



**Catholic Junior College**  
**JC 2 Preliminary Examinations**  
**Higher 2**

CANDIDATE  
 NAME

CLASS

**CHEMISTRY**

**9729/01**

Paper 1 Multiple Choice

18 September 2025  
 1 hour

Additional Materials: Multiple Choice Answer Sheet  
 Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write in soft pencil.

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

Write your name, class and NRIC/FIN number on the Answer Sheet in the spaces provided.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

**WORKED SOLUTIONS**

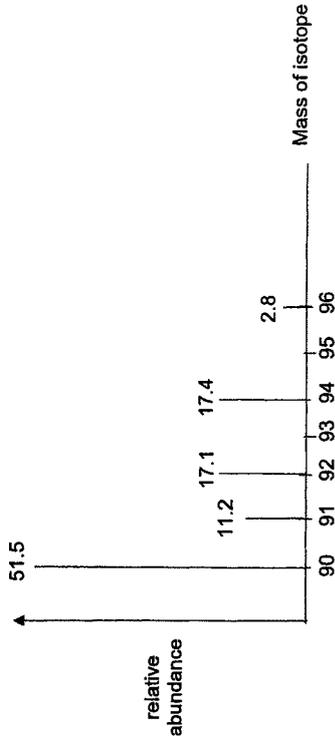
This document consists of 28 printed pages.

9729/01 CJC JC2 Preliminary Examination 2025

[Turn over

2

1 The relative abundances of all the isotopes present in a sample of zirconium are shown.



What is the relative atomic mass of zirconium calculated from these data?

- A 91.1    B 91.3    C 91.6    D 93.1

Topic: Atomic Structure

$$A_r \text{ of Zr} = \frac{51.5(90) + 11.2(91) + 17.1(92) + 17.4(94) + 2.8(96)}{100} = 91.3$$

Answer: B

2 In the interhalogen compound  $ICl_3$ , there is a single polar covalent bond.

Which of the following statement(s) helps to explain the polarity of the I–Cl covalent bond?

- 1 Cl is more electronegative than I.  
 2 The outer shell electronic configuration of both elements is  $s^2 p^6$ .  
 3 The outer shell electrons are more shielded from nuclear charge in I than they are in Cl.

- A 1, 2 and 3    B 1 and 2    C 1 and 3    D 1 only

Topic: Chemical Bonding

Polarity of a covalent bond depends on the electronegativity differences between two atoms.

Electronegativity is a measure of the ability of an atom to attract the bonding electrons.

Option 1: True; Cl is more electronegative than I.

Option 2: True but does not explain why the bond is polar.

Option 3: True; hence the attraction exerted by the nucleus of I on the shared pair of electrons is weaker than that of Cl.

Answer: C

9729/01 CJC JC2 Preliminary Examination 2025

3 In which pairs of compounds does the first molecule have a smaller bond angle than that in the second molecule?

- 1  $\text{NF}_3$   $\text{CCl}_4$   
 2  $\text{H}_2\text{S}$   $\text{H}_2\text{O}$   
 3  $\text{SF}_6$   $\text{CS}_2$
- A 1, 2 and 3    B 1 and 2    C 2 and 3    D 3 only

Topic: Chemical Bonding

molecule	shape	bond angle	molecule	shape	Bond angle
1 $\text{NF}_3$	trigonal pyramidal	107°	$\text{CCl}_4$	tetrahedral	109°
2 $\text{H}_2\text{S}$	bent	92° due to central S atom being less electronegative than O in $\text{H}_2\text{O}$	$\text{H}_2\text{O}$	bent	105°
3 $\text{SF}_6$	octahedral	90°	$\text{CS}_2$	linear	180°

Answer: A

4 The table shows the boiling point of three alcohols.

	boiling point / °C
pentan-1-ol	138
2-methylbutan-2-ol	129
2,2-dimethylpropanol	114

What is responsible for the differences in boiling point?

- A different relative molecular mass  
 B different number of carbon-carbon bonds  
 C weaker hydrogen bonding between branched chain molecules  
 D more extensive instantaneous dipoles-induced dipoles attractions between straight chain molecules

Topic: Chemical Bonding

- A False; all three alcohols are isomers with the same relative molecular mass  
 B False; same number of carbon-carbon bonds in the three isomers  
 C False; strength of intermolecular hydrogen bonding in the straight chain and branched chain isomers are similar since all three isomers, on average, will form the same number of hydrogen bonds per molecule (since each molecule consist of 1 -OH group).  
 D True; more extensive instantaneous dipoles-induced dipoles attractions between straight chain molecules (due to larger surface area of contact between the molecules).

Answer: D

5 Which statements about the behaviour of Group 17 elements from chlorine to iodine are correct?

- A The elements become stronger oxidising agents.  
 B The volatility of the elements decreases.  
 C The thermal stability of the hydrogen halides increases.  
 D The bond energy of H-X bond increases.

Topic: The Periodic Table

- A False; the elements become weaker oxidising agents from chlorine to iodine as there is a lower tendency for  $\text{X}_2$  to reduce to  $\text{X}^-$ .  
 B True; The volatility of the elements decreases down the group. As the number of electrons of the halogen molecules increases, the instantaneous dipoles induced dipoles (id-id) forces of attractions between the halogen molecules increases. Larger amount of energy is required to overcome the stronger id-id forces of attractions, resulting in higher boiling point and hence lower volatility.  
 C False; the thermal stability of the hydrogen halides decreases from H-Cl to H-I as the bond energy of H-X bond decreases, hence the ease of breaking H-X bond increases, resulting in lower thermal stability.  
 D False; the bond energy of H-X bond decreases from H-Cl to H-I due to less effective overlap of orbitals as the valence orbital used in bonding becomes bigger and more diffused from chlorine to iodine.

Answer: B

6 0.10 mol of an oxide of nitrogen ( $\text{N}_x\text{O}_y$ ) is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.

The water produced in this reaction has a mass of 7.2 g.  
 The ammonia produced requires 200  $\text{cm}^3$  of 1.0  $\text{mol dm}^{-3}$  HCl for complete neutralisation.

What is the formula of this oxide of nitrogen?

- A  $\text{N}_2\text{O}$     B NO    C  $\text{NO}_2$     D  $\text{N}_2\text{O}_5$

**Topic: The Mole Concept and Stoichiometry**

Let the oxide of nitrogen be  $N_xO_y$ .

Amt of water formed when 0.10 mol of the oxide reacted =  $\frac{7.2}{18.0} = 0.400$  mol

No of O atoms in  $N_xO_y$ ,  $y = \frac{0.400}{0.100} = 4$

Amt of HCl required for neutralisation =  $\frac{200}{1000} \times 1.0 = 0.200$  mol = amt of  $NH_3$  formed.

No of N atoms in  $N_xO_y$ ,  $x = \frac{0.200}{0.100} = 2$

Hence oxide of nitrogen is  $N_2O_4$ .

**Answer: D**

unbalanced equation:  $N_xO_y + H_2 \rightarrow NH_3 + H_2O$

Amounts / mol: 0.1 0.2 0.4

Hence:  $1N_xO_y + H_2 \rightarrow 2NH_3 + 4H_2O$

where x and y can be derived via inspection

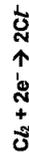
- 7 Sodium thiosulfate is used in the textile industry to remove an excess of chlorine from bleaching processes by reducing it to chloride ions.

One mole of thiosulfate ions,  $S_2O_3^{2-}$ , is able to remove 4 moles of chlorine,  $Cl_2$ , in this process. In this process,  $S_2O_3^{2-}$  is oxidised. What is the resultant sulfur-containing product in this reaction?

- A  $HSO_4^-$  B  $S_4O_6^{2-}$  C  $SO_2$  D S

**Topic: The Mole Concept and Stoichiometry (Redox)**

Half equation involving chlorine:



Hence, 4 moles of  $Cl_2$  would gain  $8e^-$ .

This means that 1 mole of  $S_2O_3^{2-}$  loses  $8e^-$ . (one S atom loses  $4e^-$ )

Oxidation state of S in  $S_2O_3^{2-} = +2$

Final OS of S in the product =  $+2 - (-4) = +6$

OS of S in

(A)  $HSO_4^-$  (+6) answer

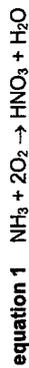
(B)  $S_4O_6^{2-}$  (+2.5)

(C)  $SO_2$  (+4)

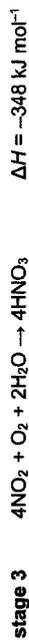
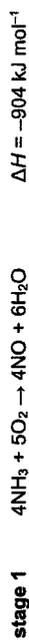
(D) S (0)

**Answer: A**

- 8 Nitric acid is made industrially by the oxidation of ammonia. The overall equation for the process is shown.

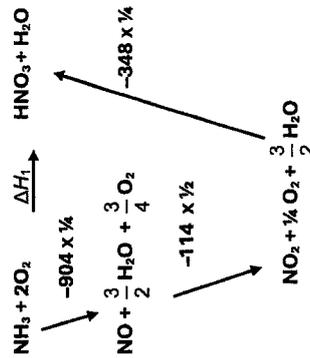


The process happens in three stages. The equations and enthalpy changes for these stages are given.

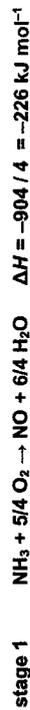


What is the enthalpy change of the process shown in equation 1?

- A  $-1480 \text{ kJ mol}^{-1}$   
 B  $-370 \text{ kJ mol}^{-1}$   
 C  $-341.5 \text{ kJ mol}^{-1}$   
 D  $+82 \text{ kJ mol}^{-1}$

**Topic: Energetics (Energy cycle and Hess' Law)**

$$\begin{aligned}
 \Delta H_1 &= -904 \times \frac{1}{4} + -114 \times \frac{1}{2} + -348 \times \frac{1}{4} \\
 &= -370 \text{ kJ mol}^{-1}
 \end{aligned}$$

**Alternative method (Mathematical method)**

Summing up the above 3 equations gives equation 1.

Hence  $\Delta H_1 = -226 + (-57) + (-87) = -370 \text{ kJ mol}^{-1}$

**Answer: B**

- 9 A radioactive element has 2 isotopes, G and H, with half-lives of 3 days and 6 days respectively. An experiment starts with 4 times as many atoms of G as of H.

Given that radioactive decay is a first-order reaction, how long will it be before the number of atoms of G left equals the number of atoms of H left?

- A 12 days      B 15 days      C 24 days      D 48 days

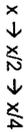
**Topic: Kinetics (first order reactions and half-life)**

Let the number of atoms of G be  $4x$  and the number of atoms of H be  $x$ .

Radioactive decay for G after 12 days (4 half-lives of 3 days):



Radioactive decay for H after 12 days (2 half-lives of 6 days):



G goes through 4 half-lives (12 days) before it can have the same amount of atoms as H at the same time.

**Answer: A**

- 10 The kinetics of the reaction between hydrogen peroxide and acidified iodide ions were investigated.

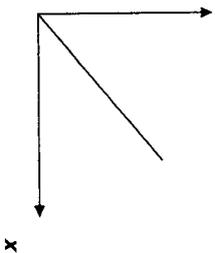


The rate equation was found to be rate =  $k[\text{H}_2\text{O}_2][\text{I}^-]$

Which of the following shows the correct labelling of the x-axis for Graph I and y-axis for Graph II?

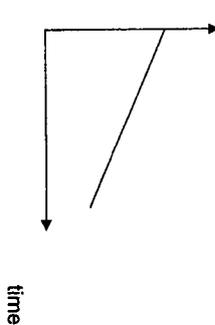
**Graph I**

rate of reaction



**Graph II**

y



x-axis for Graph I

y-axis for Graph II

- A  $[\text{I}^-]$        $[\text{H}_2\text{O}_2][\text{I}^-]$   
 B  $[\text{H}^+]$        $[\text{I}_2]$   
 C  $[\text{H}_2\text{O}_2][\text{I}^-]$        $[\text{H}^+]$   
 D  $[\text{H}_2\text{O}_2][\text{H}^+]$        $[\text{I}^-]$

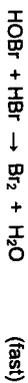
**Topic: Kinetics (shapes of graphs)**

**Graph I** : Rate =  $k[\text{H}_2\text{O}_2][\text{I}^-]$  (similar to  $y=mx$  graph)

**Graph II** : gradient of the graph shows that rate is independent of reactant I.  $\text{H}^+$  is not involved in the rate equation and thus zero order wrt  $\text{H}^+$ .

**Answer: C**

- 11 The reaction between HBr and  $\text{O}_2$  is thought to occur via a multi-step mechanism:



The overall reaction is  $4\text{HBr} + \text{O}_2 \rightarrow 2\text{Br}_2 + 2\text{H}_2\text{O}$ .

Which statement is correct?

- A The overall order of reaction is 3.  
 B  $\text{HO}_2\text{Br}$  is the only intermediate in the reaction.  
 C HOBr acts as a catalyst in the reaction.  
 D ~~Units of the rate constant is  $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$~~

**Topic: Kinetics (reaction mechanism, units of rate constant)**

Rate =  $k[\text{HBr}][\text{O}_2] \Rightarrow$  overall order of reaction is 2

$\text{HO}_2\text{Br}$  and HOBr are the intermediates in the reaction (they do not appear in the overall equation).

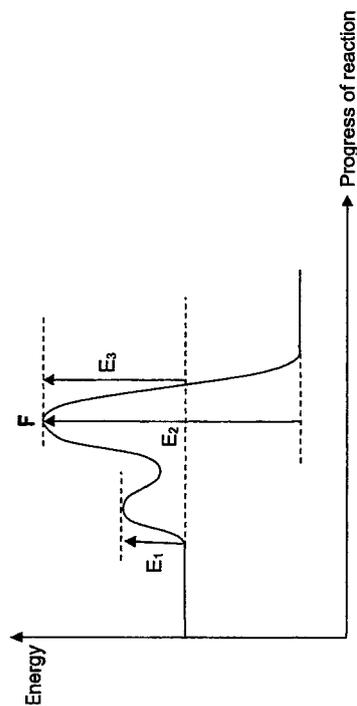
HOBr is not a catalyst as it is not regenerated.

$k = \text{rate} / [\text{HBr}][\text{O}_2]$

units of  $k = \text{mol dm}^{-3}\text{s}^{-1} / (\text{mol dm}^{-3})^2$   
 $= \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$

**Answer: D**

- 12 Which of the following statements is true about the following energy profile for a catalysed reaction shown below?



- 1 The reaction is catalysed by a heterogeneous catalyst.
- 2 The enthalpy change of the reaction is  $E_3 - E_2$ .
- 3 F is the intermediate formed.
- 4 The second step of the reaction is the rate determining step.

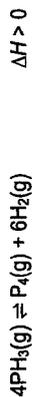
A 2 and 3    B 2 and 4    C 1 only    D 4 only

Topic: Kinetics (energy profile diagram, rate determining step and catalyst).

- 1 is wrong. The profile of the graph matches a two-step reaction. This is characteristic of a homogeneous catalyst which occurs via an intermediate.
- 2 is true. The enthalpy change of the reaction is  $E_3 - E_2$  to give the correct sign and magnitude.
- 3 is wrong as F is the transition state for Step 2 of the reaction, not the intermediate.
- 4 is true. The second step has a larger  $E_a$ , hence it is more likely to be the rate determining step compared to the first step.

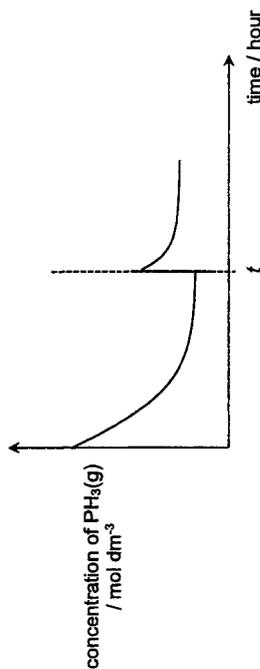
Answer: B

- 13 Phosphine,  $\text{PH}_3$ , decomposes to give phosphorus and hydrogen gas.



The graph below shows the change in concentration of  $\text{PH}_3$  over time until the reaction mixture reaches equilibrium at a constant temperature of 400 K.

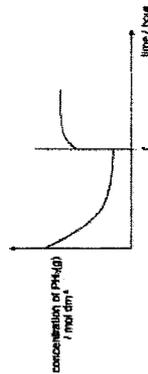
Which of the following is a possible change made at  $t$  hour?



- A reduction of volume of the vessel
- B addition of  $\text{PH}_3$
- C removal of  $\text{P}_4$
- D addition of a catalyst

Topic: Chemical equilibrium, Le Chatelier's principle

Option A: The reduction of volume (increase in overall pressure) will cause  $\text{PH}_3$  to have a sharp increase at time  $t$  as shown. However, the increase in overall pressure will result in the position of equilibrium shifting to the left to produce fewer moles of gas. This will increase in concentration of  $\text{PH}_3$  after time  $t$ , and the graph should look like this:



Option B is correct as concentration of  $\text{PH}_3$  will increase at time  $t$  and position of equilibrium shifts right leading to a subsequent decrease in its concentration.

Option C is wrong as removal of  $\text{P}_4$  will not lead to a drastic increase in concentration of  $\text{PH}_3$  at time  $t$ .

Option D is wrong as addition of a catalyst does not lead to a shift in position of equilibrium.

Answer: B

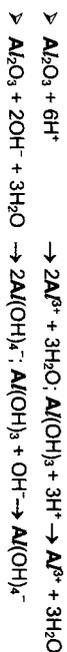
14 Which statement about the chemical properties of the oxides in the third period of the Periodic Table is true?

- A  $\text{Na}_2\text{O}$  and  $\text{MgO}$  can be mixed in water to give an approximately neutral solution.  
 B  $\text{Al}_2\text{O}_3$  is soluble in both  $\text{KOH}$  and  $\text{HCl}$ .  
 C  $\text{SO}_3$  is insoluble in water.  
 D  $\text{SiO}_2$  forms a solution of pH 2 when dissolved in water at room temperature.

Topic: The Periodic Table

Option A: False.  $\text{Na}_2\text{O}$  and  $\text{MgO}$  are basic and dissolve in water to give an alkaline solution ( $\text{NaOH}$  and  $\text{Mg(OH)}_2$ ). Moreover,  $\text{MgO}$  is sparingly soluble only.

Option B: True.  $\text{Al}_2\text{O}_3$  is amphoteric. It reacts with  $\text{KOH}$  to give  $\text{Al(OH)}_4^-$  and  $\text{HCl}$  to give  $\text{AlCl}_3$ , hence  $\text{Al}_2\text{O}_3$  does dissolve in both  $\text{KOH}$  and  $\text{HCl}$ .



Option C: False.  $\text{SO}_3$  dissolves in water to give  $\text{H}_2\text{SO}_4$ .  $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

Option D: False.  $\text{SiO}_2$  giant covalent and hence is insoluble in water, therefore the pH of solution will be 7.

15 Which one of the following statements about the behaviour of the Group 2 elements from magnesium to barium is correct?

- A They become weaker reducing agents.  
 B The electronegativity increases.  
 C The thermal stability of the metal carbonate increases.  
 D The enthalpy change of hydration of the ions become more exothermic.

Topic: The Periodic Table

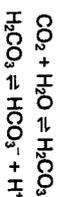
Option A and B: Incorrect. Down the group, due to increasing size and an increase in shielding effect (due to increasing number of electron shells), the nucleus has lower attraction for the valence electrons (electronegativity decreases). As a result, the tendency for the element to lose the valence electrons increases, and therefore the reducing power increases.

Option C: Correct. Down the group, the size of cation increases, thus charge density decreases, leading to lower polarising power of the cation. As a result, the  $\text{CO}_3^{2-}$  ion is polarised to a smaller extent, C—O bond weakened to a smaller extent and harder to break. Decomposition of the metal carbonate occurs with greater difficulty hence thermal stability increases.

Option D: Incorrect. Down the group, the size of cation increases, thus charge density decreases. The hydration energy of an ion is proportional to the charge density of the ion. The ion-dipole attractions formed between the ions and water molecules become increasingly weaker, and thus the hydration energy becomes less exothermic.

Answer: C

16 The concentration of carbon dioxide in the blood is regulated by the following equilibria.



During exercise, the production of lactic acid decreases the pH of blood. Which statements about these equilibria are correct when this happens?

1. The positions of both equilibria shift.

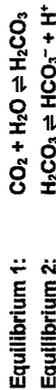
2.  $[\text{H}^+]$  decreases.

3.  $\text{HCO}_3^-$  acts as a Bronsted-Lowry acid.

- A 1 only      B 2 only      C 1 and 3 only      D 1, 2 and 3

**Topic: Chemistry of Aqueous Solutions**

When the pH of blood decreases, the  $[H^+]$  increases. (Option 2 is wrong)



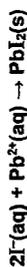
When  $[H^+]$  increases,  $HCO_3^-$  will accept the  $H^+$  ( $HCO_3^-$  is a Bronsted-Lowry base, hence option 3 is wrong). Position of eqm 2 will shift left to decrease the amount of  $H^+$ . This will result in an increase in  $H_2CO_3$ . Subsequently, eqm 1 will respond by shifting left as well. (Option 1 is correct.)

Answer: A

- 17 Equal volumes of aqueous KI and  $0.200 \text{ mol dm}^{-3}$  of  $Pb(NO_3)_2$  are mixed together to precipitate  $PbI_2$ . Given that the  $K_{sp}$  value of  $PbI_2$  is  $8.70 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$ , which one of the following could have been the initial concentration of KI?

- A  $8.70 \times 10^{-9} \text{ mol dm}^{-3}$   
 B  $2.95 \times 10^{-4} \text{ mol dm}^{-3}$   
 C  $5.50 \times 10^{-4} \text{ mol dm}^{-3}$   
 D  $1.50 \times 10^{-2} \text{ mol dm}^{-3}$

**Topic: Chemistry of Aqueous Solutions**



For precipitation of  $PbI_2$  to occur, ionic product  $[Pb^{2+}][I^-]^2$  must be greater than the

$K_{sp}$  value of  $PbI_2$ .  $\Rightarrow [Pb^{2+}][I^-]^2 > K_{sp}$

Let  $x$  be  $[I^-]_{\text{initial}}$

$$\frac{0.200}{2} \times \left(\frac{x}{2}\right)^2 > 8.70 \times 10^{-9}$$

$$[I^-]_{\text{initial}} > 5.90 \times 10^{-4} \text{ mol dm}^{-3}$$

Option D is the only one that has a value higher than  $5.90 \times 10^{-4} \text{ mol dm}^{-3}$

Answer: D

- 18 Which of the following reactions is ammonia acting as a Bronsted-Lowry base?

- A  $NH_3 + HF \rightleftharpoons NH_4^+ + F^-$   
 B  $NH_3 + CH_3Br \rightarrow CH_3NH_2 + HBr$   
 C  $4NH_3 + [Cu(H_2O)_6]^{2+} \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$   
 D  $NH_3 + BC l_3 \rightarrow NH_3 \cdot BC l_3$

**Topic: Theories of Acids and Bases involving concepts from multiple topics**

A:  $NH_3$  is behaving as a Bronsted-Lowry base as it accepts a proton,  $H^+$  from  $HF$  to form  $NH_4^+$ .

B:  $NH_3$  is behaving as a Lewis base where it donates a pair of electrons to electron deficient C atom in  $CH_3Br$  in a nucleophilic substitution ( $S_N2$ ) reaction.

C:  $NH_3$  is behaving as a Lewis base where it donates a pair of electrons to  $Cu^{2+}$  in a ligand displacement reaction.

D:  $NH_3$  is behaving as a Lewis base where it donates a pair of electrons to electron deficient B atom in  $BCl_3$  to form a tetrahedral adduct.

Answer: A

- 19 Which statement about benzene and cyclohexene is correct?

- A Both are planar molecules.  
 B Both possess delocalised  $\pi$  electrons.  
 C Both decolourise aqueous bromine in the presence of finely divided iron.  
 D Both undergo complete combustion give the same products.

**Topic: Properties of Alkenes vs Arenes**

A: Cyclohexene is not planar, it has four  $sp^3$ -hybridised carbon atoms which are tetrahedral about each of them.

B: Only benzene has delocalised electrons where the six  $\pi$  electrons are delocalised over the six carbon atoms in the structure. The two  $\pi$  electrons in cyclohexene are localised between two  $sp^2$ -hybridised carbon atoms.

C: Cyclohexene decolorises orange-red aqueous bromine at room temperature in an electrophilic addition reaction but benzene decolorises reddish-brown liquid bromine upon warming with  $Fe(s)$  or  $FeBr_3(s)$  under anhydrous conditions.

D: Carbon dioxide and water will be formed from complete combustion.

Answer: D

- 20 Ocimenes are a group of isomeric hydrocarbons with a sweet herbal scent and are commonly used in perfumes. The structure of one of its isomers is shown below.



$\beta$ -ocimene

Which statements are correct?

- 1  $\beta$ -ocimene has a total of four stereoisomers.
- 2  $\beta$ -ocimene reacts with HBr to produce a major product containing two chiral centres.
- 3  $\beta$ -ocimene undergoes both electrophilic addition and free radical substitution in the presence of excess bromine in the dark.
- 4  $\beta$ -ocimene reacts with cold dilute alkaline potassium manganate(VII) to produce a major product with six  $-OH$  groups.

A 1 and 3      B 2 and 4      C 1, 2 and 3      D 1, 2, 3 and 4

Topic: Alkenes



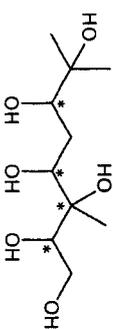
- 1: Incorrect. Only one C=C can exhibit cis-trans isomerism, hence total number of stereoisomers in  $\beta$ -ocimene =  $2^1 = 2$  stereoisomers.

- 2: Correct – The major product as shown below has 2 chiral centres.



- 3: Incorrect. Free radical substitution of bromine requires UV light to react with  $\beta$ -ocimene.

- 4: Correct. The product of mild oxidation produces 6-OH groups.



Answer: B – similar to 2018/P2/Q3(b)(ii); 2019/P3/Q3(d)(ii); 2013/P3/4(a)

- 21 Methylbenzene reacts with bromine chloride,  $BrCl$ , in different ways, depending on the conditions used. A reaction is carried out using an excess of methylbenzene in the absence of sunlight and in the presence of an iron-containing catalyst.

What is the main reaction taking place?

- A substitution of one bromine atom into the  $-CH_3$  side-chain
- B substitution of one chlorine atom into the  $-CH_3$  side-chain
- C substitution of one bromine atom into the benzene ring
- D substitution of one chlorine atom into the benzene ring

Topic: Arenes

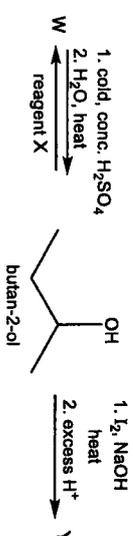
Electrophilic substitution of the benzene ring with the electrophile  $Br^+$  being generated in the presence of an Iron-containing catalyst, which then attacks the C atom in the benzene ring.

In absence of sunlight (uv light), FRS of the side-chain cannot take place. So, A and B are incorrect.

$Cl^+$  is not the electrophile as it is more electronegative than Br as can be seen from  $Br-Cl$ . So, D can be ruled out.

Answer: C

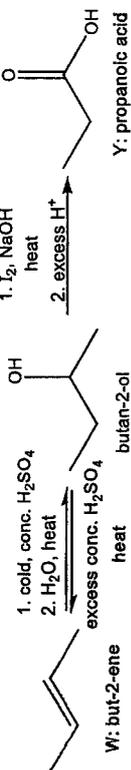
- 22 The diagram shows reactions involving butan-2-ol.



Which row correctly identifies the unknown compounds and reagents?

	W	reagent X	Y
A	2-chlorobut-2-ene	$PCl_5$	butanoic acid
B	but-2-ene	ethanolic KOH	propanoic acid
C	2-chlorobutane	$PCl_5$	butanoic acid
D	but-2-ene	conc. $H_2SO_4$	propanoic acid

**Topic: Reactions of alcohols**



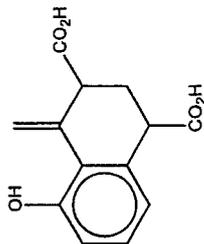
2-chlorobutane is not a possible answer for W as it does not undergo electrophilic addition with steam to form butan-2-ol.

Ethanoic KOH is not a possible answer for reagent X as it is only used for the elimination of halogenoalkane to an alkene.

Mild oxidation with iodine in alkaline media reduces the number of carbon atom by 1 to generate propanoic acid. Hence, butanoic acid is not produced as compound Z.

Answer: D

23 Compound A dissolves in heavy water,  $\text{D}_2\text{O}$ , to form compound B. Compound B contains a number of hydrogen atoms which can be replaced by deuterium, D. [D, deuterium =  ${}^2_1\text{H}$ ]



Compound A

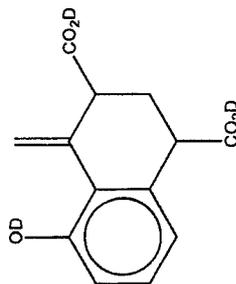
What is the maximum number of deuterium atoms present in one molecule of compound B?

- A 1      B 2      C 3      D 4

**Topic: Acidity of Carboxylic Acids and Phenols**

When compound A is dissolved in  $\text{D}_2\text{O}$ , the following reactions will take place:

- proton exchange of the 2 acidic functional groups (phenol and carboxylic acid)



Compound B

Answer: C

- 24 Methanal, HCHO is the simplest aldehyde. Which statements about methanal is correct?

- All four atoms in methanal lie in the same plane.
- The carbon atom in methanal has an oxidation number of 0.
- Complete combustion of 1 mol of methanal requires 1 mol of oxygen gas.

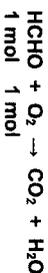
A 1, 2 and 3      B 1 and 2      C 2 and 3      D 1 only

Topic: Carbonyl Compounds

Methanal is trigonal planar in shape, the central C atom is  $sp^2$  hybridised.



The O.N. of C = 0 since the O.N. of H is +1 and that of O is -2. The molecule is not charged.



Answer: A (1, 2, 3 are correct)

- 25 A liquid P is sparingly soluble in water. It dissolves readily in cold hydrochloric acid. Evaporation of this solution yields a crystalline solid. Which could be P?

A  $\text{C}_6\text{H}_5\text{COCH}_3$       B  $\text{C}_6\text{H}_5\text{CONH}_2$       C  $\text{C}_6\text{H}_5\text{NH}_2$       D  $\text{C}_6\text{H}_5\text{OH}$

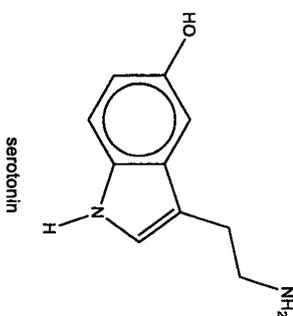
Topic: Nitrogen compounds

Liquid P is sparingly soluble in water since it contains the hydrophobic phenyl group,  $\text{C}_6\text{H}_5$ . P dissolves readily in cold hydrochloric acid, suggesting that it is basic. Only phenylamine is basic, and a very soluble ionic salt,  $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-(\text{aq})$  is formed as neutralisation takes place. The crystalline solid,  $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-(\text{s})$  is produced upon evaporation of the aqueous solution.

The ketone, amide are neutral and phenol is acidic so they do not react with cold HCl.

Answer: C

- 26 Serotonin is a neurotransmitter molecule.



Which one of the following reagents will not react with serotonin?

- A  $\text{CH}_3\text{COCl}$   
 B HCl  
 C NaOH  
 D  $\text{PCl}_5$

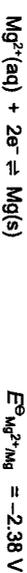
Topic: Organic Reactions with different functional groups

$\text{CH}_3\text{COCl}$  reacts with the amines and phenols to give the corresponding amides and esters. HCl undergoes EA reaction with the alkene; it also reacts with the basic amines via neutralisation. NaOH reacts with acidic phenol.

$\text{PCl}_5$  does not react with any of the functional groups present in serotonin. In addition, no reaction with phenol due the partial C—O double bond arising as a result of the overlapping of the p-orbital of the oxygen atom with the  $\pi$  orbitals of the carbon atoms of the benzene ring. So, there is no reaction involving cleavage of C—O bond.

Answer: D

- 27 A voltaic cell is set up using the  $\text{Mg}^{2+}/\text{Mg}$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-cells.



Under standard conditions, the cell e.m.f. would be 3.15 V. However, the voltmeter recorded a reading of 3.05 V.

What is the best explanation for this lower e.m.f.?

- a higher concentration of  $\text{Fe}^{3+}$  was used
- a higher concentration of  $\text{Mg}^{2+}$  was used
- a smaller magnesium electrode was used

A 1 only      B 2 only      C 1 and 2 only      D 1, 2 and 3

**Topic: Electrochemistry [modified from 2021 CJC Prelim]**

- incorrect – a higher concentration of  $\text{Fe}^{3+}$  would result in an even greater tendency for reduction, so  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}$  becomes more positive, and cell e.m.f. becomes more positive as well.
- correct – a higher concentration of  $\text{Mg}^{2+}$  shifts the position of equilibrium of  $\text{Mg}^{2+}/\text{Mg}$  to the right.  $E_{\text{Mg}^{2+}/\text{Mg}}$  becomes less negative and cell e.m.f. becomes less positive.
- incorrect – changing the size of the electrode does not shift the position of equilibrium.

Answer: B

**28 Use of the Data Booklet is relevant to this question.**

The table below shows the properties of four metals K, Ca, Cr and Ga. Which set of properties belong to Cr?

	melting point / °C	density / g cm <sup>-3</sup>
A	1860	7.19
B	30	5.91
C	63	0.86
D	842	1.55

**Topic: Transition Elements**

	melting point / °C	density / g cm <sup>-3</sup>	Element
A	1860	7.19	Cr
B	30	5.91	Ga
C	63	0.86	K
D	842	1.55	Ca

Transition elements have higher melting points because the 3d and 4s electrons are involved in delocalisation in metallic bonding (due to their proximity in energies). For main group metals, eg For s-block elements, only the s electrons are involved in delocalisation in metallic bonding. Hence, larger amount of energy is required to overcome the stronger electrostatic forces of attraction between the cations and the sea of delocalised electrons in transition elements.

Transition elements are denser than main group metals because transition metals have: Relatively smaller atomic radius, hence a closer-packed structure. Higher relative atomic mass, hence higher mass per unit volume.

Answer: A

**29 Which statement best explains why the  $[\text{TiCl}_6]^{2-}$  complex ion is expected to be colourless?**

- The 3d subshell of the transition metal ion is empty.
- Electrons from the lower energy level absorb energy outside the visible spectrum.
- There is a large energy gap between the non-degenerate orbitals.
- There is no d-orbital splitting in the transition metal ion.

**Topic: Transition Elements**

The electronic configuration of Ti is  $[\text{Ar}]3d^2 4s^2$ .

The oxidation state of Ti in  $[\text{TiCl}_6]^{2-}$  is +4.

The electronic configuration of Ti in the +4 oxidation state is  $[\text{Ar}]3d^0 4s^0$

The 3d (and 4s) subshells are empty.

The d – d\* electronic transition cannot take place because of the absence of electrons, even though the orbitals are expected to split into two non-degenerate levels.

Answer: A

**30 The cathode of an electrolytic cell is a square piece of copper with dimensions 0.1 m x 0.1 m. The electrolyte is copper(II) sulfate.**

Assume that each copper atom occupies a cube of length  $3.0 \times 10^{-12}$  m, the piece of copper has no thickness and that there is a uniform coverage.

How long will it take a current of 4.0 A to cover both sides of the piece of copper with new copper to a total of depth of 1000 atoms?

- A 178 s    B 24.7 h    C 49.4 h    D 98.9 h

**Topic: Electrochemistry**

The surface area on one side of the copper piece =  $(0.1 \times 0.1) = 0.01 \text{ m}^2$

The surface area of one copper atom on one side =  $(3.0 \times 10^{-12})^2 = 9.0 \times 10^{-24} \text{ m}^2$

Number of copper atoms to cover one side with depth of a single atom

$$= \frac{0.01}{9.0 \times 10^{-24}} = 1.11 \times 10^{21}$$

Total number of copper atoms to cover two sides with depth of 1000 atoms each =  $(1.11 \times 10^{21} \times 2 \times 1000) = 2.22 \times 10^{24}$

Amount of copper atoms to be deposited =  $\frac{2.22 \times 10^{24}}{6.02 \times 10^{23}} = 3.69 \text{ mol}$

At the cathode,  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$

Amount of electrons required =  $(3.69 \times 2) = 7.38 \text{ mol}$

$Q = (7.38 \times 9.65 \times 10^4) = 7.12 \times 10^5 \text{ C}$

$Q = I \times t$

$$t = \frac{7.12 \times 10^5}{4.0} = 1.78 \times 10^5 \text{ s}$$

$$= \left( \frac{1.78 \times 10^5}{60 \times 60} \right)$$

$$= 49.4 \text{ h}$$

Answer: C





(ii) By using the standard enthalpy change of formation,  $\Delta H_f^\circ$  values given below, calculate the standard Gibbs free energy change,  $\Delta G^\circ$ , in  $\text{kJ mol}^{-1}$  for the reaction of  $(\text{CH}_3)_2\text{N}_2\text{H}_2$  with  $\text{N}_2\text{O}_4$  at 298 K

substance	$(\text{CH}_3)_2\text{N}_2\text{H}_2(\text{l})$	$\text{N}_2\text{O}_4(\text{l})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$\Delta H_f^\circ / \text{kJ mol}^{-1}$	+48.9	-19.6	-393.5	-241.8

$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$= [2(-393.5) + 0 + 4(-241.8)] - [(+48.9) + 2(-19.6)]$$

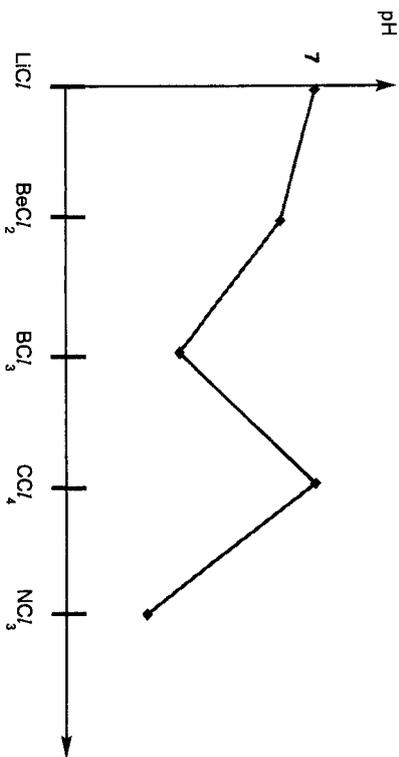
$$= -1763.9 \text{ kJ mol}^{-1}$$

$$\text{Now, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -1763.9 - [298(+1141.2 \times 10^{-3})]$$

$$= -2.10 \times 10^3 \text{ kJ mol}^{-1}$$

(c) (i) The chlorides of Period 2 elements behave similarly to chlorides of Period 3 elements. Based on your knowledge of chlorides of Period 3 elements, sketch a graph of pH against the chlorides of lithium to nitrogen. In your sketch, consider the chloride of carbon is immiscible with water. [3]



(ii) Write an equation with state symbols to account for the pH of liquid  $\text{NCl}_3$  when dissolved in water. Aqueous  $\text{HNO}_2$  and steamy white fumes are formed in the reaction.



(d) Describe and explain how the thermal stability of the hydrogen halides varies down Group 17. Include an equation for the thermal decomposition reaction in your answer.

Describe:

- Hydrogen halides decompose on heating to give hydrogen gas and halogens.



- The thermal stability decreases down from  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{HI}$ .

Explain:

- Down the group, as the size of the halogen atom increases.
- The  $\text{H-X}$  bond length increases and is weaker due to less effective orbital overlap.
- Hence, the bond energy of  $\text{H-X}$  decreases, and thermal stability decreases down the group.

[Total: 16]

2 Ammonia gas, NH<sub>3</sub>, is used in industrial refrigeration systems. A refrigeration chamber contains 0.686 mol of ammonia gas at a temperature of 360K. The chamber volume is 2.25 dm<sup>3</sup>.

(a) State two main assumptions of kinetic theory of gases.

- The individual gas particles have negligible volume as compared to the overall gas volume.
  - There are negligible forces of attraction between the gas particles.
- ..... [2]

(b) Calculate the pressure of ammonia, in kPa, in the chamber using the ideal gas equation.

$$pV = nRT$$

$$p(2.25 / 1000) = 0.686(8.31)(360)$$

$$p = 912 \text{ kPa}$$

[1]

(c) To determine the pressure of ammonia in the chamber more precisely, the van der waals' equation shown below is used.

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \text{ (where } a \text{ and } b \text{ are constants)}$$

Given that the pressure obtained using van der waals' equation is lower than your answer in (b), explain the difference.

The pressure is lower due to the presence of hydrogen bonding between ammonia molecules.

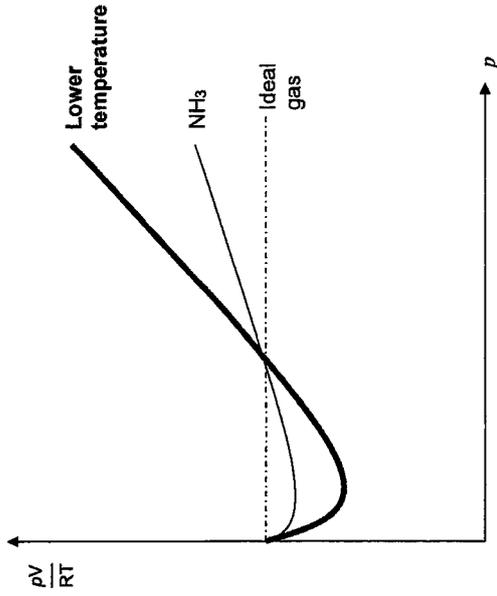
..... [1]

(d) Under what conditions of temperature and pressure would you expect ammonia to be most like that of an ideal gas?

high temperature and low pressure.

..... [1]

(e) The graph below shows the compressibility curve of 1 mole of ammonia gas. On the same axes, draw the compressibility curve for 1 mole of ammonia at a lower temperature in the graph below and explain the shape of your graph. Your answer should include reference to intermolecular forces.



At lower temperature, the gas particles have lower kinetic energy, and hence do not have sufficient energy to overcome the intermolecular forces of attraction between one another. Thus, the intermolecular forces of attraction between the gas particles are more significant at lower temperature.

..... [2]

[Total: 8]

- 3 (a) A 2.67 g sample of a Period 3 chloride is heated to 227°C in a sealed flask. At this temperature, the chloride is a gas of volume 250 cm<sup>3</sup> and the pressure in the flask is 323 kPa. Using the general gas equation, calculate the *M<sub>r</sub>* of the Period 3 chloride. Deduce its formula. [3]

$$pV = nRT$$

$$323 \times 10^3 \times 250 \times 10^{-6} = n \times 8.31 \times (227 + 273)$$

$$n = 0.01943 \text{ mol}$$

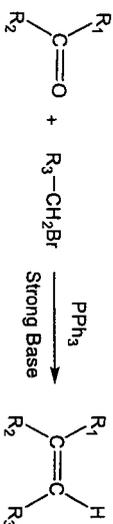
$$n = \text{mass} / M_r$$

$$0.01943 = 2.67 / M_r$$

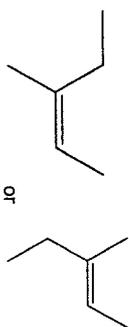
$$M_r = 137.4$$

Based on *M<sub>r</sub>*, the period 3 chloride is likely to contain 3 Cl.  
*A<sub>r</sub>* of period 3 element = 137.4 – 35.5 × 3 = 30.9  
 PCl<sub>3</sub>

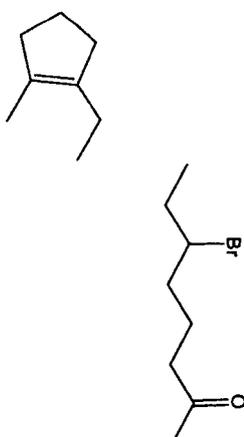
- (b) Triphenylphosphine (represented as PPh<sub>3</sub>) is used in a type of reaction known as a Wittig reaction. In the Wittig reaction, a carbonyl compound reacts with a halogenoalkane to form an alkene. The conversion is shown in the following unbalanced equation.



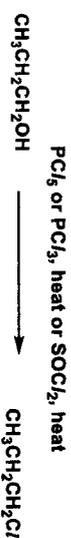
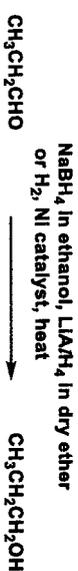
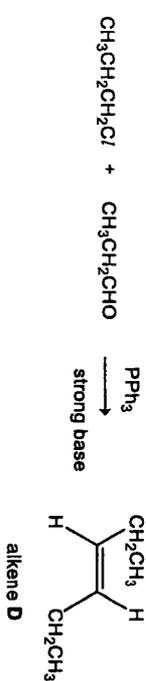
- (i) Draw the structure of the product formed from the Wittig reaction of the following compounds. [1]



- (ii) Predict the structural formula of the product formed when the following compound undergoes the Wittig reaction. [1]



- (iii) Alkene D can be formed from propanal, CH<sub>3</sub>CH<sub>2</sub>CHO via the Wittig reaction. Propose a 2-step synthesis to form 1-chloropropane, from propanal, for the Wittig reaction to take place. [2]



(c) Many transition metals and their complexes are paramagnetic. Paramagnetism is a property of a substance which allows it to be weakly attracted to a magnet. This property is due to the presence of unpaired electrons in the substance.

Nickel forms many complexes with a co-ordination number of 4. Complexes with a co-ordination number of 4 can take on either the tetrahedral or the square planar geometry.

Table 3.1 shows the relative paramagnetism of two nickel complexes with different geometry, which contain  $Ni^{2+}$  ion with a co-ordination number of 4.

Table 3.1

formula of complex	relative paramagnetism
$[NiCl_4]^{2-}$	2
$[Ni(CN)_4]^{2-}$	0

Fig. 3.2 shows how the d-orbitals of a transition metal ion such as nickel are split in complexes with these two different geometries.

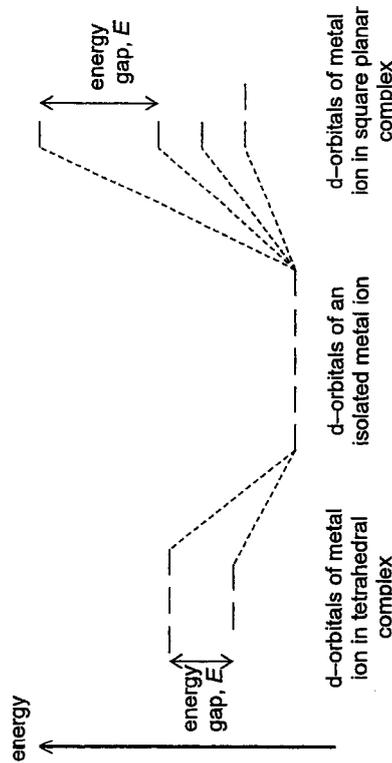
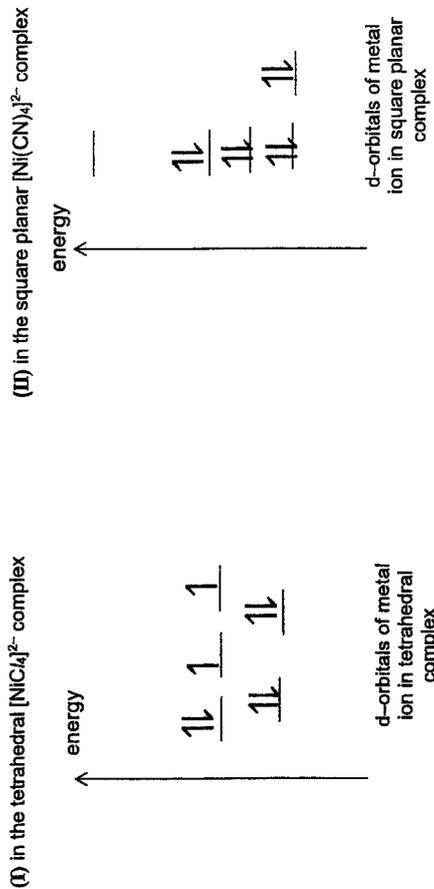


Fig. 3.2

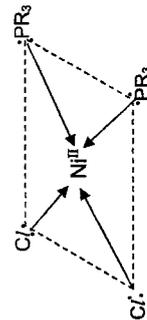
(i) Complete the diagram in Fig. 3.3 to show how the d electrons are arranged in the five non-degenerate d-orbitals



[2]

Fig. 3.3

(ii) Nickel(II) chloride forms a square planar complex,  $Ni(PR_3)_2Cl_2$ , with the monodentate organic ligand, triethylphosphine which can be represented as  $PR_3$ . The complex can occur in two forms, G and H, where G has an overall dipole and H has none. Suggest the structure of G.

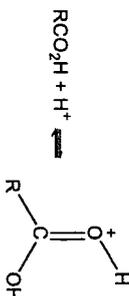


[Total: 10]

- 4 Esters are derivatives of carboxylic acids. Simple esters tend to have pleasant, fruity odours and are widely used as flavours and fragrances. Esterification generally refers to the formation of esters from alcohol and carboxylic acids, as shown in **Equation 1**. This Fischer esterification mechanism is thought to involve 5 steps.



**Step 1 :** The carboxyl oxygen on the carboxylic acid gains a proton.



**Step 2 :** Next, the electron-rich oxygen atom of the alcohol attacks the carbon atom of the carboxylic acid to form a positively-charged tetrahedral intermediate.

**Step 3 :** This is followed by transferring a proton to the hydroxyl oxygen of the carboxyl group.

**Step 4 :** Subsequently, water is removed to form the positively charged ester.

**Step 5 :** The ester is formed when a proton is transferred to the base.

- (a) (i) Suggest why protonation in **Step 1** is required before nucleophilic attack in **Step 2** can occur.

The protonation **activates the carbonyl carbon** toward nucleophilic attack. This is because O would withdraw electrons from C, making it even **more partial positive**.

[1]

(ii) State whether the acid catalyst acts as a homogeneous or heterogeneous catalyst in this reaction. Explain your answer.

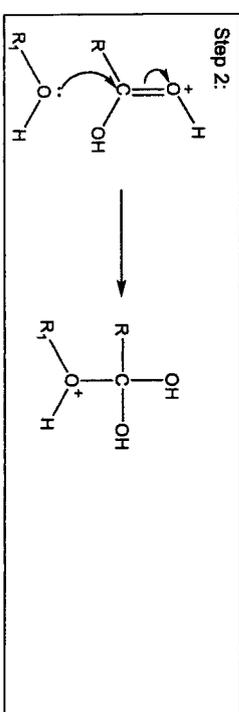
Homogeneous. Both the catalyst and the reactants are in the same phase. The acid catalyst is also regenerated at the end of the process.

[1]

- (iii) Using the information given, propose the mechanism for **Step 2** in the given boxes below. The structure of the alcohol,  $\text{R}'\text{-OH}$  is shown below.

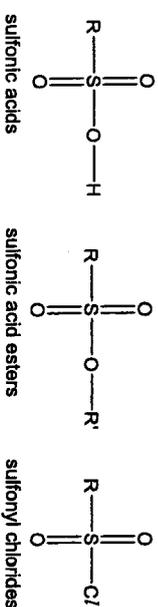


Suggest the mechanism for this reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]



- (iv) Suggest the type of reaction taking place in **Step 2**  
Nucleophilic addition ..... [1]

- (b) Organic sulfonic acids,  $\text{RSO}_2\text{OH}$ , sulfonic acid esters,  $\text{RSO}_2\text{OR}'$ , and sulfonyl chlorides,  $\text{RSO}_2\text{Cl}$ , show similar chemical properties to those of carboxylic acids, esters and acyl chlorides respectively. R and R' can represent alkyl groups or H atoms.

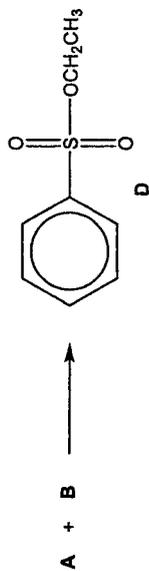


- (i) Based on your answer in (a)(i), explain why the rate of esterification will be faster when sulfonic acid is used instead of carboxylic acid.

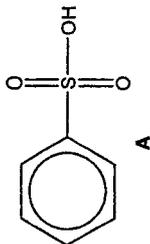
Sulfur atom in sulfonic acid is more electrophilic/ electron deficient than the carbon in carboxylic acid as it is bonded to 1 more electronegative O atom and thus is more susceptible to nucleophilic attack by the alcohol.

[1]

- (ii) The sulfonic acid ester **D** is synthesised from the corresponding sulfonic acid **A** and another organic molecule **B**.

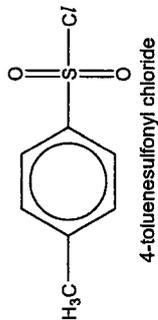


Suggest the structures of A and B. [2]

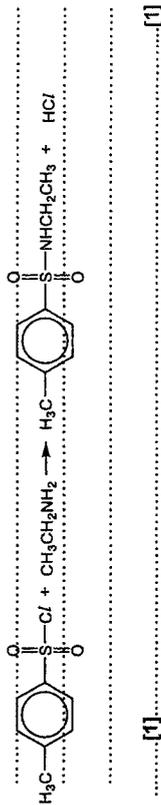


B:  $\text{CH}_3\text{CH}_2\text{OH}$

(iii) Sulfonyl chlorides react with amines in a manner similar to acyl chlorides to form sulfonamide. 4-toluenesulfonyl chloride reacts readily with ethylamine,  $\text{CH}_3\text{CH}_2\text{NH}_2$ , at room temperature.

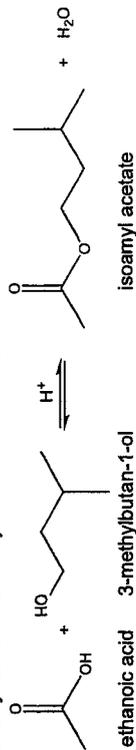


Suggest an equation for the reaction of 4-toluenesulfonyl chloride with ethylamine.



(c) At the newly opened Minion Land in Universal Studios Singapore, many banana-flavoured treats can be found at the stalls for visitors to immerse themselves in the Minions experience. The ester, isoamyl acetate with molecular formula  $\text{C}_7\text{H}_{14}\text{O}_2$  is the compound responsible for the fruit's distinctive taste.

Isoamyl acetate can be synthesised via esterification as follows:



(i) When isoamyl acetate undergoes acid hydrolysis in a solution containing  $\text{H}_2\text{O}^{18}$ , atoms of the  $^{18}\text{O}$  isotope appear in the product as

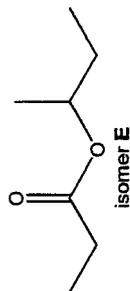


Explain why this is the case.

The C-O single bond in the

[2018P1Q28]

(ii) An isomer of isoamyl acetate with molecular formula,  $\text{C}_7\text{H}_{14}\text{O}_2$ , E has the following structure. Describe a reaction by which you could distinguish between isoamyl acetate and isomer E. [1]



To two separate test tubes containing isoamyl acetate and isomer E, add aqueous

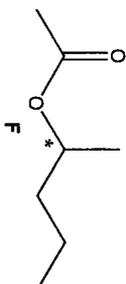
iodine and aqueous sodium hydroxide, and heat in a hot water bath. Test tube

containing isomer E will form a yellow ppt of  $\text{CHI}_3$ . No yellow ppt will be seen in the test

tube containing isoamyl acetate. [2]

15

- (iii) Another isomer with molecular formula  $C_7H_{14}O_2$ , **F** contains a chiral centre. Use an asterisk (\*) to mark the chiral centre present on the molecule of **F**. [1]



- (d) Ethanoyl chloride instead of ethanoic acid may be used to synthesise isoamyl acetate.

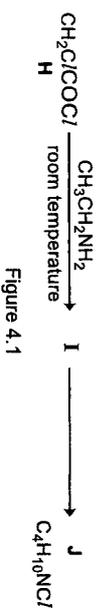
- (i) Write an equation for the reaction of ethanoyl chloride with water and hence explain why the solution has a lower pH as compared to ethanoic acid.



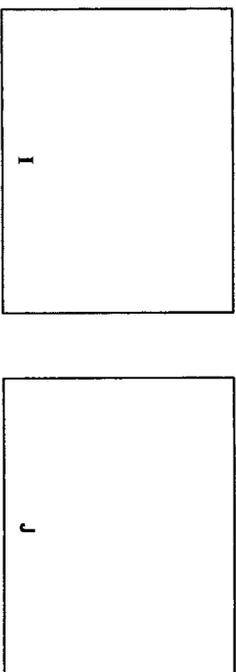
Ethanoyl chloride undergoes hydrolysis readily with water to form a strongly acidic solution of HCl. Ethanoic acid only partially dissociate in water to give  $H_3O^+$ . [2]

- (ii) Chloroethanoyl chloride,  $CH_2ClCOCl$ , **H**, can be obtained from ethanoic acid by heating it with  $Cl_2$  and  $PCl_5$ .

**H** can then be used to produce **J**,  $C_4H_{10}NCI$ , via compound **I**, as shown in Figure 4.1.



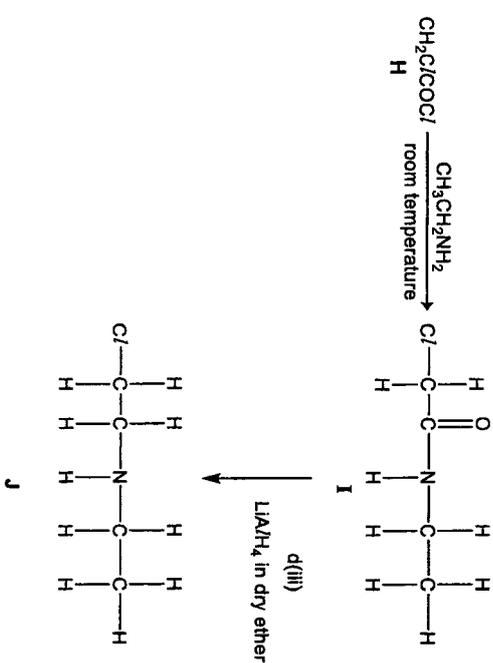
Suggest structures for compounds **I** and **J** in Figure 4.1. [2]



- (iii) State the reagents and conditions to convert **I** to **J**.

.....[1]

16



[Total: 18]

- 5 (a) Ammonia in aqueous solution is a weak base, its dissociation constant,  $K_b$ , being  $1 \times 10^{-5} \text{ mol dm}^{-3}$ .

What is the pH of a  $0.100 \text{ mol dm}^{-3}$  aqueous solution of ammonia? [2]

$$\begin{aligned} \text{NH}_3 + \text{H}_2\text{O} &\rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\ [\text{OH}^-] &= \sqrt{K_b \times [\text{base}]} \\ &= \sqrt{(1 \times 10^{-5}) \times 0.100} \\ &= 1 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{pOH} &= -\lg(1 \times 10^{-3}) = 3.00 \\ \text{pH} &= (14 - 3.00) = 11.0 \end{aligned}$$

- (b)  $45.4 \text{ cm}^3$  of ammonia gas is passed into  $25.00 \text{ cm}^3$  of  $0.0400 \text{ mol dm}^{-3}$  of sulfuric acid at standard temperature and pressure (s.t.p). All the ammonia is neutralised by the acid to form ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ .

- (i) Write a balanced equation, with state symbols, for the reaction between ammonia and sulfuric acid. [1]



- (ii) Calculate the amount of ammonia gas passed into the acid. [1]

$$\text{Amount of NH}_3 = \left(\frac{45.4}{22700}\right) = 0.00200 \text{ mol}$$

- (iii) Calculate the concentration of  $\text{NH}_4^+$  ions formed in the solution. [1]

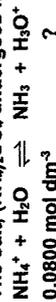
$$\text{Amount of H}_2\text{SO}_4 = \left(\frac{25.00}{1000} \times 0.0400\right) = 0.00100 \text{ mol}$$

$$\text{Amount of } (\text{NH}_4)_2\text{SO}_4 = \frac{0.00200}{2} = 0.00100 \text{ mol}$$

$$[\text{NH}_4^+] = (2 \times 0.00100 \times \frac{1000}{25.00}) = 0.0800 \text{ mol dm}^{-3}$$

- (iv) Calculate the pH of the aqueous solution of the salt formed, assuming  $K_w$  is  $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ . [2]

The salt,  $(\text{NH}_4)_2\text{SO}_4$ , undergoes hydrolysis in water.



$$0.0800 \text{ mol dm}^{-3} \quad ?$$

$$K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1 \times 10^{-5}} = 1.00 \times 10^{-9}$$

$$[\text{H}^+] = \sqrt{K_a \times [\text{NH}_4^+]}$$

$$= \sqrt{(1.00 \times 10^{-9}) \times (0.0800)}$$

$$= 8.94 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg [\text{H}^+]$$

$$= -\lg(8.94 \times 10^{-6}) = 5.05$$

- (c) The Haber process is the principal commercial method used to manufacture ammonia gas from nitrogen and hydrogen, as shown in the following equation:



The table below shows the percentage of ammonia gas by volume in the equilibrium mixtures at various temperatures and pressures. In all cases, the molar ratio of  $\text{N}_2$  and  $\text{H}_2$  in the mixtures is 1:3.

Temperature/ °C	% of ammonia gas		
	at 1 atm	at 10 atm	at 100 atm
200	1.10	7.42	25.8
300	0.22	1.94	12.6
400	0.07	0.61	5.2

- (i) State Le Chatelier's principle.

Le Chatelier's principle states that if a change (e.g., change in concentration, pressure or temperature) is made to a system in dynamic equilibrium, the system reacts in such a way to oppose the change, and a new equilibrium is formed. [1]

- (ii) From the data provided above, state how the percentage of ammonia gas varies with changes in temperature, at a fixed pressure and how the percentage of ammonia gas varies with changes in pressure, at a fixed temperature, in the equilibrium mixture.

The percentage of ammonia gas decreases with increasing temperature, at a fixed pressure.

The percentage of ammonia gas increases with increasing pressure, at a fixed temperature. [1]

- (iii) Hence, explain how changes in temperature and pressure affect the percentage of ammonia, in the equilibrium mixture, with reference to Le Chatelier's principle.

By Le Chatelier's principle, since the forward reaction is exothermic, so when

temperature is increased, the position of equilibrium shifts to the left, as heat

energy is absorbed by the reverse endothermic reaction, resulting in decrease

in percentage of ammonia gas.

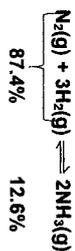
By Le Chatelier's principle, when pressure is increased, the position of

equilibrium shifts to the right to decrease the number of gaseous molecules

so as to reduce the pressure, resulting in increase in percentage of ammonia

gas.

- (iv) Calculate the partial pressure of each gas in the equilibrium mixture at a pressure of 100 atm and a temperature of 300 °C. Hence, determine  $K_p$  at 300 °C, stating the units. [2]



$$P_{\text{NH}_3} = \left(\frac{12.6}{100} \times 100\right) \text{ atm} = 12.6 \text{ atm}$$

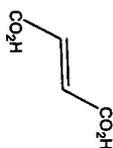
$$P_{\text{N}_2} = \left(\frac{1}{4} \times \frac{87.4}{100} \times 100\right) \text{ atm} = 21.9 \text{ atm}$$

$$P_{\text{H}_2} = \left(\frac{3}{4} \times \frac{87.4}{100} \times 100\right) \text{ atm} = 65.6 \text{ atm}$$

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{12.6^2}{21.9 \times (65.6)^3} = 2.57 \times 10^{-5} \text{ atm}^{-2}$$

[Total: 13]

- 6 Double indicator acid-base titrations can be used to determine the composition of a mixture of acids in addition to the pH of buffer solutions formed from polyprotic acids. Maleic acid is a diprotic weak acid,  $\text{H}_2\text{A}$  and its structure is as shown below.



- (a) The table below gives the  $pK_a$  values of maleic acid at 298 K.

Equation	$pK_a$
$\text{H}_2\text{A} \rightleftharpoons \text{HA}^- + \text{H}^+$	1.90 ( $pK_{a1}$ )
$\text{HA}^- \rightleftharpoons \text{A}^{2-} + \text{H}^+$	6.20 ( $pK_{a2}$ )

Explain why the value of  $pK_{a2}$  is higher than that of  $pK_{a1}$ .

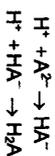
A higher  $pK_{a2}$  implies it is **more difficult to lose** (the second) **proton** due to the **stronger electrostatic force of attraction between the increasing negatively charged anion and the proton**..... [1]

- (b) A double indicator titration was performed to determine the pH of the buffer solution that was prepared by mixing unknown volumes of  $\text{Na}_2\text{A}$  and  $\text{NaHA}$ .

25.0  $\text{cm}^3$  of the buffer solution was titrated against 0.200  $\text{mol dm}^{-3}$  HCl using bromocresol green as an indicator for the first end-point. 16.90  $\text{cm}^3$  of the titrant was required for this titration.

An additional titre volume of 19.20  $\text{cm}^3$  was required to reach the second end point using thymol blue as an indicator.

The reaction between  $\text{A}^{2-}$  and  $\text{H}^+$  from HCl occurs in two steps:



- (i) Calculate the concentration of  $\text{A}^{2-}$  present in the buffer solution initially.

$$\begin{aligned} \text{Amount of } \text{A}^{2-} &= \left(\frac{16.90}{1000} \times 0.200\right) = \text{Amount of HCl} = 3.38 \times 10^{-3} \text{ mol} \\ [\text{A}^{2-}] &= \left(3.38 \times 10^{-3} \times \frac{1000}{25.0}\right) = 0.135 \text{ mol dm}^{-3} \end{aligned}$$

[1]

(ii) Calculate the volume of hydrochloric acid used to fully react with the  $\text{HA}^-$  present in the buffer solution initially and hence calculate the initial concentration of  $\text{HA}^-$ .

Amount of  $\text{HCl}$  required to react with  $\text{HA}^-$  from  $\text{A}^{2-}$  at the second end-

$$\text{point} = \left(\frac{25.00}{1000} \times 0.1352\right)$$

$$= 3.38 \times 10^{-3} \text{ mol}$$

= Amount of  $\text{A}^{2-}$

$$\text{Vol. of HCl required to react with } \text{HA}^- \text{ from } \text{A}^{2-} = \left(\frac{3.38 \times 10^{-3}}{0.200} \times 1000\right) \\ = 16.90 \text{ cm}^3$$

$$\text{Vol. of HCl required to react with } \text{HA}^- \text{ present initially} = 19.20 - 16.90 \\ = 2.30 \text{ cm}^3$$

$$\text{Amount of } \text{HA}^- = \left(\frac{2.30}{1000} \times 0.200\right) = \text{Amount of HCl} = 4.60 \times 10^{-4} \text{ mol}$$

$$[\text{HA}^-] = \left(4.60 \times 10^{-4} \times \frac{1000}{25.0}\right) = 0.0184 \text{ mol dm}^{-3}$$

(iii) Using your answers to (b)(i) and (ii), calculate the initial pH of the buffer solution. [2]

$$\text{pH} = \text{p}K_{a2} + \lg \frac{[\text{A}^{2-}]}{[\text{HA}^-]}$$

$$= 6.20 + \lg \frac{[0.1352]}{[0.0184]}$$

$$= 7.07$$

[1]

(iv) Hence using your calculations from (b)(i) and (ii), calculate the concentration of  $\text{H}_2\text{A}$  at the second equivalence point.

$$\text{Amount of } \text{H}_2\text{A} \text{ at 2}^{\text{nd}} \text{ EP} = \text{Amt of } \text{A}^{2-} \text{ ions} + \text{Amt of } \text{HA}^- \text{ ions in original mixture} \\ = 3.38 \times 10^{-3} + 4.60 \times 10^{-4} \text{ mol}$$

$$= 3.84 \times 10^{-3} \text{ mol}$$

$$[\text{H}_2\text{A}] = \left(3.84 \times 10^{-3} \times \frac{1000}{25.0+36.10}\right) = 0.06284 \text{ mol dm}^{-3}$$

[1]

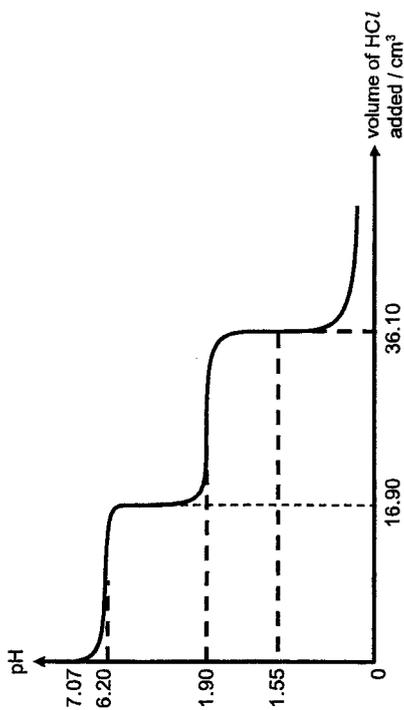
(v) Hence, calculate the pH of  $\text{H}_2\text{A}$  at the second equivalence point.

$$[\text{H}^+] = (K_a \times [\text{H}_2\text{A}])^{0.5} \\ = (10^{-1.90} \times 0.06284)^{0.5} \\ = 0.0281 \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(0.0281) \\ = 1.55$$

[1]

(c) Using the information provided in the question in addition to your answers from (b)(iii) – (b)(v), sketch a graph to show the pH changes that occur when 50.00  $\text{cm}^3$  of 0.200  $\text{mol dm}^{-3}$   $\text{HCl}$  is added to 25.0  $\text{cm}^3$  of the initial buffer solution. Indicate clearly in your sketch, all relevant pH and volumes of  $\text{HCl}$  used.



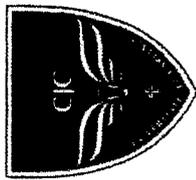
(d) Explain why a weak acid cannot be used in place of hydrochloric acid as a titrant for this titration. [3]

There will be **no sharp decrease of pH** that is typically found along with the end-point, hence there is **no indicator that can be used to produce a distinct colour change to identify the end-point**.

..... [1]

[Total: 11]





**Catholic Junior College**  
**JC2 Preliminary Examination**  
**Higher 2**

CANDIDATE NAME		INDEX NUMBER	
CLASS	2T		

**CHEMISTRY**

Paper 3 Free Response

**9729/03**

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.

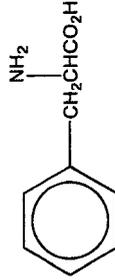
For Examiner's Use	
Q1	/21
Q2	/20
Q3	/19
Q4	/20
Section A	
Section B	OR
Q5	/20
TOTAL	80

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  $C_9H_9NO_2$ . It cannot be synthesised by the human body and need to be obtained through diet.



phenylalanine

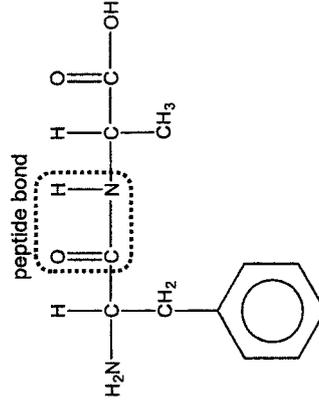
Phenylalanine can react with alanine,  $CH_3CH(NH_2)CO_2H$ , to form a mixture of dipeptides.

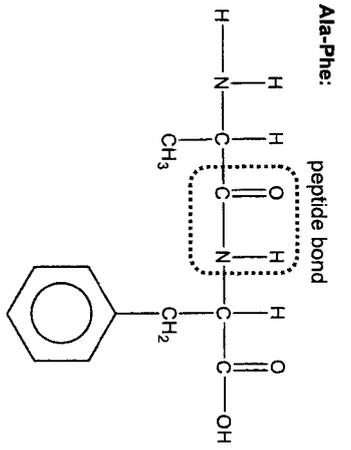
- (i) Name the type of reaction when phenylalanine reacts with alanine. [1]  
 (ii) State the number of possible different constitutional isomers that can be formed in this reaction. [1]  
 (iii) Draw the structures of the constitutional isomers with the molecular formula  $C_{12}H_{18}N_2O_3$  that 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:





(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]

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

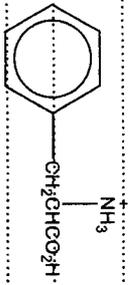
Table 1.1

(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]

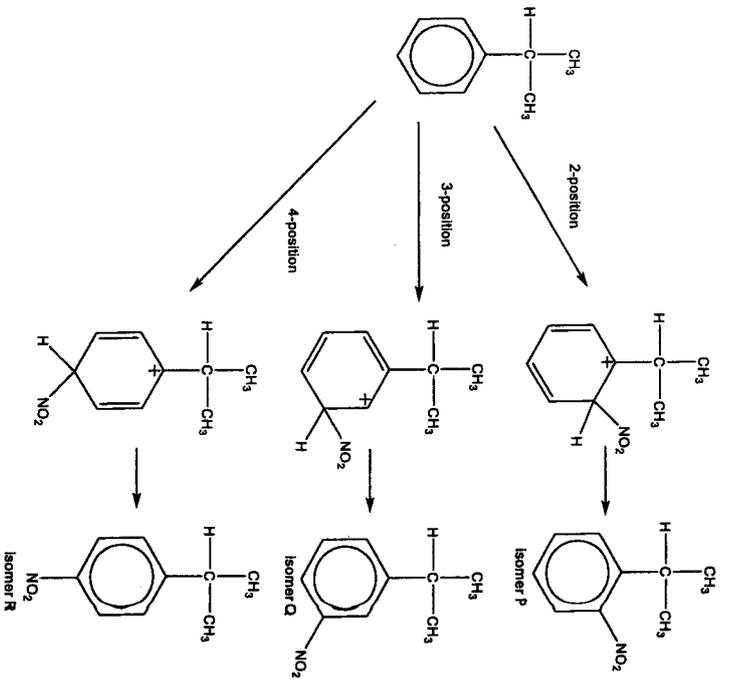


Fig. 1.1

(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  $NO_2$  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.

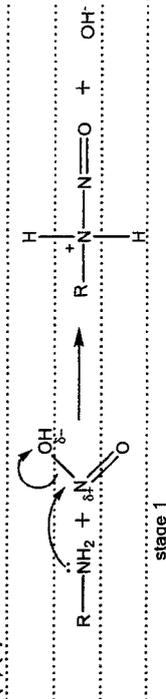
Table 1.2

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	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}^+-\text{N}=\text{O} \\   \\ \text{H} \end{array} \longrightarrow \text{R}-\text{N}-\text{N}=\text{O} + \text{H}^+$
3	protonation and electron pair movement	$\text{R}-\text{N}-\text{N}=\text{O} + \text{H}^+ \longrightarrow \begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}^+-\text{N}-\text{O} \end{array}$
4	deprotonation and protonation	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}^+-\text{N}-\text{O} \end{array} \longrightarrow \begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}=\text{N}-\text{O}^+ \\   \\ \text{H} \end{array}$
5	Electron pair movement and heterolytic cleavage of N-O bond	$\begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}=\text{N}-\text{O}^+ \\   \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \text{H} \\   \\ \text{R}-\text{N}^+-\text{N} \\   \\ \text{H} \end{array} + \begin{array}{c} \text{H} \\   \\ \text{O}^+ \\   \\ \text{H} \end{array}$

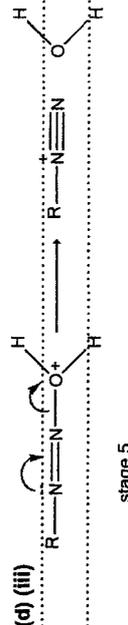
- (f) Name the type of reaction in stage 1. [1]  
 (ii) Complete the mechanism in stage 1 by adding a lone pair and curly arrows in Table 1.2. [2]  
 (iii) Complete the mechanisms in stage 3 and stage 5 by adding lone pairs and relevant curly arrows. [2]

- (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.

$\text{MgO}$  has giant ionic lattice structure and is basic oxide. It reacts readily with acids to give salts and water.

$\text{MgO} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{H}_2\text{O}$

$\text{Al}_2\text{O}_3$  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.

$\text{Al}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$

$\text{Al}_2\text{O}_3 + 2\text{KOH} + 3\text{H}_2\text{O} \rightarrow 2\text{KAl}(\text{OH})_4$







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.  
 $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$

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, HCN, is a weak acid.

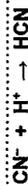
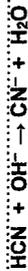


A mixture containing both HCN and  $\text{CN}^-$  ions is a useful reagent in organic chemistry.

(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.

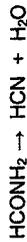
(ii) Acid buffer,

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

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

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

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



(i) Ethanal undergoes nucleophilic addition reaction with 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]

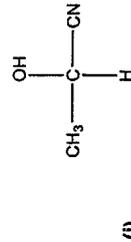
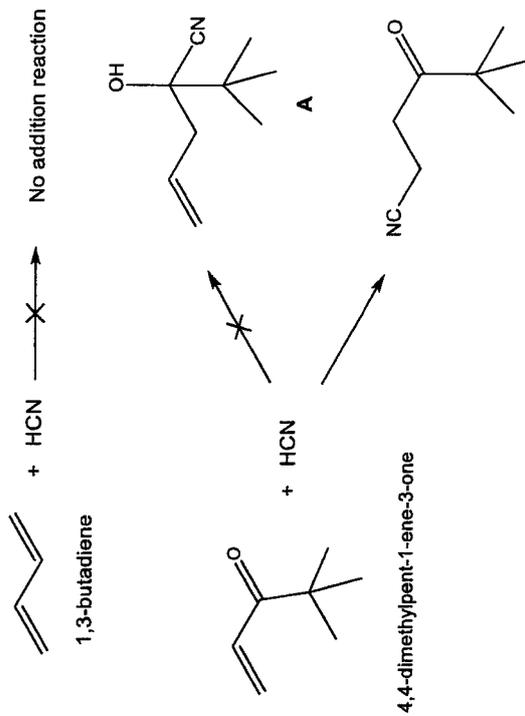


Fig. 3.1

(ii) Nucleophilic addition between 1,3-butadiene and HCN does not take place as the C atoms in the  $\text{C}=\text{C}$  double bonds have the same electronegativity. Therefore, the 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 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 :CN<sup>-</sup> 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 C=C double bond more susceptible to attack by :CN<sup>-</sup> nucleophile. Nucleophilic addition can occur between the C=C double bond and HCN.

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

hydroxide	solubility/ mol dm <sup>-3</sup>
Mg(OH) <sub>2</sub>	1.6 x 10 <sup>-4</sup>
Ca(OH) <sub>2</sub>	2.5 x 10 <sup>-2</sup>
Ba(OH) <sub>2</sub>	4.1 x 10 <sup>-1</sup>

- (i) Suggest a value for the solubility of strontium hydroxide, Sr(OH)<sub>2</sub>. [1]
- (ii) Calculate the solubility product, K<sub>sp</sub>, for Mg(OH)<sub>2</sub>. [1]
- (iii) Given that the K<sub>sp</sub> for Ba(OH)<sub>2</sub> is 0.276 mol<sup>3</sup> dm<sup>-9</sup> and using your answer in d(i), describe what you would observe if equal volumes of saturated solutions of Mg(OH)<sub>2</sub> and Ba(OH)<sub>2</sub> were mixed. Explain your answer with appropriate calculations. [2]

(i) 2.0 x 10<sup>-1</sup> mol dm<sup>-3</sup>

(Accept any value between 2.5 x 10<sup>-2</sup> and 4.1 x 10<sup>-1</sup> mol dm<sup>-3</sup>)

(ii) Mg(OH)<sub>2</sub>(s) ⇌ Mg<sup>2+</sup>(aq) + 2OH<sup>-</sup>(aq)

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

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

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

$$\text{IP of Mg(OH)}_2 = (1.6 \times 10^{-4}/2) [(3.2 \times 10^{-4} + 8.2 \times 10^{-4})/2]^2$$

$$= 1.35 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9} > K_{sp} \text{ Mg(OH)}_2$$

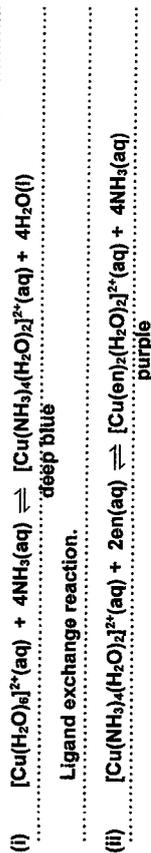
White ppt of Mg(OH)<sub>2</sub> will be observed.

$$\text{IP of Ba(OH)}_2 = (4.1 \times 10^{-1}/2) [(8.2 \times 10^{-1} + 3.2 \times 10^{-1})/2]^2$$

$$= 0.0345 \text{ mol}^3 \text{ dm}^{-9} < K_{sp} \text{ Ba(OH)}_2$$

No ppt of Ba(OH)<sub>2</sub> will be observed.

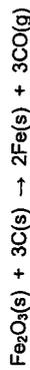
- (e) The addition of  $\text{NH}_3(\text{aq})$  to a solution containing  $\text{Cu}^{2+}(\text{aq})$  produces a deep blue solution.
- (i) Write an equation for this reaction and state the type of reaction occurring. [2]
- (ii) This solution changes from deep blue to purple when the bidentate ligand, 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]



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.

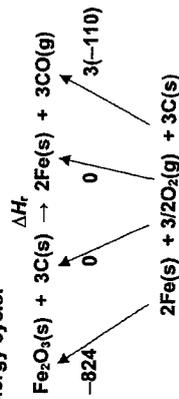
Use the information below to determine the enthalpy change for the following reaction. [2]



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

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

Or using an energy cycle:



Hess' Law,

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

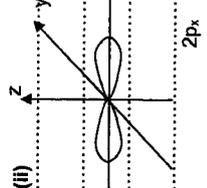
[Total: 19]

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]

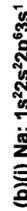


It is the energy required/absorbed/needed/supplied to remove 1 mole of electrons from 1 mole of gaseous  $\text{Na}^+$  ions to form 1 mole of gaseous  $\text{Na}^{2+}$  ions.

- (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/ionise 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 Na<sub>2</sub>O and SO<sub>2</sub> with water. Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur. [2]

Na<sub>2</sub>O reacts with water and pH of the resulting solution = 14 (accept 13 or 14).

Na<sub>2</sub>O(s) + 2H<sub>2</sub>O(l) → 2NaOH(aq).

SO<sub>2</sub> reacts violently with water and pH of the resulting solution = 2

SO<sub>2</sub>(g) + H<sub>2</sub>O(l) → H<sub>2</sub>SO<sub>3</sub>(aq)

(d) The manufacture of sulfuric acid involves the reaction between sulfur dioxide and oxygen gas.  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

When an equimolar mixture of SO<sub>2</sub> and O<sub>2</sub> is passed over a catalyst at an initial pressure of 2 atm, the percentage conversion of SO<sub>2</sub>(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<sub>p</sub>, for this reaction. Use your answer in (d)(i) to calculate the value of K<sub>p</sub> for this reaction including its units. [2]

	2SO <sub>2</sub>	O <sub>2</sub>	⇌	2SO <sub>3</sub>
Initial pressure / atm	1	1		0
Change in pressure / atm	-0.98 x 1	-½ (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 SO<sub>2</sub> to y atm at constant temperature. The system was then allowed to establish a new equilibrium. The partial pressure of SO<sub>2</sub> was found to be 1.50 atm at this new equilibrium.

Calculate the value of y in atm. [2]

	2SO <sub>2</sub>	O <sub>2</sub>	⇌	2SO <sub>3</sub>
Initial pressure / atm	y	0.510		0.980
Change in pressure / atm	-0.520	-½ (0.520)		+ 0.520
Equilibrium pressure / atm	y - 0.520	0.250		1.50

Since temperature remains constant, K<sub>p</sub> 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 π electron cloud in the benzene ring, thus losing its aromatic character.

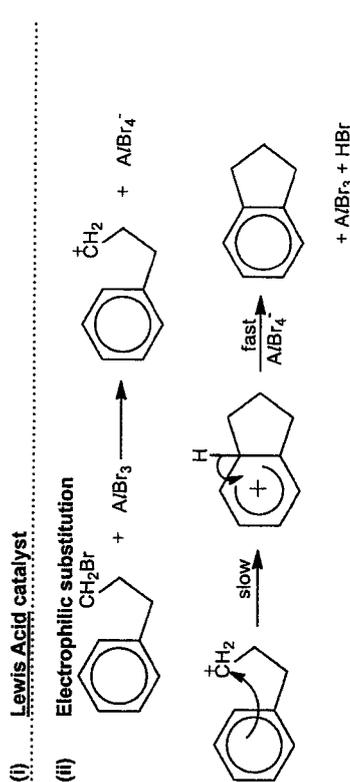
Benzene undergo substitution reactions under suitable conditions because such reactions retains its resonance-stabilised ring system

(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 AlBr<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]

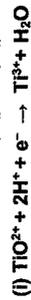


[Total: 20]

5 Titanium is a transition element, commonly found as TiO<sub>2</sub> in minerals.

- (a) When TiO<sub>2</sub> reacts with an excess of sulfuric acid, TiO<sup>2+</sup> ion is formed. TiO<sup>2+</sup> can be reduced to form a purple solution containing Ti<sup>3+</sup>(aq). [1]  
 (i) Construct the half-equation for the reduction of TiO<sup>2+</sup> to Ti<sup>3+</sup> in acidic conditions. [1]  
 (ii) Explain why Ti<sup>3+</sup>(aq) is violet. [3]  
 (iii) Acidified Ti<sup>3+</sup>(aq) reacts with oxygen dissolved in water as shown.  $4\text{Ti}^{3+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{TiO}^{2+} + 4\text{H}^+$   $\Delta G^\ominus = -436.1 \text{ kJ mol}^{-1}$

Calculate E<sup>o</sup>cell for the above reaction and hence determine the standard reduction potential of TiO<sup>2+</sup>(aq)/Ti<sup>3+</sup>(aq). [2]



(ii) In the presence of H<sub>2</sub>O ligands, the partially filled degenerate d-orbitals of

Ti<sup>3+</sup> 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 d\* orbital via d-d\* electronic transition. The complementary violet colour will then be observed as the colour of Ti<sup>3+</sup>(aq).

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

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

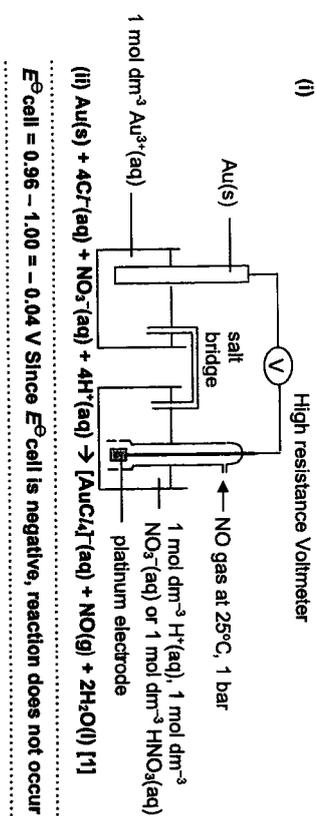
$E^\ominus_{\text{cell}} = E^\ominus(\text{O}_2/\text{H}_2\text{O}) - E^\ominus(\text{TiO}^{2+}/\text{Ti}^{3+}) = 1.23 - E^\ominus(\text{TiO}^{2+}/\text{Ti}^{3+})$  [subst +1.23V]

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

- (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

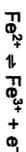
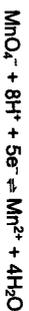
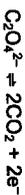
- (i) Draw a fully labelled diagram of the experimental set-up used to measure the standard cell potential,  $E^\ominus_{\text{cell}}$ , of  $\text{Au}^{3+}(\text{aq})/\text{Au}(\text{s})$  and  $\text{HNO}_3(\text{aq})/\text{NO}(\text{g})$ . Include all necessary chemicals. [2]
- (ii) Gold can be only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



- (iii) adding conc  $\text{HNO}_3$  increases concentration of  $\text{H}^{+}$  and  $\text{NO}_3^{-}$  and shifts position of equilibrium 3 to the right,  $E_{\text{HNO}_3(\text{aq})/\text{NO}(\text{g})}$  more positive  
 adding conc  $\text{HCl}$  increases concentration of  $\text{Cl}^{-}$  and shifts position of equilibrium 2 to the left,  $E_{[\text{AuCl}_4]^{-}(\text{aq})/\text{Au}(\text{s})}$  less positive or more negative  
 New  $E_{\text{cell}}$  becomes more positive and hence gold dissolves

- (c) An impure sample of  $\text{BaCO}_3$ , of mass  $0.500 \text{ g}$ , is added to  $50.0 \text{ cm}^3$  of  $0.020 \text{ mol dm}^{-3}$  acidified  $\text{MnO}_4^{-}$  (aq), which is in excess. A redox reaction occurs and all the  $\text{BaCO}_3$  reacts. The resulting solution, containing unreacted acidified  $\text{MnO}_4^{-}$  is then titrated with  $0.050 \text{ mol dm}^{-3} \text{Fe}^{2+}(\text{aq})$ .

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



- Calculate the percentage by mass of  $\text{BaCO}_3$  in the  $0.500 \text{ g}$  impure sample. Show your working. [M<sub>r</sub>:  $\text{BaCO}_3$ , 225.3] [3]
- Initial moles of  $\text{MnO}_4^{-} = 0.0200 \times 50/1000 = 1.00 \times 10^{-3}$
- 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  $\text{BaCO}_3 = 1.00 \times 10^{-3} - 2.68 \times 10^{-4} = 7.32 \times 10^{-4}$
- moles  $\text{C}_2\text{O}_4^{2-}$  reacted =  $7.32 \times 10^{-4} \times 5/2 = 1.83 \times 10^{-3}$
- mass of  $\text{BaCO}_3 = 225.3 \times 1.83 \times 10^{-3} = 0.412 \text{ g}$
- % Purity of  $\text{BaCO}_3 = 100 \times 0.412/0.50 = 82.5\%$

- (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.

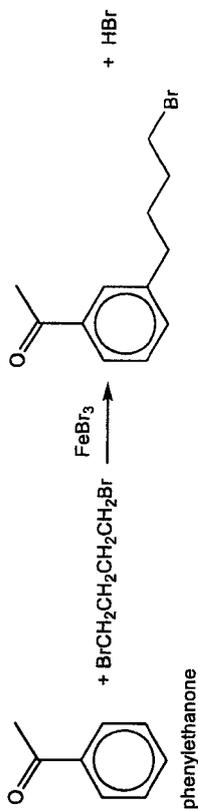
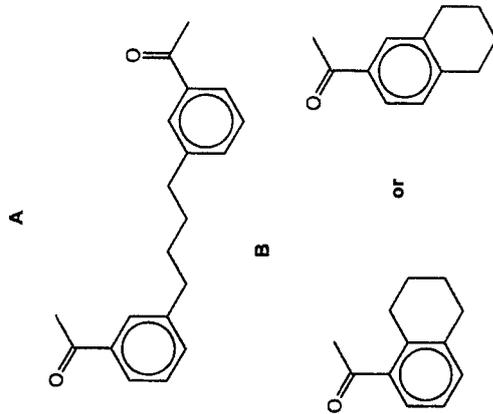


Fig. 5.1

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** ( $\text{C}_{12}\text{H}_{14}\text{O}$ ).  
[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.





