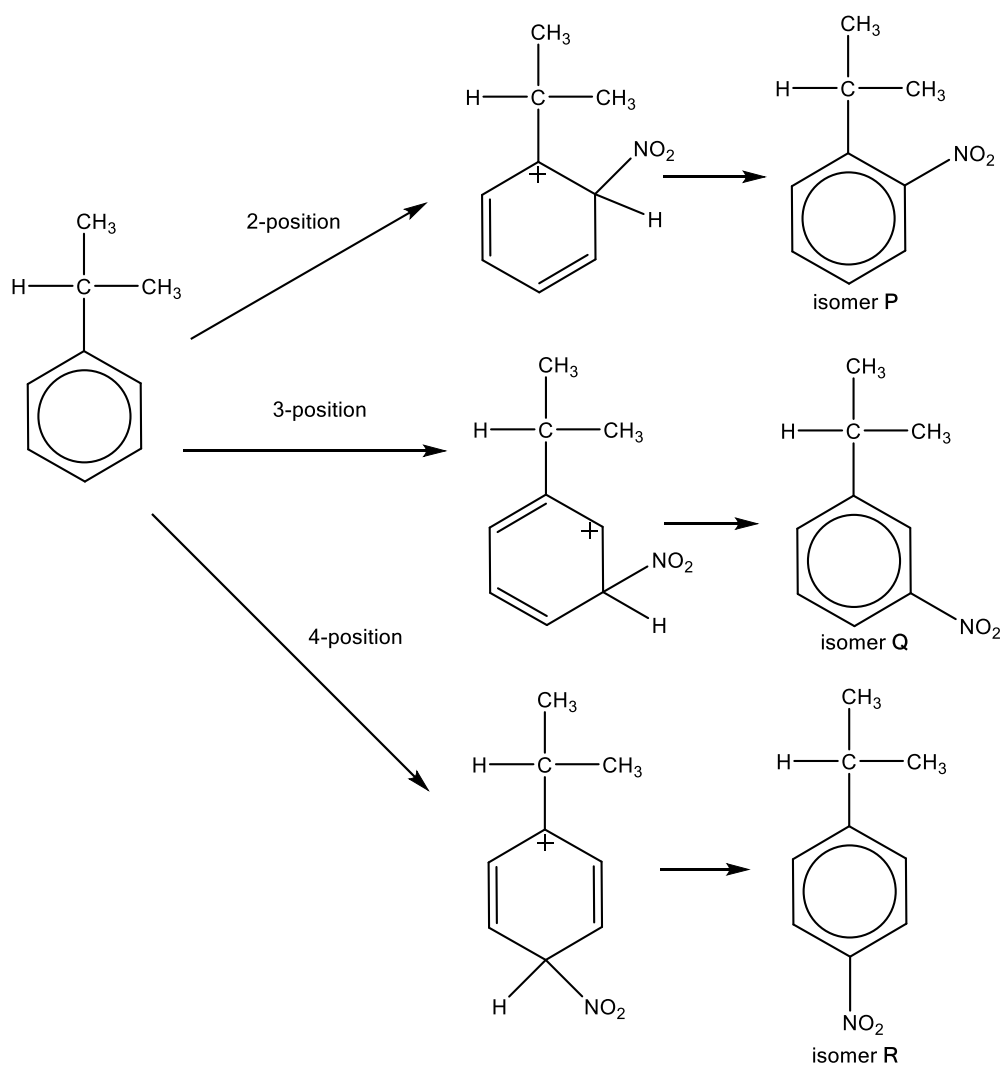


Fig. 1.1

(c) Formed the least: isomer **Q**. Formed the most: isomer **R**

In carbocation of isomer **Q**, the alkyl group which is activating/electron-donating is unable to stabilise the carbocation significantly as the positively charged carbon is not directly bonded to alkyl group, whereas isomers **P** and **R** will be formed as major products because the activating alkyl group is able to stabilize the carbocation as the positively charged carbon is directly bonded to the alkyl group.

However, isomer **R** is likely to be formed the most as it does not have steric hindrance between the  $\text{NO}_2$  and alkyl group, like isomer **P** does.

- (d) Diazonium salts are commonly used to produce synthetic dyes with intense colours that do not occur naturally. The cation of a diazonium salt can be made by reacting an arylamine,  $\text{RNH}_2$ , with nitrous acid,  $\text{HNO}_2$ .

The five stages of the reaction are described in Table 1.2.

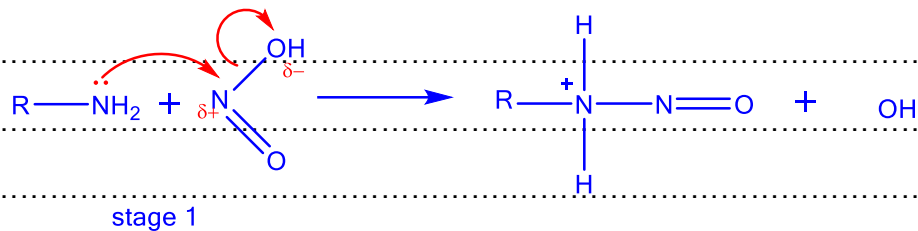
**Table 1.2**

stage	description of stage	equation
1		$\text{R}-\text{NH}_2 + \begin{array}{c} \text{OH} \\ \delta^- \\ \text{N}^{\delta+}=\text{O} \end{array} \longrightarrow \begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}^+-\text{N}=\text{O} \\   \\ \text{H} \end{array} + \text{OH}^-$
2	deprotonation	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}^+-\text{N}=\text{O} \\   \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}-\text{N}=\text{O} \\   \\ \text{H} \end{array} + \text{H}^+$
3	protonation and electron pair movement	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}-\text{N}=\text{O} \\   \\ \text{H} \end{array} + \text{H}^+ \longrightarrow \begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}^+=\text{N}-\text{OH} \\   \\ \text{H} \end{array}$
4	deprotonation and protonation	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}^+=\text{N}-\text{OH} \\   \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}=\text{N}-\text{O}^+ \\   \\ \text{H} \end{array}$
5	Electron pair movement and heterolytic cleavage of N-O bond	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}=\text{N}-\text{O}^+ \\   \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}^+=\text{N} \\   \\ \text{H} \end{array} + \begin{array}{c} \text{H} \\   \\ \text{O} \\   \\ \text{H} \end{array}$

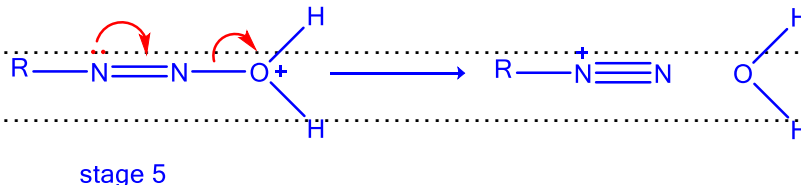
- (i) Name the type of reaction in stage 1. [1]
- (ii) Complete the mechanism in stage 1 by adding a lone pair and curly arrows in Table 1.2. [2]
- (iii) Complete the mechanisms in stage 3 and stage 5 by adding lone pairs and relevant curly arrows. [2]

(d) (i) nucleophilic substitution

(d) (ii)



(d) (iii)



- (e) Describe the variation in the acid-base behaviour of the Period 3 oxides by reference to the reactions of  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  separately with sulfuric acid,  $\text{H}_2\text{SO}_4$ , and with potassium hydroxide,  $\text{KOH}$ .

Write equations for any reactions described.

[6]

(e). Across Period 3, the nature of the oxides changes from basic to amphoteric to acidic.

**MgO** has giant ionic lattice structure and is basic oxide. It reacts readily with acids to give salts and water.



**$\text{Al}_2\text{O}_3$**  is an ionic oxide with partial covalent character.  $\text{Al}^{3+}$ , with its high charge density, will be able to polarise the  $\text{O}^{2-}$  ions to some extent, pulling electron density back to itself, giving rise to some covalent character. It is an amphoteric oxide and reacts with both acids and bases.



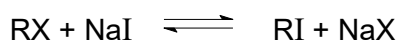
$\text{SiO}_2$  has a giant molecular structure and is acidic oxide. It reacts readily with bases to give salts and water. [1]



[Total: 21]

2 Halogenoalkanes are often used as refrigerants, propellants for aerosols and for generating foamed plastics like expanded polystyrene, and intermediates in the synthesis of polyvinyl chloride.

- (a) Finkelstein reaction involves the replacement of the halogen atom in a halogenoalkane by an iodide ion from a solution of sodium iodide dissolved in propanone. This reaction goes almost to completion and a precipitate of sodium halide is formed as shown below.



A series of experiments can be carried out to determine the order of reaction with respect to a halogenoalkane,  $\text{C}_4\text{H}_9\text{Br}$ , and iodide ion. Different concentrations of  $\text{C}_4\text{H}_9\text{Br}$  and sodium iodide were used, and the following initial rates were obtained in Table 2.1.

Table 2.1

Experiment	$[\text{C}_4\text{H}_9\text{Br}] / \text{mol dm}^{-3}$	$[\text{NaI}] / \text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.04	0.60	$5.68 \times 10^{-5}$
2	0.02	0.30	$1.42 \times 10^{-5}$
3	0.60	0.60	$8.52 \times 10^{-4}$

- (i) The halogenoalkane,  $\text{C}_4\text{H}_9\text{Br}$  which is used in the above reaction, contains a chiral carbon. Deduce a structure for the halogenoalkane. [1]

- (ii) Use the data in Table 2.1 to deduce the order of reaction with respect to each reactant, showing how you arrive at your answers. Hence, write a rate equation for the reaction. [3]
- (iii) Using your answer in (a)(i) and (a)(ii), describe a mechanism that is consistent with your rate equation. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs. [3]

(i)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$

(ii) Let  $\text{rate} = k [\text{C}_4\text{H}_9\text{Br}]^x [\text{I}^-]^y$

Comparing experiments 1 and 3,

$$\frac{\text{rate 1}}{\text{rate 3}} = \frac{k(0.04)^x (0.6)^y}{k(0.6)^x (0.6)^y}$$

$$\frac{5.68 \times 10^{-5}}{8.52 \times 10^{-4}} = \left( \frac{0.04}{0.6} \right)^x$$

$$x = 1$$

$\therefore$  Order of reaction w.r.t.  $\text{C}_4\text{H}_9\text{Br} = 1$

Comparing experiments 1 and 2,

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{k(0.04)^1 (0.6)^y}{k(0.02)^1 (0.3)^y}$$

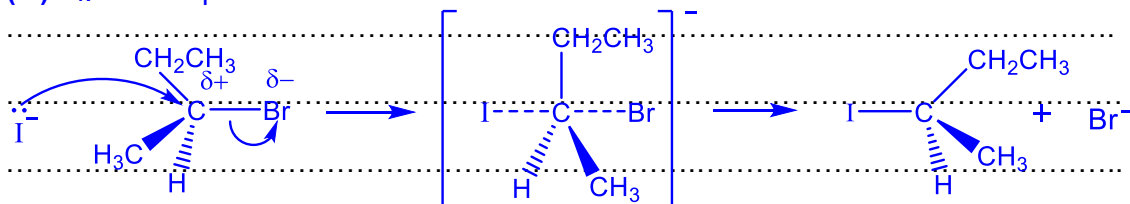
$$\frac{5.68 \times 10^{-5}}{1.42 \times 10^{-5}} = \left( \frac{0.04}{0.02} \right) \left( \frac{0.6}{0.3} \right)^y$$

$$y = 1$$

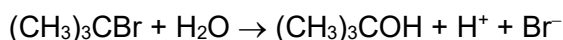
$\therefore$  Order of reaction w.r.t. iodide = 1

$\text{rate} = k [\text{C}_4\text{H}_9\text{Br}] [\text{I}^-]$

(iii)  $\text{S}_{\text{N}}2$  nucleophilic substitution



- (b) The hydrolysis of another isomer, 2-bromo-2-methylpropane takes place as follows.



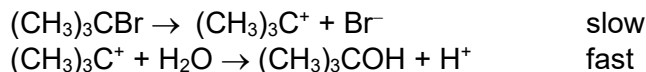
An experiment was conducted to determine the order of reaction with respect to 2-bromo-2-methylpropane. The following results were obtained for the product,  $(\text{CH}_3)_3\text{COH}$ .

time/ s	19	28	50	70	154
$[(\text{CH}_3)_3\text{COH}] / \text{mol dm}^{-3}$	0.0030	0.0040	0.0060	0.0072	0.0095



It was found that the order of reaction with respect to 2-bromo-2-methylpropane is one and the half-life of the reaction is 35 s.

- (i) Using a non-graphical method, show that the concentration of 2-bromo-2-methylpropane at the start of the experiment is  $0.0096 \text{ mol dm}^{-3}$ . [2]
- (ii) Hence, deduce how long the reaction has proceeded when concentration of  $(\text{CH}_3)_3\text{COH}$  obtained is  $0.0084 \text{ mol dm}^{-3}$ . [1]
- (iii) The following mechanism for the above reaction is as shown.



Explain why the mechanism shows an overall first order kinetics. [1]

- (i) The first  $t_{1/2}$  corresponds to the time taken for half the final  $[(\text{CH}_3)_3\text{COH}]$  to be formed, while the sum of two  $t_{1/2}$  corresponds to the time taken for  $\frac{3}{4}$  of the final  $[(\text{CH}_3)_3\text{COH}]$  to be formed.

The  $[(\text{CH}_3)_3\text{COH}]$  at time = 35 s is not given in the table but the  $[(\text{CH}_3)_3\text{COH}]$  at time =  $2 \times 35 = 70 \text{ s}$  is given.

Hence,  $\frac{3}{4} \times \text{final } [(\text{CH}_3)_3\text{COH}] = 0.0072 \text{ mol dm}^{-3}$ ,

$\therefore \text{final } [(\text{CH}_3)_3\text{COH}] = \frac{4}{3} \times 0.0072 = 0.0096 \text{ mol dm}^{-3}$

Since the mole ratio of  $(\text{CH}_3)_3\text{CBr} : (\text{CH}_3)_3\text{COH} = 1:1$  and assuming that the total volume of the reaction mixture remains constant,

$[(\text{CH}_3)_3\text{CBr}]$  at the start of the experiment = final  $[(\text{CH}_3)_3\text{COH}]$   
 $= 0.0096 \text{ mol dm}^{-3}$

- (ii)  $0.0084 = \frac{7}{8} \times 0.0096$

Hence, three half-lives have passed by.

Reaction has proceed for  $3 \times 35 = 105 \text{ s}$

- (iii) In the mechanism, the slow step involves 1 molecule of  $(\text{CH}_3)_3\text{CBr}$ . Hence the rate equation is  $\text{rate} = k[(\text{CH}_3)_3\text{Br}]$  which shows that the reaction is overall first order kinetics.

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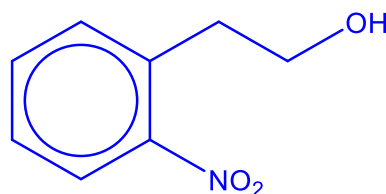
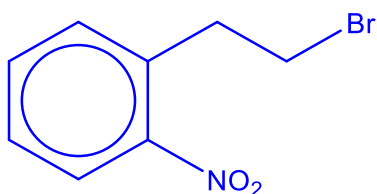
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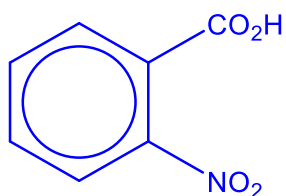
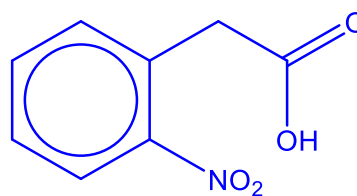
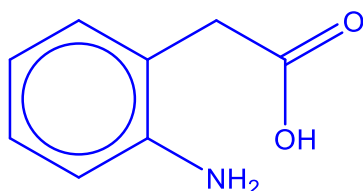
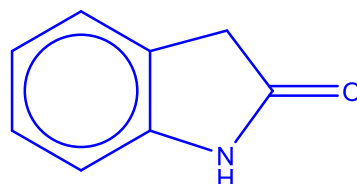
- (c) Compound **J**,  $\text{C}_8\text{H}_8\text{NO}_2\text{Br}$ , is a primary halogenoalkane. **J** undergoes nucleophilic substitution with hot aqueous potassium hydroxide to produce compound **K** which has a molecular formula  $\text{C}_8\text{H}_9\text{NO}_3$ . Compound **K** undergoes side-chain oxidation with hot acidified potassium manganate(VII) to give compound **L**,  $\text{C}_7\text{H}_5\text{NO}_4$  and carbon dioxide gas is produced. **L** produces effervescence with sodium hydrogencarbonate.

Heating compound **K** under reflux with acidified potassium dichromate(VI) gives compound **M**,  $\text{C}_8\text{H}_7\text{NO}_4$ . When compound **M** is treated with tin and concentrated hydrochloric acid, followed by careful neutralisation using an aqueous alkali, a salt of compound **N**,  $\text{C}_8\text{H}_9\text{NO}_2$ , is obtained.

1 mole of compound **N** reacts with 2 moles of aqueous bromine. Treatment of compound **N** with anhydrous phosphorus pentachloride produces compound **O**,  $\text{C}_8\text{H}_7\text{NO}$ .

Suggest the structures of **J** to **O** and explain the reactions that compounds **K**, **L**, **M** and **N** undergo. [9]



**J****K****L****M****N****O**

Reaction	Type of reaction	Deduction
<b>L</b> produces effervescence with sodium hydrogen carbonate.	acid–base reaction	Carboxylic acid group in <b>L</b> reacted with sodium hydrogen carbonate.  <b>L</b> contains carboxylic acid group, –COOH.
Heating compound <b>K</b> under reflux with acidified potassium dichromate(VI) gives compound <b>M</b> , C <sub>8</sub> H <sub>7</sub> NO <sub>4</sub> .	oxidation	gain in 1 O, loss of 2 H ⇒ 1° alcohol in <b>K</b> is oxidised to –COOH in <b>M</b> .
Compound <b>M</b> is treated with tin and concentrated hydrochloric acid, followed careful neutralisation, compound <b>N</b> , C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub> is obtained.	reduction	–NO <sub>2</sub> group in <b>M</b> is reduced to –NH <sub>2</sub> group in <b>N</b> .
1 mole of compound <b>N</b> reacts with 2 moles of aqueous bromine.	Electrophilic substitution	<b>N</b> is a phenylamine. –Br is substituted at positions 2, 4 or 2, 6 w.r.t the –NH <sub>2</sub> group

<p>Treatment of compound <b>N</b> with anhydrous phosphorus pentachloride produces compound <b>O</b>, <math>C_8H_7NO</math>.</p>	<p><b>N</b> is first converted to acyl chloride, by <math>PCl_5</math> via nucleophilic substitution.</p> <p>The acyl chloride formed then undergoes intra-molecular condensation with the <math>-NH_2</math> group to form a cyclic amide <b>O</b>.</p>	<p>The <math>-CH_2COOH</math> group must be adjacent to the <math>-NH_2</math> group in <b>N</b> to enable ring formation/formation of a cyclic amide</p>
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[Total: 20]

- 3 (a) Ammonia in aqueous solution is a Lewis base.  
Explain what is meant by this statement. Illustrate your answer with an equation for a suitable reaction. [2]

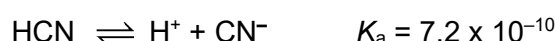
A Lewis base is an electron pair donor.



The N atom in  $\text{NH}_3$  donates a lone pair of electrons to a  $\text{H}^+$  ion from  $\text{HCl}$ , to give  $\text{NH}_4^+$ .

Accept any suitable reaction

- (b) Hydrogen cyanide,  $\text{HCN}$ , is a weak acid.

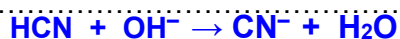


A mixture containing both  $\text{HCN}$  and  $\text{CN}^-$  ions is a useful reagent in organic chemistry.

- (i) What is meant by a buffer solution? Write equations to show clearly how the mixture can act as a buffer solution. [2]

- (ii) Calculate the  $[\text{CN}^-] / [\text{HCN}]$  ratio in such a mixture whose pH is 10.0. [1]

- (i) A buffer solution is one whose pH remains nearly constant when small amount of acid or alkali are added to it (or on dilution).



When a small amount of  $\text{H}^+$  or  $\text{OH}^-$  is added to the buffer solution it is removed.

Hence, the pH of the solution is kept relatively / nearly constant.

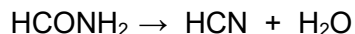
- (ii) Acid buffer,

$$\text{pH} = \text{p}K_a + \lg \frac{[\text{CN}^-]}{[\text{HCN}]}$$

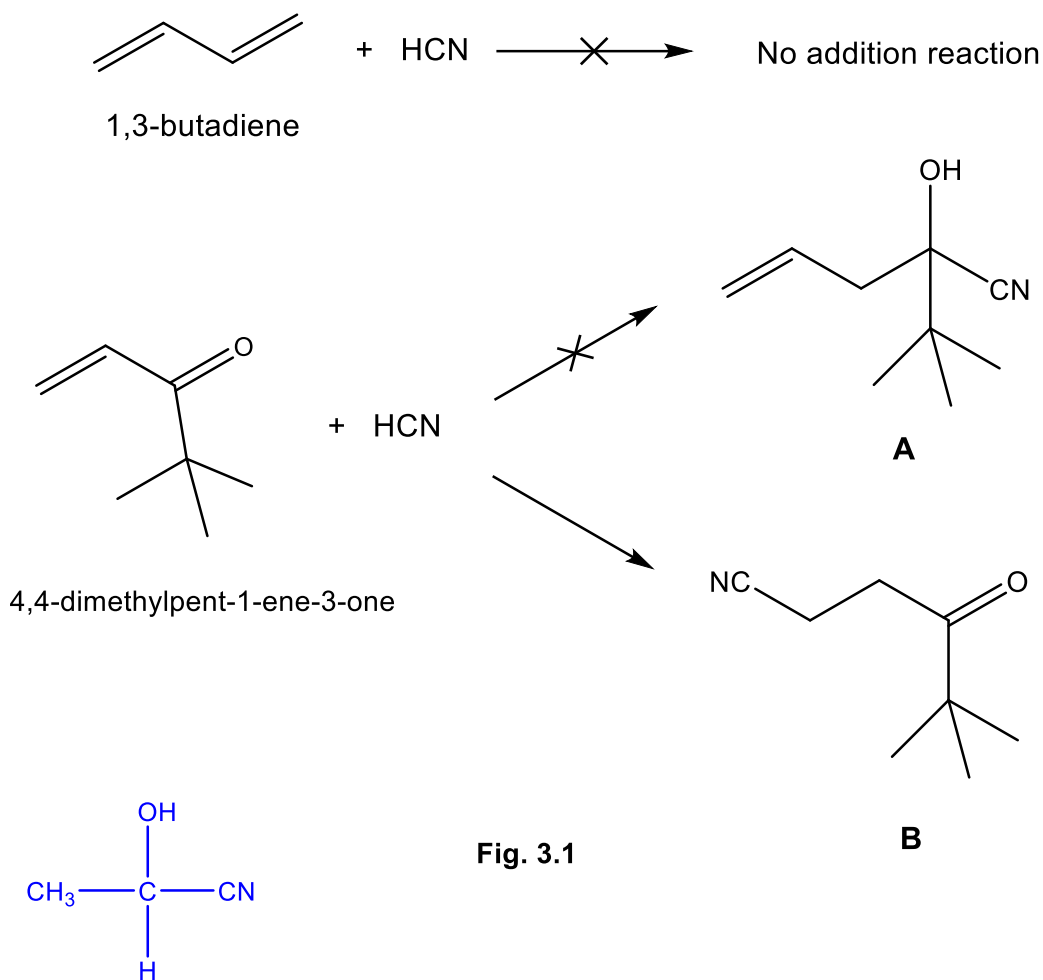
$$10.0 = -\lg(7.2 \times 10^{-10}) + \lg \frac{[\text{CN}^-]}{[\text{HCN}]}$$

$$\frac{[\text{CN}^-]}{[\text{HCN}]} = 7.20$$

- (c) The simplest amide, methanamide,  $\text{HCONH}_2$ , can be dehydrated to hydrogen cyanide,  $\text{HCN}$ .



- (i) Ethanal undergoes nucleophilic addition reaction with  $\text{HCN}$ . Give the product formed for the reaction. [1]
- (ii) In some circumstances, double bonds will undergo a nucleophilic addition reaction. Suggest reasons to explain the figure below. Use the concepts of electronegativity, electronic and steric effects, and delocalisation in your answer. [3]



(i)

- (ii) Nucleophilic addition between 1,3-butadiene and  $\text{HCN}$  does not take place as the  $\text{C}$  atoms in the  $\text{C}=\text{C}$  double bonds have the same electronegativity. Therefore, the  $\text{C}$  atoms do not have a partial positive charge and so are not electron deficient. So, will not be attacked by the  $\text{:CN}^-$  nucleophile.
- (Accept: The  $\pi$  electrons of the  $\text{C}=\text{C}$  double bonds of the diene are delocalised and therefore increases the electron density of  $\text{C}$  atoms so they are not susceptible to attack by the  $\text{:CN}^-$  nucleophile.)

Compound A is not obtained due to presence of the bulky alkyl groups bonded to the carbonyl C atom; thus preventing the attack by the  $\text{:CN}^-$  nucleophile as a result of steric hindrance.

Compound B is formed due to the presence of the adjacent strong electron withdrawing carbonyl functional group which renders the  $\text{C}=\text{C}$  double bond more susceptible to attack by  $\text{:CN}^-$  nucleophile. Nucleophilic addition can occur between the  $\text{C}=\text{C}$  double bond and HCN.

- (d) The hydroxides of Group 2 vary in their solubilities in water.

hydroxide	solubility/ $\text{mol dm}^{-3}$
$\text{Mg(OH)}_2$	$1.6 \times 10^{-4}$
$\text{Ca(OH)}_2$	$2.5 \times 10^{-2}$
$\text{Ba(OH)}_2$	$4.1 \times 10^{-1}$

- (i) Suggest a value for the solubility of strontium hydroxide,  $\text{Sr(OH)}_2$ . [1]

- (ii) Calculate the solubility product,  $K_{\text{sp}}$ , for  $\text{Mg(OH)}_2$ . [1]

- (iii) Given that the  $K_{\text{sp}}$  for  $\text{Ba(OH)}_2$  is  $0.276 \text{ mol}^3 \text{ dm}^{-9}$  and using your answer in **d(ii)**, describe what you would observe if equal volumes of saturated solutions of  $\text{Mg(OH)}_2$  and  $\text{Ba(OH)}_2$  were mixed. Explain your answer with appropriate calculations. [2]

- (i)  $2.0 \times 10^{-1} \text{ mol dm}^{-3}$

(Accept any value between  $2.5 \times 10^{-2}$  and  $4.1 \times 10^{-1} \text{ mol dm}^{-3}$ )

- (ii)  $\text{Mg(OH)}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$

$$1.6 \times 10^{-4} \quad (2 \times 1.6 \times 10^{-4})$$

$$K_{\text{sp}} = [\text{Mg}^{2+}] [\text{OH}^-]^2 = (1.6 \times 10^{-4})(3.2 \times 10^{-4})^2 = 1.64 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$

- (iii) When equal volumes of the two solutions were mixed, the concentration of each solution will be halved.

$$\begin{aligned} \text{IP of Mg(OH)}_2 &= (1.6 \times 10^{-4}/2) [(3.2 \times 10^{-4} + 8.2 \times 10^{-1})/2]^2 \\ &= 1.35 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9} > K_{\text{sp}} \text{ Mg(OH)}_2 \end{aligned}$$

White ppt of  $\text{Mg(OH)}_2$  will be observed.

$$\begin{aligned} \text{IP of Ba(OH)}_2 &= (4.1 \times 10^{-1}/2) [(8.2 \times 10^{-1} + 3.2 \times 10^{-4})/2]^2 \\ &= 0.0345 \text{ mol}^3 \text{ dm}^{-9} < K_{\text{sp}} \text{ Ba(OH)}_2 \end{aligned}$$

No ppt of  $\text{Ba(OH)}_2$  will be observed.

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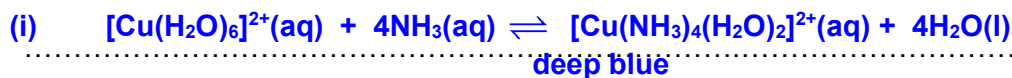


(e) The addition of  $\text{NH}_3(\text{aq})$  to a solution containing  $\text{Cu}^{2+}(\text{aq})$  produces a deep blue solution.

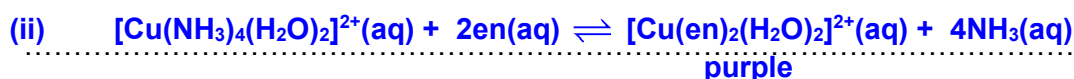
(i) Write an equation for this reaction and state the type of reaction occurring. [2]

(ii) This solution changes from deep blue to purple when the bidentate ligand, **en**, ethane-1,2-diamine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , is added.

Suggest an explanation for this observation and write an equation for the reaction occurring. (The formula of ethane-1,2-diamine can be shortened to **en** in the formulae and equations of your answer.) [2]



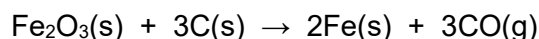
Ligand exchange reaction.



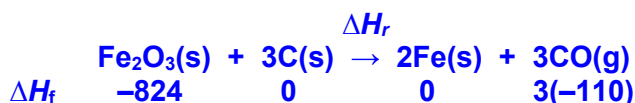
En being a stronger ligand than  $\text{NH}_3$  displaces it to form the purple  $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}(\text{aq})$  complex.

(f) Iron is the most abundant element on Earth, constituting about 80% of the inner and outer cores of Earth. Iron exists in a wide range of oxidation states, although the +2 and +3 states are the most common.

Use the information below to determine the enthalpy change for the following reaction. [2]

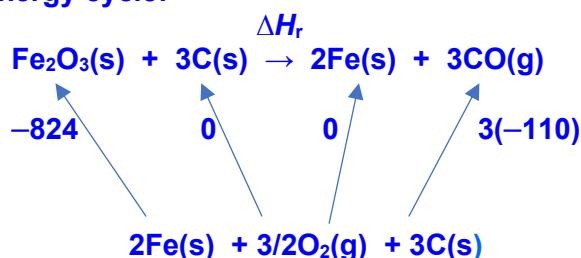


enthalpy change of formation of $\text{Fe}_2\text{O}_3(\text{s})$	$-824 \text{ kJ mol}^{-1}$
enthalpy change of formation of $\text{CO}(\text{g})$	$-110 \text{ kJ mol}^{-1}$



$$\begin{aligned} \Delta H_r &= \Sigma \Delta H_f \text{ of products} - \Sigma \Delta H_f \text{ of reactants} \\ &= [3(-110) + 0] - [(-824) + 0] \\ &= +494 \text{ kJ mol}^{-1} \end{aligned}$$

Or using an energy cycle:



Hess' Law,

$$\begin{aligned} -824 + 0 + \Delta H_r &= 0 + 3(-110) \\ \Delta H_r &= +494 \text{ kJ mol}^{-1} \end{aligned}$$

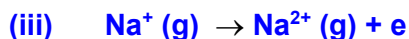
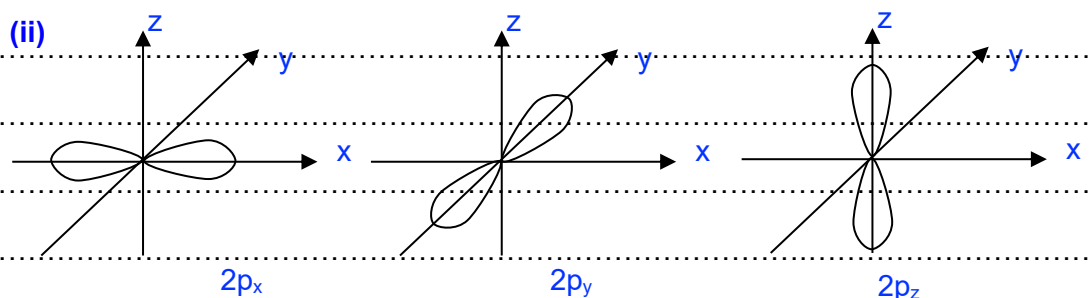
[Total: 19]

## Section B

Answer **one** question in this section.

4 Use of the Data Booklet is relevant to this question.

- (a) (i) State the *spdf* electronic configuration of sodium. [1]
- (ii) Draw and label an orbital from which the second electron of sodium is removed. [1]
- (iii) With the aid of a relevant equation, explain what is meant by the second ionisation energy of sodium. [2]



It is the energy required/absorbed/needed/supplied to remove 1 mole of electrons from 1 mole of gaseous  $Na^+$  ions to form 1 mole of gaseous  $Na^{2+}$  ions.

- (b) Sodium vapour lamp is a gas-discharge lamp that is commonly used in street lighting due to its characteristic yellow-orange hue. These lamps consist of a gas tube containing solid sodium and a small amount of neon gas.

The process of producing light involves the ionisation of gaseous sodium and neon atoms in an electric field.

- (i) Explain why sodium has a lower first ionisation energy than neon. [1]
- (ii) Suggest why the pinkish glow of neon is observed before the orange glow of sodium when the lamp is first turned on. [1]

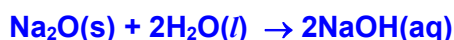


Na has 1 more principal quantum shell than Ne, hence the distance between the nucleus and valence electron is greater.  
Electrostatic attraction between the nucleus and valence electrons is weaker, resulting in a lower energy required to remove the valence electron from Na than in Ne.

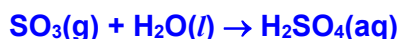
(b)(ii) Na is a solid at room temperature. Hence energy must be absorbed to vaporise/atomise sodium prior to ionisation. When the lamp was first turned on, ionisation of neon takes place first before ionisation of sodium.

- (c) Describe the reactions, if any, of the oxides  $\text{Na}_2\text{O}$  and  $\text{SO}_3$  with water. Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur. [2]

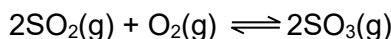
$\text{Na}_2\text{O}$  reacts with water and pH of the resulting solution = 14 (accept 13 or 14)



$\text{SO}_3$  reacts violently with water and pH of the resulting solution = 2



- (d) The manufacture of sulfuric acid involves the reaction between sulfur dioxide and oxygen gas.



When an equimolar mixture of  $\text{SO}_2$  and  $\text{O}_2$  is passed over a catalyst at an initial pressure of 2 atm, the percentage conversion of  $\text{SO}_2\text{(g)}$  is 98%.

- (i) Calculate the equilibrium partial pressure of each of the three gases. [2]
- (ii) Write the expression for the equilibrium constant,  $K_p$ , for this reaction. Use your answer in (d)(i) to calculate the value of  $K_p$  for this reaction including its units. [2]

	$2\text{SO}_2$	$\text{O}_2$	$\rightleftharpoons$	$2\text{SO}_3$
Initial pressure / atm	1	1		0
Change in pressure / atm	$-0.98 \times 1$	$-\frac{1}{2} (0.98)$		+ 0.98
Equilibrium pressure / atm	0.0200	0.510		+ 0.980

$$K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2 (p_{\text{O}_2})}$$

$$K_p = \frac{(0.980)^2}{(0.510)(0.0200)^2} = 4707$$

$$= \underline{4710 \text{ atm}^{-1}}$$

- (iii) Some sulfur dioxide gas was added to the existing equilibrium system to increase the partial pressure of  $\text{SO}_2$  to  $y$  atm at constant temperature. The system was then allowed to establish a new equilibrium. The partial pressure of  $\text{SO}_3$  was found to be 1.50 atm at this new equilibrium.

Calculate the value of  $y$  in atm.

[2]

	$2\text{SO}_2$	$\text{O}_2$	$\rightleftharpoons$	$2\text{SO}_3$
Initial pressure / atm	$y$	0.510		0.980
Change in pressure / atm	- 0.520	- $\frac{1}{2}$ (0.520)		+ 0.520
Equilibrium pressure / atm	$y - 0.520$	0.250		1.50

Since temperature remains constant,  $K_p$  remains constant,

$$K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2 (p_{\text{O}_2})} = 4707$$

$$K_p = \frac{(1.50)^2}{(0.250)(y-0.520)^2} = 4707$$

$$y = 0.5637$$

$$= \underline{0.564}$$

- (e) Explain why benzene has a tendency to undergo substitution reactions rather than addition reactions. [1]

..... Addition reactions on benzene will destroy the extra stability brought about by the delocalisation of the  $\pi$  electron cloud in the benzene ring, thus losing its aromatic character.

..... Benzene undergo substitution reactions under suitable conditions because such reactions retains its resonance-stabilised ring system

- (f) Compound **B** can be synthesised from (3-bromopropyl)benzene in one step as shown in Fig. 4.1 below.

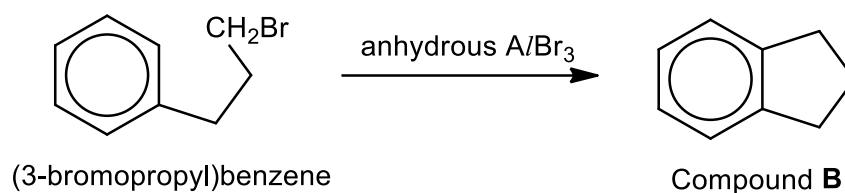
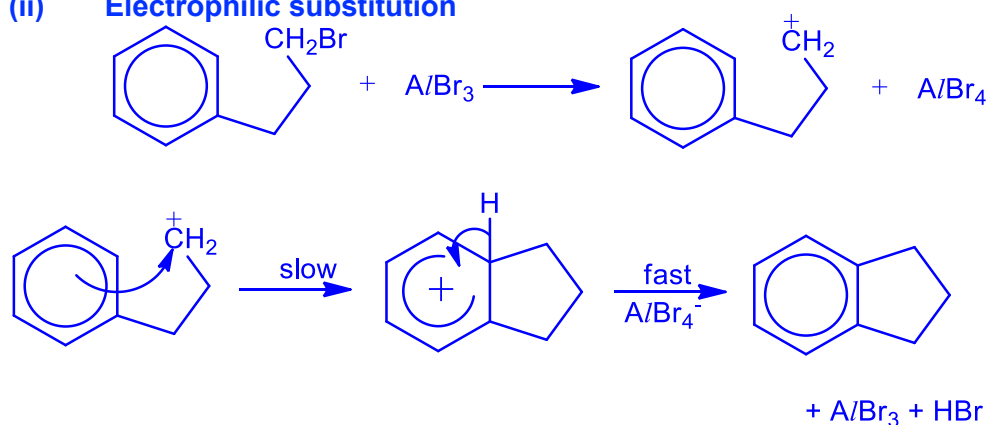


Fig. 4.1

- (i) State the role of Al/Br<sub>3</sub> in this reaction. [1]  
 (ii) Describe the mechanism of the above reaction, including curly arrows to show movement of electrons, and all charges. [4]

(i) Lewis Acid catalyst

(ii) Electrophilic substitution



[Total: 20]

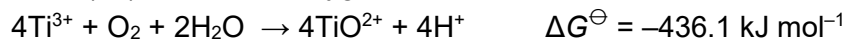
5 Titanium is a transition element, commonly found as  $\text{TiO}_2$  in minerals.

(a) When  $\text{TiO}_2$  reacts with an excess of sulfuric acid,  $\text{TiO}^{2+}$  ion is formed.  $\text{TiO}^{2+}$  can be reduced to form a purple solution containing  $\text{Ti}^{3+}(\text{aq})$ .

(i) Construct the half-equation for the reduction of  $\text{TiO}^{2+}$  to  $\text{Ti}^{3+}$  in acidic conditions. [1]

(ii) Explain why  $\text{Ti}^{3+}(\text{aq})$  is violet. [3]

(iii) Acidified  $\text{Ti}^{3+}(\text{aq})$  reacts with oxygen dissolved in water as shown.



Calculate  $E^\ominus_{\text{cell}}$  for the above reaction and hence determine the standard reduction potential of  $\text{TiO}^{2+}(\text{aq})/\text{Ti}^{3+}(\text{aq})$ . [2]

(i)  $\text{TiO}^{2+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{Ti}^{3+} + \text{H}_2\text{O}$

(ii) In the presence of  $\text{H}_2\text{O}$  ligands, the partially filled degenerate d-orbitals of  $\text{Ti}^{3+}$  split into 2 groups of non-degenerate d orbitals with a small energy gap. In the presence of visible light, d electron in a d orbital of lower energy absorbs energy in the yellow region and is promoted to the higher energy  $\text{d}^*$  orbital via d-d\* electronic transition. The complementary violet colour will then be observed as the colour of  $\text{Ti}^{3+}(\text{aq})$ .

(iii)  $\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$  ( $n = 4$ )

$$E^\ominus_{\text{cell}} = -436100 / -4(96500) = +1.13 \text{ V}$$

$$E^\ominus_{\text{cell}} = E^\ominus(\text{O}_2|\text{H}_2\text{O}) - E^\ominus(\text{TiO}^{2+}|\text{Ti}^{3+}) = 1.23 - E^\ominus(\text{TiO}^{2+}|\text{Ti}^{3+}) \text{ [subst +1.23V]}$$

$$\therefore E^\ominus(\text{TiO}^{2+}|\text{Ti}^{3+}) = +0.10\text{V}$$

.....

.....

.....

.....

.....

.....

.....

.....

- (b) Gold is an unreactive metal that can only be oxidised under specific conditions. Some relevant half-equations and their standard electrode potentials are given.

	half-equation	$E^{\ominus} / \text{V}$
1	$\text{Au}^{3+}(\text{aq}) + 3\text{e}^{-} \rightleftharpoons \text{Au}(\text{s})$	+1.50
2	$[\text{AuCl}_4]^{-}(\text{aq}) + 3\text{e}^{-} \rightleftharpoons \text{Au}(\text{s}) + 4\text{Cl}^{-}(\text{aq})$	+1.00
3	$\text{NO}_3^{-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 3\text{e}^{-} \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+0.96

- (i) Draw a fully labelled diagram of the experimental set-up used to measure the standard cell potential,  $E^{\ominus}_{\text{cell}}$ , of  $\text{Au}^{3+}(\text{aq})/\text{Au}(\text{s})$  and  $\text{HNO}_3(\text{aq})/\text{NO}(\text{g})$ . Include all necessary chemicals. [2]

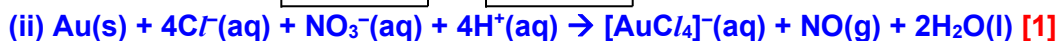
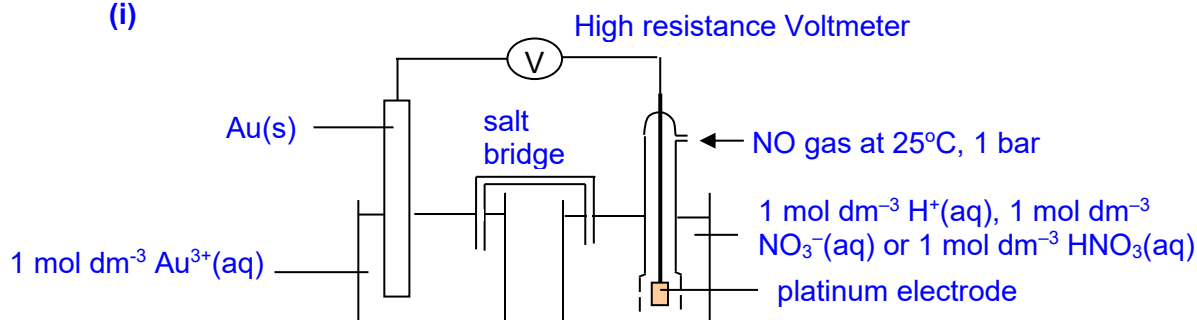
- (ii) Gold can be only oxidised by a mixture of concentrated hydrochloric acid and concentrated nitric acid, known as aqua regia.

Using the half-equations 2 and 3, construct a balanced equation for the reaction and explain why it would be expected that this redox reaction would **not** occur if it is carried out under standard conditions. [2]

- (iii) In fact, gold dissolves when the concentration of hydrochloric acid is  $12 \text{ mol dm}^{-3}$  and the concentration of nitric acid is  $16 \text{ mol dm}^{-3}$ .

State and explain what effect the use of concentrated hydrochloric acid and concentrated nitric acid in aqua regia have on the electrode potential,  $E$  values, of half-equations 2 and 3 respectively and thus the overall  $E_{\text{cell}}$ . [2]

(i)



$E^\ominus_{\text{cell}} = 0.96 - 1.00 = -0.04 \text{ V}$  Since  $E^\ominus_{\text{cell}}$  is **negative**, reaction **does not occur**

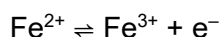
(iii) adding conc  $\text{HNO}_3$  increases concentration of  $\text{H}^+$  and  $\text{NO}_3^-$  and shifts position of equilibrium 3 to the right,  $E_{\text{HNO}_3(\text{aq})/\text{NO(g)}}$  more positive

adding conc  $\text{HCl}$  increase concentration of  $\text{Cl}^-$  and shifts position of equilibrium 2 to the left,  $E_{[\text{AuCl}_4]^-(\text{aq})/\text{Au(s)}}$  less positive or more negative

New  $E_{\text{cell}}$  becomes more positive and hence gold dissolves

- (c) An impure sample of  $\text{BaC}_2\text{O}_4$ , of mass 0.500 g, is added to 50.0 cm<sup>3</sup> of 0.020 mol dm<sup>-3</sup> acidified  $\text{MnO}_4^-$  (aq), which is in excess. A redox reaction occurs and all the  $\text{BaC}_2\text{O}_4$  reacts. The resulting solution, containing unreacted acidified  $\text{MnO}_4^-$  is then titrated with 0.050 mol dm<sup>-3</sup>  $\text{Fe}^{2+}(\text{aq})$ .

The end-point is reached when 26.80 cm<sup>3</sup> of 0.050 mol dm<sup>-3</sup>  $\text{Fe}^{2+}(\text{aq})$  has been added.



Calculate the percentage by mass of  $\text{BaC}_2\text{O}_4$  in the 0.500 g impure sample. Show your working. [ $M_r$ :  $\text{BaC}_2\text{O}_4$ , 225.3]

initial moles of  $\text{MnO}_4^- = 0.0200 \times 50/1000 = 1.00 \times 10^{-3}$

[3]

moles of  $\text{Fe}^{2+} = 0.050 \times (26.80/1000) = 1.34 \times 10^{-3}$

moles of  $\text{MnO}_4^-$  (reacted with  $\text{Fe}^{2+}$ ) =  $1.34 \times 10^{-3} / 5 = 2.68 \times 10^{-4}$

moles  $\text{MnO}_4^-$  reacted with  $\text{BaC}_2\text{O}_4 = 1.00 \times 10^{-3} - 2.68 \times 10^{-4} = 7.32 \times 10^{-4}$

moles  $\text{C}_2\text{O}_4^{2-}$  reacted =  $7.32 \times 10^{-4} \times 5/2 = 1.83 \times 10^{-3}$

mass of  $\text{BaC}_2\text{O}_4 = 225.3 \times 1.83 \times 10^{-3} = 0.412 \text{ g}$

% Purity of  $\text{BaC}_2\text{O}_4 = 100 \times 0.412/0.50 = 82.5\%$





- (d) The reaction of phenylethanone with 1,4-dibromobutane,  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  in the presence of  $\text{FeBr}_3$  is shown below in Fig. 5.1.

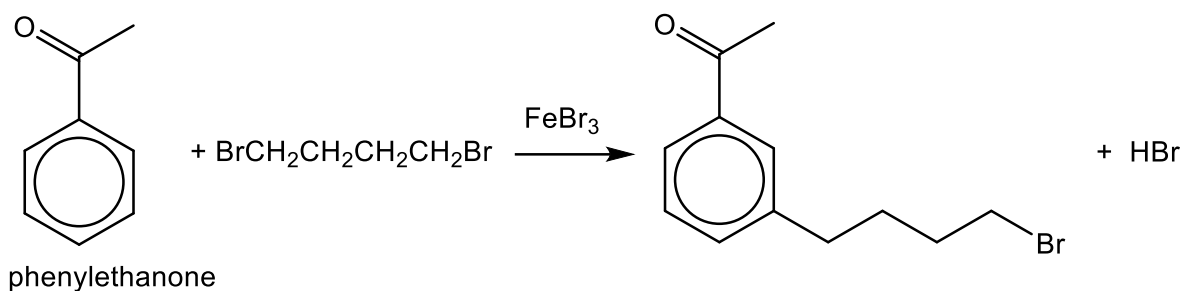
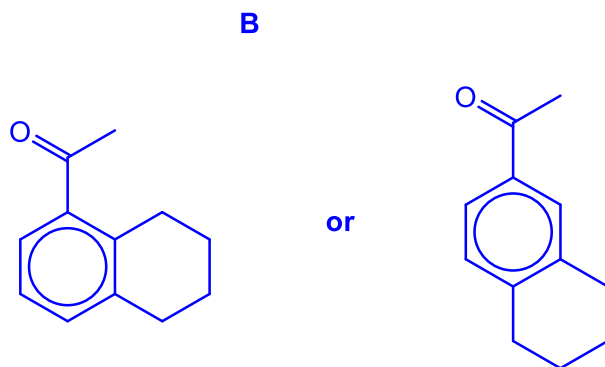
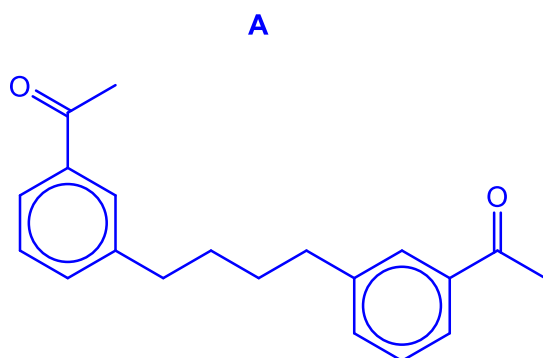


Fig. 5.1

The mechanism of this reaction is similar to that of the alkylation of benzene.

- (i) The reaction forms small amounts of two by-products, **A** ( $\text{C}_{20}\text{H}_{22}\text{O}_2$ ) and **B** ( $\text{C}_{12}\text{H}_{14}\text{O}$ ). Suggest structures for **A** and **B**. [2]



- (ii) Compound **F** can be synthesised from benzene in three steps by the route shown in Fig. 5.2. Give the structure of intermediate compounds **D** and **E** and the reagents and conditions for step 2. [3]

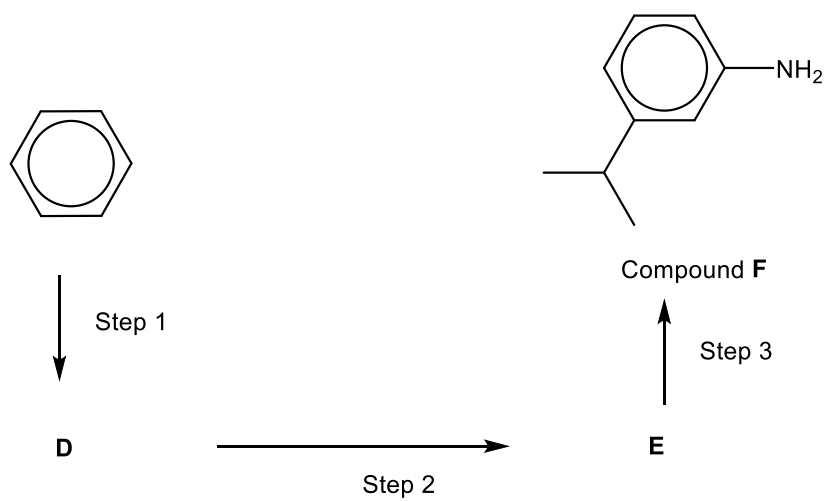


Fig. 5.2

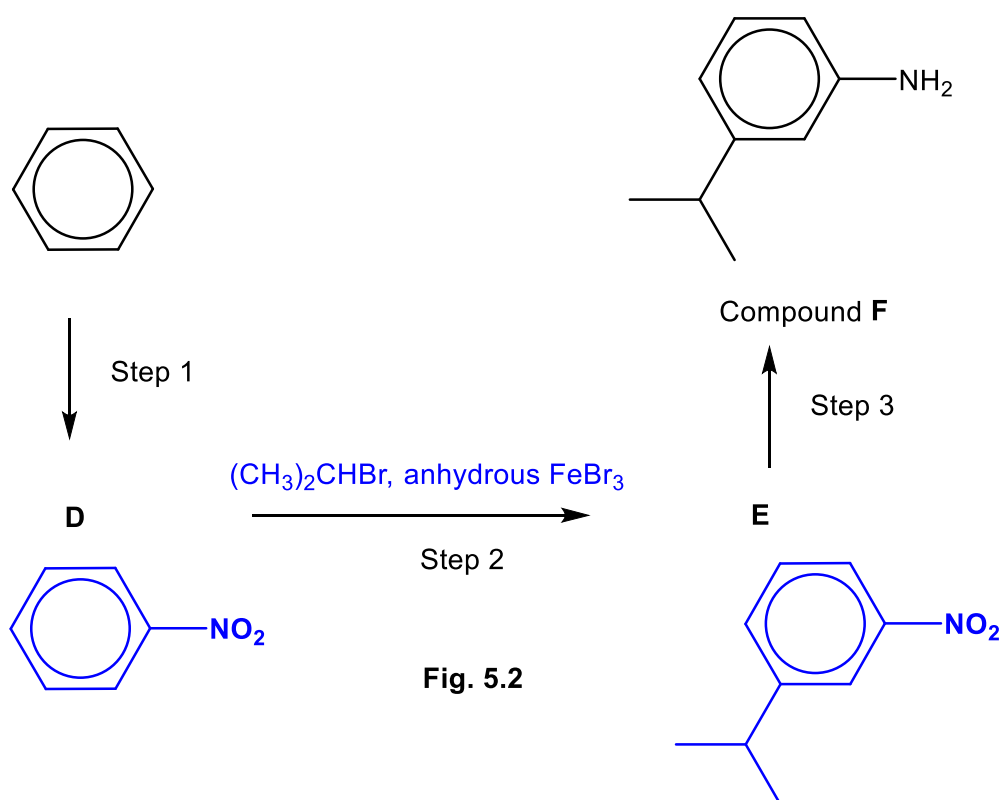


Fig. 5.2

[Total: 20]

Additional answer space

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