



Catholic Junior College
JC 2 Preliminary Examinations
Higher 2

CANDIDATE
NAME

CLASS

CHEMISTRY

9729/01

Paper 1 Multiple Choice

Wednesday 29 August 2018

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.

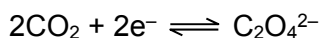
- 1 A sample of tungsten contains four naturally occurring isotopes, ^{182}W , ^{183}W , ^{184}W and ^{186}W .

The relative atomic mass of tungsten in this sample is 183.9. What is the percentage of the isotope ^{182}W in this sample?

Isotope	Relative Abundance (%)
^{182}W	?
^{183}W	?
^{184}W	30.6
^{186}W	28.6

- A 10.5 C 26.4
 B 14.4 D 40.8
- 2 20 cm^3 of 0.100 mol dm^{-3} of potassium ferrate(VI), K_2FeO_4 , reacts with sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$, in an acidic medium to produce 144 cm^3 of carbon dioxide gas at room temperature and pressure.

The half equation of $\text{C}_2\text{O}_4^{2-}$ is shown as follows:



What is the final oxidation state of the iron-containing species after the reaction?

- A +1 B +2 C +3 D +4
- 3 When attracted by a strong magnet, some species are able to exhibit paramagnetism. Such species contain unpaired electrons which are able to spin in a way which aligns parallel to the magnetic field.

Which of the following species in the ground state is able to exhibit paramagnetism?

- 1 O 2 Al^+ 3 Ti^{2+} 4 Cu^+

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

- 4 Phosphorus(V) chloride, PCl_5 dissolves in a suitable polar solvent to produce two ions, $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$.

Which of the following shows the correct shape for PCl_5 , $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$?

	PCl_5	$[\text{PCl}_4]^+$	$[\text{PCl}_6]^-$
A	trigonal planar	square planar	square pyramidal
B	trigonal bipyramidal	square planar	octahedral
C	trigonal planar	distorted tetrahedral	square pyramidal
D	trigonal bipyramidal	tetrahedral	octahedral

- 5 The table shows the boiling point of some halogenoalkanes.

compound	boiling point/ °C
$\text{CH}_3\text{CH}_2\text{Cl}$	12.3
$\text{CH}_3\text{CH}_2\text{Br}$	34.8
$\text{CH}_3\text{CH}_2\text{I}$	70.0

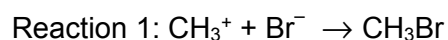
Which of the following correctly explains the difference in the boiling point?

- 1 the electronegativity difference between the halogen and carbon increases from C-Cl to C-I
 - 2 the strength of permanent dipole-permanent dipole attraction increases from C-Cl to C-I
 - 3 the strength of instantaneous dipole-induced dipole attraction increases from $\text{CH}_3\text{CH}_2\text{Cl}$ to $\text{CH}_3\text{CH}_2\text{I}$
 - 4 the bond energy of C-X bond decreases from C-Cl to C-I
- A** 1 and 2 only
B 2 and 4 only
C 3 only
D 3 and 4 only

- 6 Which of the following changes will result in the greatest decrease in the density of a fixed mass of ideal gas?

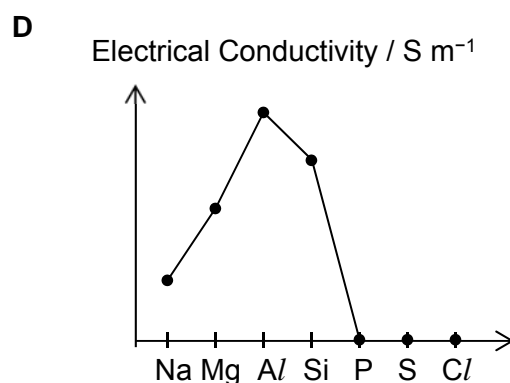
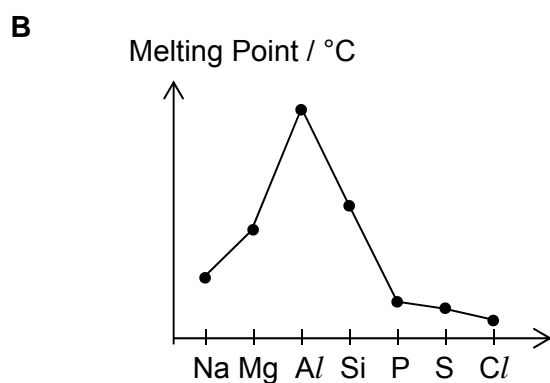
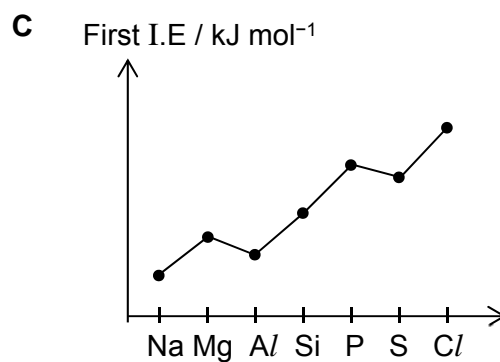
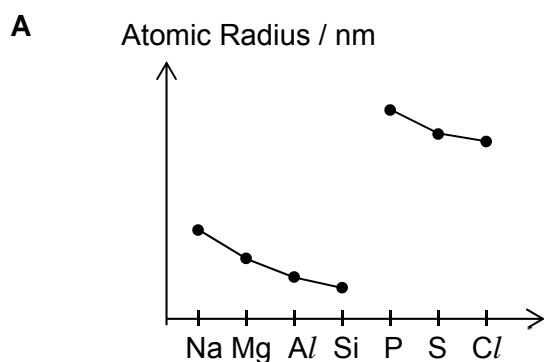
	Pressure	Temperature/ K
A	halves	halves
B	halves	doubles
C	doubles	halves
D	doubles	doubles

- 7 Consider the following reactions.



Which of the following statement is **not** true about the reactions above?

- A Both reactions are acid-base reactions.
 B In reaction 2, HPO_4^{2-} acts as the Brønsted-Lowry base.
 C In reaction 2, HBO_3^{2-} is the conjugate acid of H_2BO_3^- .
 D In reaction 1, a dative covalent bond is formed between CH_3^+ and Br^- .
- 8 Which of the following sketches shows the correct trend in the stated property for the elements in the third period of the Periodic Table?

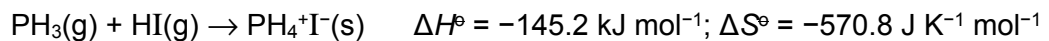


- 9 Compounds of Period 3 elements dissolve in water to form aqueous solutions that are acidic, basic or neutral.

Which of the following sequence shows the order of **increasing** resultant pH when the compounds are added to water?

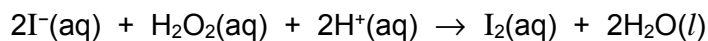
- A NaCl, MgCl₂, SiCl₄
B AlCl₃, SiCl₄, PCl₅
C Al₂O₃, MgO, SO₂
D P₄O₁₀, SiO₂, MgO

- 10 Phosphine reacts with hydrogen iodide to form phosphonium iodide in the reaction shown below:

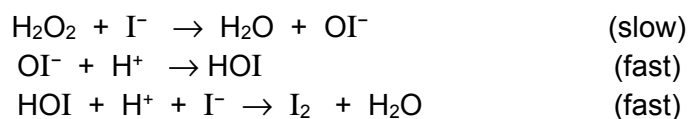


Which of the following statement is true for the above reaction?

- 1 The products are less disordered than the reactants.
 - 2 The reaction is non-spontaneous under standard conditions.
 - 3 As temperature increases, the reaction becomes more spontaneous.
- A 1 only
B 2 only
C 1 and 2 only
D 1, 2 and 3 only
- 11 The reaction of acidified aqueous potassium iodide with aqueous hydrogen peroxide:



is thought to involve the following steps:



Which of the following conclusion can be drawn from this information?

- 1 The acid is acting as a catalyst only.
 - 2 The reaction is pseudo-first order with respect to H₂O₂.
 - 3 The reaction rate is independent of the pH of the solution.
- A 1 only
B 3 only
C 1 and 2 only
D 1,2 and 3 only

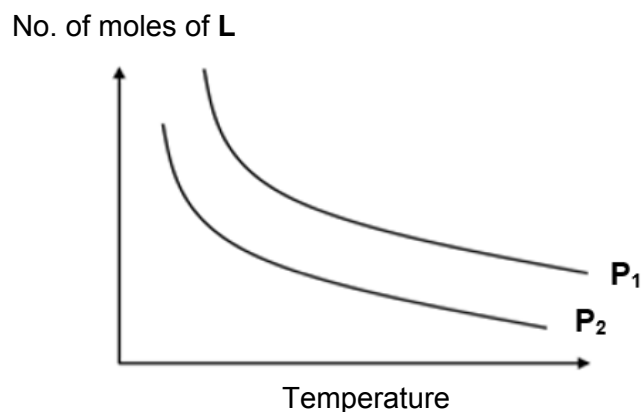
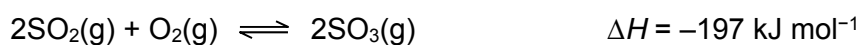
- 12 A first-order decomposition reaction is shown below.



The half-life of the reaction was found to be 3.47 s.

What is the time taken for AB(g) to reach one-third of its initial concentration?

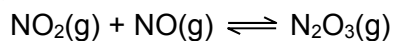
- A** 3.0 s **B** 3.5 s **C** 5.5 s **D** 7.0 s
- 13 The graph below shows how the number of moles of compound **L** varies with temperature at two different pressures of **P₁** and **P₂** respectively. **L** could be any of the following compounds shown in the equation at equilibrium.



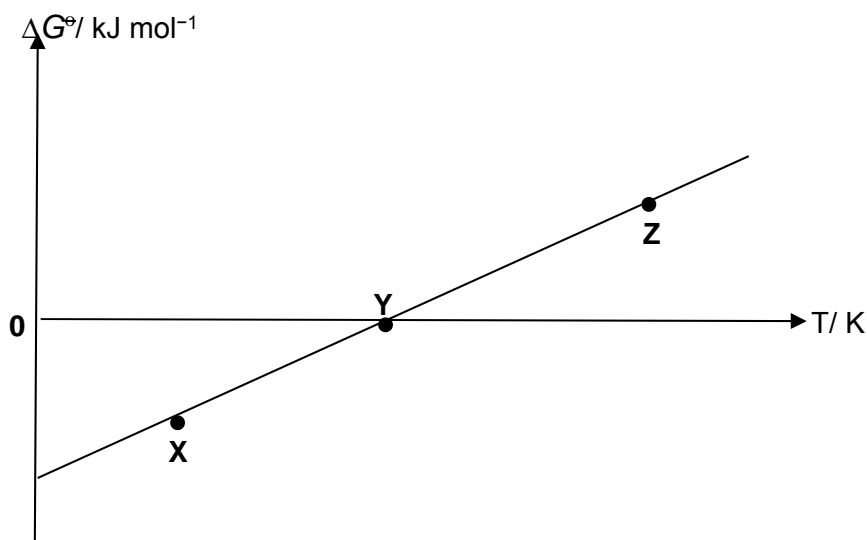
What is the correct identity of **L** and the correct magnitude of pressures **P₁** and **P₂**?

Identity of L	magnitude of pressures P₁ and P₂
A SO ₂	P₁ > P₂
B SO ₂	P₁ < P₂
C SO ₃	P₁ > P₂
D SO ₃	P₁ < P₂

- 14 When nitrogen dioxide, NO_2 , and nitrogen monoxide, NO , is mixed, the gases react to form dinitrogen trioxide, N_2O_3 . The reaction is shown in the following equilibrium.



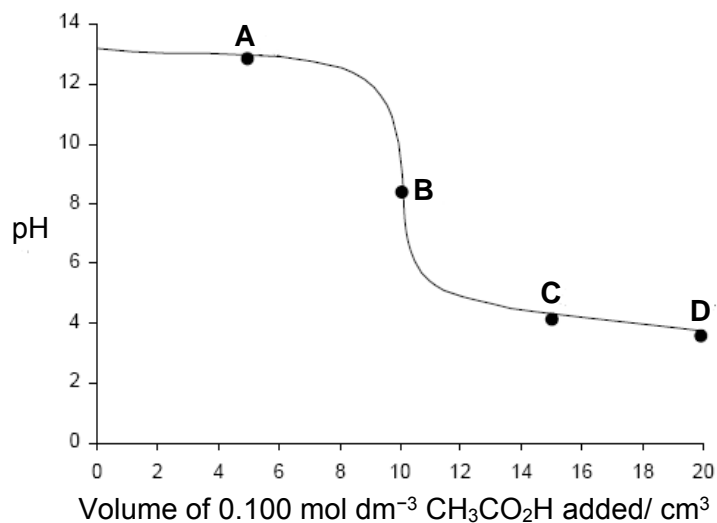
The graph below shows how the ΔG^\ominus varies with temperature for the above reaction.



Using the graph above, deduce which of the following statement is true about the reaction at equilibrium?

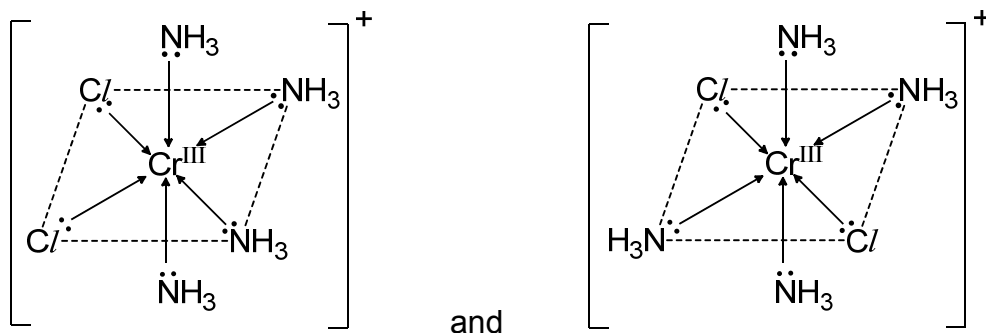
- A At point X, more NO_2 is present as compared to that at point Y.
 B At point X, the K_c value is likely to be greater than 1.
 C At point Y, the rate of forward reaction is greater than that of backward reaction.
 D At point Z, more N_2O_3 is present compared to that at point Y.
- 15 The pH changes when $0.100 \text{ mol dm}^{-3} \text{ CH}_3\text{CO}_2\text{H}$ is added dropwise to 10.0 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ NaOH}(\text{aq})$ as shown below.

At which point on the graph does $\text{pH} = \text{p}K_a$, where K_a is the acid dissociation constant of the weak acid?



- 16 Coordination complexes with more than one type of ligand can exist in a number of stereoisomeric forms.

For example, the chromium(III) complex $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ can refer to the two stereoisomers as shown:

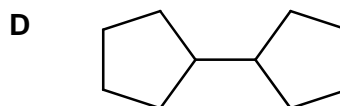
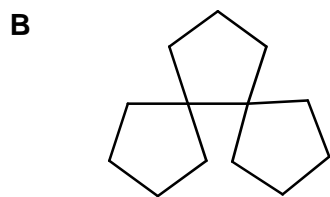
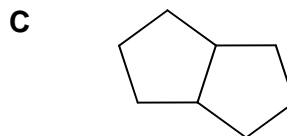
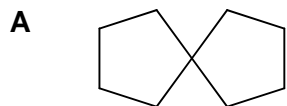


How many stereoisomers can the cobalt(III) complex $[\text{Co}(\text{trien})\text{Cl}_2]^+$ have?
(trien = $(\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2)_2$, a tetradentate ligand)

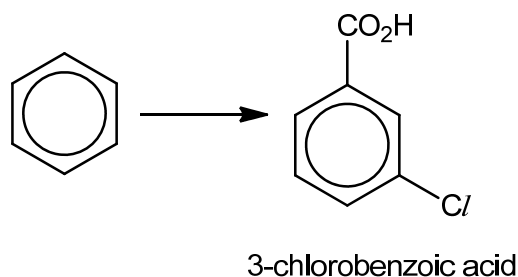
- A** 1 **B** 2 **C** 3 **D** 4

- 17 Cyclopentane undergoes substitution with bromine.

What is a possible by-product of this reaction?



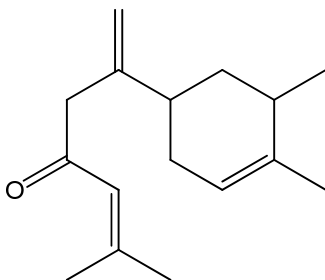
- 18 3-chlorobenzoic acid can be synthesized from benzene in three steps.



Which of the following is the best method for this synthesis?

	Step 1	Step 2	Step 3
A	$Cl_2, AlCl_3$	$CH_3Cl, AlCl_3$	$KMnO_4, H_2SO_4$
B	$Cl_2, AlCl_3$	$KMnO_4, H_2SO_4$	$CH_3Cl, AlCl_3$
C	$CH_3Cl, AlCl_3$	$KMnO_4, H_2SO_4$	$Cl_2, AlCl_3$
D	$CH_3Cl, AlCl_3$	$Cl_2, AlCl_3$	$KMnO_4, H_2SO_4$

- 19 The structure of a β -atlantone derivative is shown below.

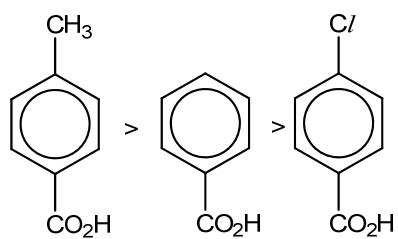


When it is completely reacted with hydrogen in the presence of platinum when heated, how many chiral centres does the product molecule possess?

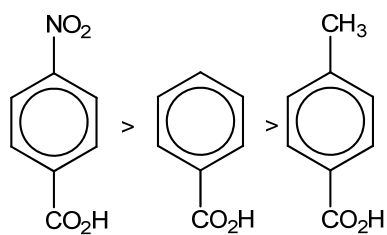
- A** 2 **B** 3 **C** 4 **D** 5

20 Which of the following correctly lists the compounds in order of decreasing acidity in aqueous solution?

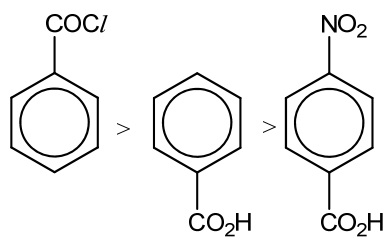
A



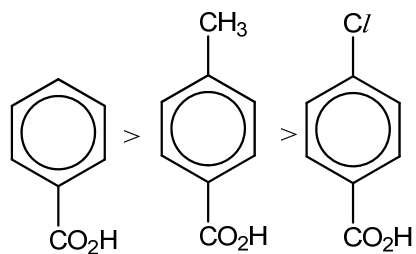
B



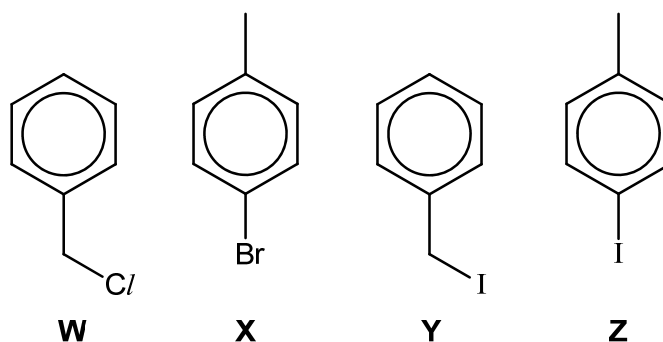
C



D



- 21 Equal amounts of compounds **W**, **X**, **Y** and **Z** are added separately to four test-tubes containing equal concentrations of ethanolic silver nitrate solution in a heated water bath. No precipitate forms in two of the tubes. In the other two tubes, precipitates form at different rates.

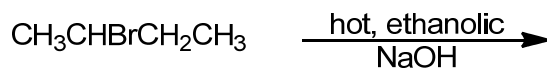


Which statements are correct?

- 1 The compounds which do not form a precipitate are **X** and **Z**.
- 2 The colour of the precipitate which forms the fastest is white.
- 3 The precipitate which forms the fastest weighs more than the other precipitate.

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

- 22 The following reaction gives a mixture of organic products.



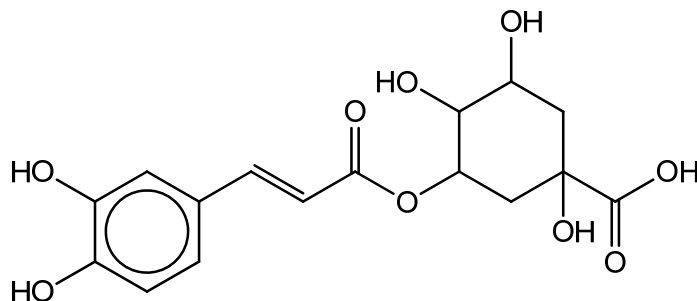
Which of the following statements are true?

- 1 The organic products formed are mainly alcohols.
- 2 The predominant type of reaction occurring is nucleophilic substitution.
- 3 There is a pair of cis-trans isomers among the organic products.

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

- 23** Chlorogenic acids account for up to 8% of the composition of unroasted coffee beans. More than 40 different varieties have been identified in green coffee beans, with 5-caffeoylquinic acid being the most prevalent.

The structure of 5-caffeoylquinic acid is shown below.

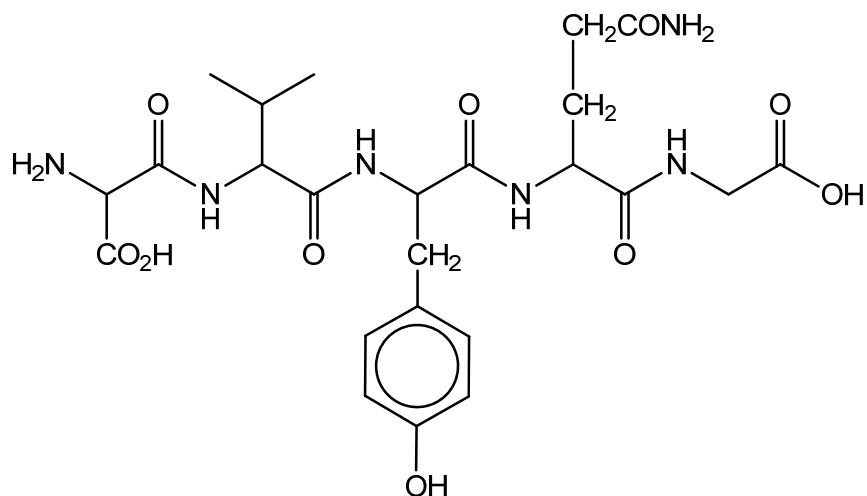


5-caffeoylquinic acid

How many moles of aqueous sodium hydroxide, sodium hydrogencarbonate and phosphorus(V) chloride will react with one mole of 5-caffeoylquinic acid at room temperature?

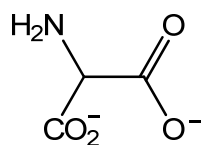
	NaOH(aq)	NaHCO ₃ (aq)	PCl ₅ (s)
A	6	3	6
B	5	1	3
C	4	3	4
D	3	1	4

24 The structure of a polypeptide chain is shown below.

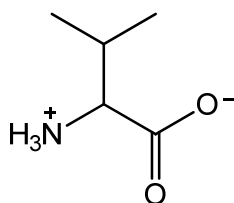


Which of the following will be formed when this polypeptide chain is heated under reflux with 6 mol dm^{-3} of NaOH(aq) ?

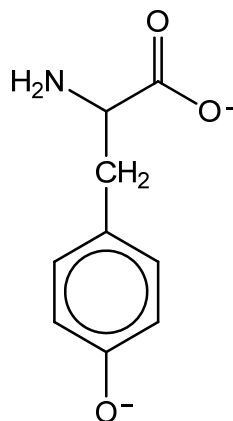
1



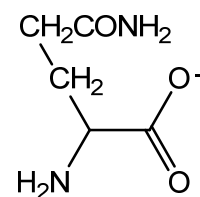
2



3

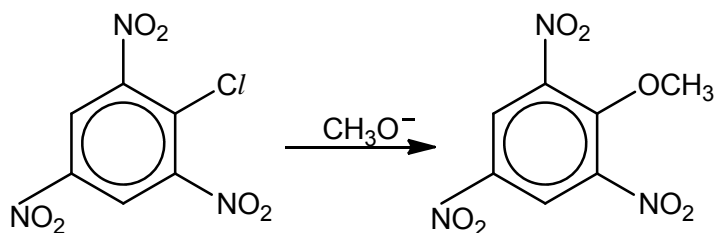


4



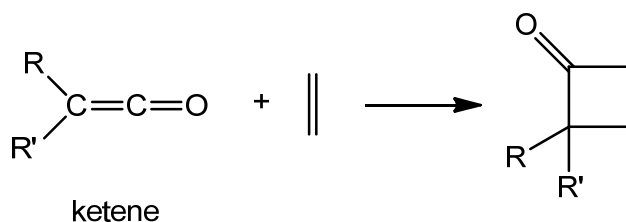
- A 1 and 3 only
 B 2 and 4 only
 C 1, 3 and 4 only
 D 1, 2, 3 and 4

- 25 Methoxide anion, CH_3O^- , can be generated when methanol reacts with sodium metal. The following reaction shows how methoxide anion reacts with an organic compound under suitable conditions.

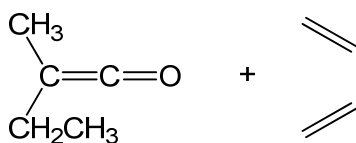


Which of the following is the correct mechanism for the above reaction?

- A electrophilic addition
 B electrophilic substitution
 C nucleophilic addition
 D nucleophilic substitution
- 26 Ketenes contain a carbon involved in both alkene and ketone functional groups. It is a reactive compound which undergoes cycloaddition reaction readily with unsaturated compounds to form cyclic rings. One example of such a reaction is shown below.



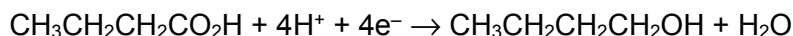
Which of the following is the correct product formed for the following cycloaddition reaction?



- A B C D

- 27 Use of the Data Booklet is relevant to this question.

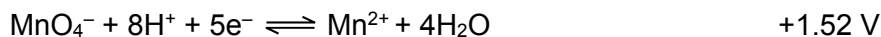
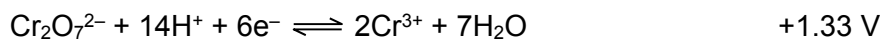
When a current is passed through a solution of butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, the following reaction occurs at the cathode.



Oxygen is produced at the anode.

Which volume of oxygen, measured at room temperature and pressure, is produced when 0.015 mol of butanoic acid is electrolysed?

- A 90 cm³ B 180 cm³ C 360 cm³ D 720 cm³
- 28 Some standard reduction potentials are given below.



Which oxidation is **not** feasible under standard conditions?

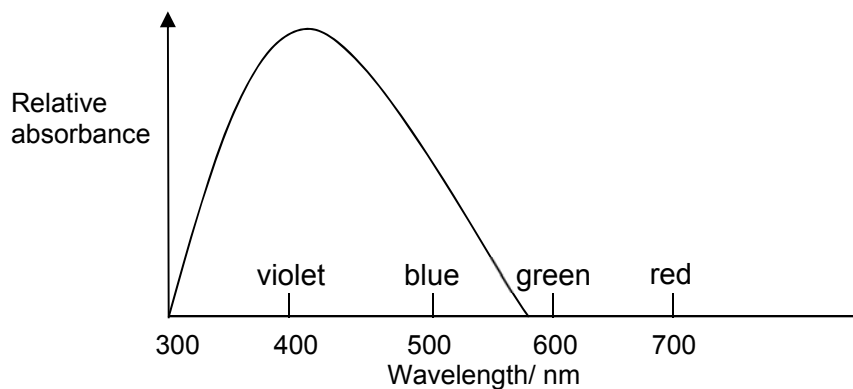
- A chloride ions by acidified manganate(VII) ions
 B bromide ions by chlorine
 C manganese(II) ions by acidified dichromate(VI) ions
 D chromium(III) ions by chlorine
- 29 A compound of chromium with the general formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ forms an aqueous solution. When this solution is treated with an excess of aqueous silver nitrate, only two third of the total chloride present is precipitated as AgCl .

Which of the following represents the structure of the chromium-containing ion present in the original compound?

- A Cr^{3+} C $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$
 B $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ D $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$

- 30** The chromium picolinate complex is soluble in water and the visible absorption spectrum of the complex is shown below:

[A visible absorption spectrum is a graph depicting the absorption of radiation by a material over a range of visible light wavelengths.]



What is the most likely colour of the chromium picolinate complex?

- | | | | |
|----------|--------|----------|--------|
| A | violet | C | yellow |
| B | blue | D | green |



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CANDIDATE
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CHEMISTRY

Paper 1 Multiple Choice

9729/01

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Data Booklet

**WORKED
SOLUTIONS**

- 1 A sample of tungsten contains four naturally occurring isotopes, ^{182}W , ^{183}W , ^{184}W and ^{186}W .

The relative atomic mass of tungsten in this sample is 183.9. What is the percentage of the isotope ^{182}W in this sample?

Isotope	Relative Abundance (%)
^{182}W	?
^{183}W	?
^{184}W	30.6
^{186}W	28.6

- A 10.5 **C 26.4**
B 14.4 D 40.8

Answer: C

Let the percentage of ^{182}W be x .

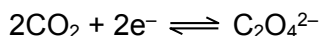
The percentage of ^{183}W would be $100 - 30.6 - 28.6 - x = 40.8 - x$

Thus,

$$183.9 = \frac{182x + 183(40.8 - x) + 184(30.6) + 186(28.6)}{100}$$
$$x = 26.4$$

- 2 20 cm³ of 0.100 mol dm⁻³ of potassium ferrate(VI), K_2FeO_4 , reacts with sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$, in an acidic medium to produce 144 cm³ of carbon dioxide gas at room temperature and pressure.

The half equation of $\text{C}_2\text{O}_4^{2-}$ is shown as follows:



What is the final oxidation state of the iron-containing species after the reaction?

- A +1 B +2 **C +3** D +4

Answer: C

Oxidation state of Fe in $\text{K}_2\text{FeO}_4 = +6$

$$\text{Amt of } \text{FeO}_4^{2-} \text{ reacted} = \frac{20}{1000} \times 0.100 = 0.002 \text{ mol}$$

$$\text{Amt of } \text{CO}_2 \text{ formed} = 144 \div 24\,000 = 0.006 \text{ mol}$$

$$\text{Amt of } \text{C}_2\text{O}_4^{2-} \text{ reacted} = \frac{1}{2} \times 0.006 = 0.003 \text{ mol}$$

Ratio of $\text{FeO}_4^{2-} : \text{C}_2\text{O}_4^{2-} = 0.002 : 0.003$



3 mol of $\text{C}_2\text{O}_4^{2-}$ will produce 6 mol of e^- and 2 mol of FeO_4^{2-} will accept 6 mol of e^- .

Therefore, 1 mol of FeO_4^{2-} will accept 3 mol of e^- .

Since FeO_4^{2-} is reduced from an oxidation state of +6 to +3.

- 3 When attracted by a strong magnet, some species are able to exhibit paramagnetism. Such species contain unpaired electrons which are able to spin in a way which aligns parallel to the magnetic field.

Which of the following species in the ground state is able to exhibit paramagnetism?

1 O

2 Al^+

3 Ti^{2+}

4 Cu^+

A 1 and 3 only

B 2 and 4 only

C 1, 3 and 4 only

D 2, 3 and 4 only

Answer: A (1 and 3 only)

1 O : $1s^2 2s^2 2p^4$ ($2p_x^2, 2p_y^1, 2p_z^1$) there are 2 unpaired electrons in 2p orbital

2 Al^+ : $1s^2 2s^2 2p^6 3s^2$ there are no unpaired electrons

3 Ti^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ there are 2 unpaired electrons in 3d orbital

4 Cu^+ : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ there are no unpaired electrons

- 4 Phosphorus(V) chloride, PCl_5 dissolves in a suitable polar solvent to produce two ions, $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$.

Which of the following shows the correct shape for PCl_5 , $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$?

	PCl_5	$[\text{PCl}_4]^+$	$[\text{PCl}_6]^-$
A	trigonal planar	square planar	square pyramidal
B	trigonal bipyramidal	square planar	octahedral
C	trigonal planar	distorted tetrahedral	square pyramidal
D	trigonal bipyramidal	tetrahedral	octahedral

Answer: D

PCl_5 : 5 bond pairs 0 lone pairs of electrons; shape is trigonal bipyramidal

$[PCl_4]^+$: 4 bond pairs 0 lone pairs of electrons; shape is tetrahedral

$[PCl_6]^-$: 6 bond pairs 0 lone pairs of electrons; shape is octahedral



- 5 The table shows the boiling point of some halogenoalkanes.

compound	boiling point/ °C
CH_3CH_2Cl	12.3
CH_3CH_2Br	34.8
CH_3CH_2I	70.0

Which of the following correctly explains the difference in the boiling point?

- 1 the electronegativity difference between the halogen and carbon increases from C-Cl to C-I
- 2 the strength of permanent dipole-permanent dipole attraction increases from C-Cl to C-I
- 3 the strength of instantaneous dipole-induced dipole attraction increases from CH_3CH_2Cl to CH_3CH_2I
- 4 the bond energy of C-X bond decreases from C-Cl to C-I

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

Answer: C (3 only)

N.B. H-bonding > pd-pd > id-id only if size of electron cloud of molecules are similar.

- 1 the electronegativity difference between the halogen and carbon should decrease from C-Cl to C-I
 Statement **does not** explain for the trend of increasing boiling point from CH_3CH_2Cl to CH_3CH_2I .
- 2 the strength of permanent dipole-permanent dipole attraction decreases from C-Cl to C-I

The statement of option 2 is **incorrect** and **does not** explain for the trend of **increasing** boiling point from $\text{CH}_3\text{CH}_2\text{Cl}$ to $\text{CH}_3\text{CH}_2\text{I}$.

- 3 the strength of instantaneous dipole-induced dipole attraction increases from $\text{CH}_3\text{CH}_2\text{Cl}$ to $\text{CH}_3\text{CH}_2\text{I}$
Statement is **correct** as the total number of electrons increases from $\text{CH}_3\text{CH}_2\text{Cl}$ to $\text{CH}_3\text{CH}_2\text{I}$ and due to the increase in id-id attraction, the boiling point increases from $\text{CH}_3\text{CH}_2\text{Cl}$ to $\text{CH}_3\text{CH}_2\text{I}$.
- 4 the bond energy of C-X bond decreases from C-Cl to C-I
Statement is correct but boiling does not break the C-X bond, so this **does not** explain for the trend of **increasing** boiling point from $\text{CH}_3\text{CH}_2\text{Cl}$ to $\text{CH}_3\text{CH}_2\text{I}$.

- 6 Which of the following changes will result in the greatest decrease in the density of a fixed mass of ideal gas?

	Pressure	Temperature/ K
A	halves	halves
B	halves	doubles
C	doubles	halves
D	doubles	doubles

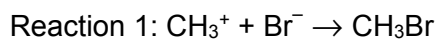
Answer: B

$$\text{Density, } \rho = \frac{m}{V}$$

$$\text{Hence, } \rho = \frac{pM_r}{RT}$$

From the formula above, the greatest decrease in density is brought about when **pressure decreases** and **temperature increases**.

- 7 Consider the following reactions.



Which of the following statement is **not** true about the reactions above?

- A Both reactions are acid-base reactions.
- B In reaction 2, HPO_4^{2-} acts as the Brønsted-Lowry base.
- C In reaction 2, HBO_3^{2-} is the conjugate acid of H_2BO_3^- .
- D In reaction 1, a dative covalent bond is formed between CH_3^+ and Br^- .

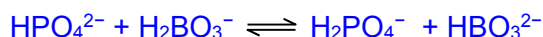
Answer: C

For Reaction 1:



CH_3^+ behaves as the Lewis acid (electron pair acceptor) while Br^- behaves as the Lewis base (electron pair donor). Hence it is an acid-base reaction (option A is true) which involves the formation of a dative covalent bond. (option D is true)

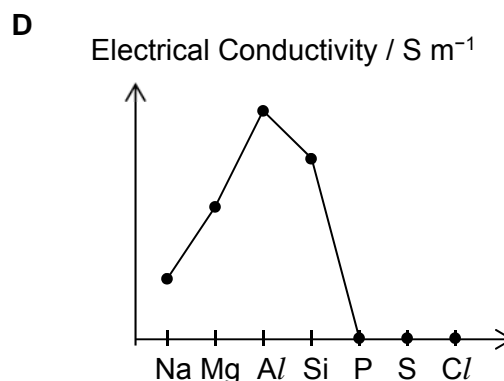
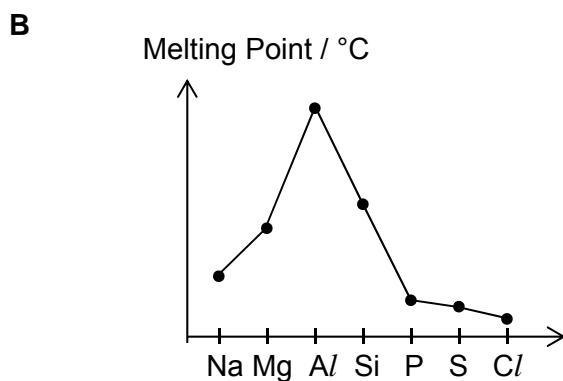
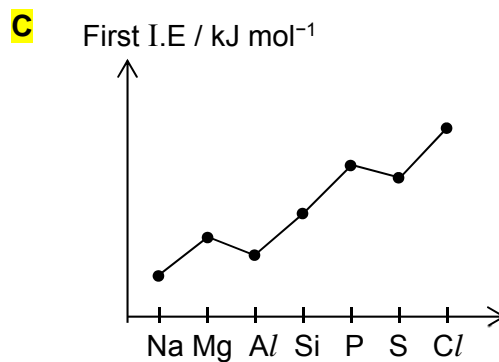
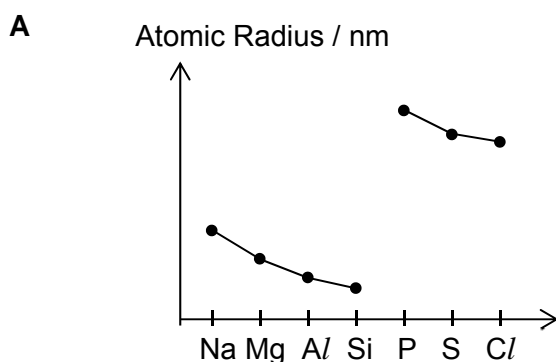
For Reaction 2:



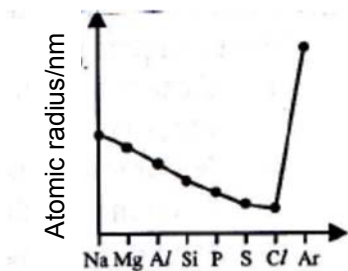
H_2BO_3^- behaves as the Brønsted-Lowry acid (H^+ donor) while HPO_4^{2-} behaves as the Brønsted-Lowry base (H^+ acceptor). Hence it is an acid-base reaction. (option B is true)

HBO_3^{2-} is the conjugate **base** of H_2BO_3^- (option C is not true)

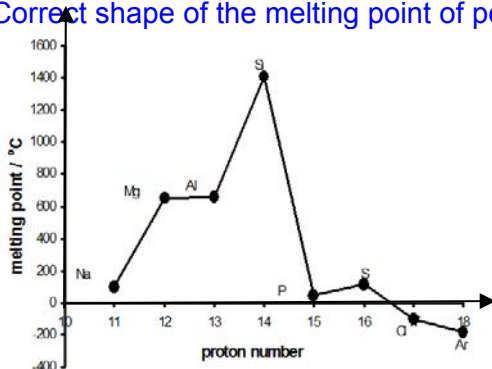
- 8 Which of the following sketches shows the correct trend in the stated property for the elements in the third period of the Periodic Table?

**Answer: C**

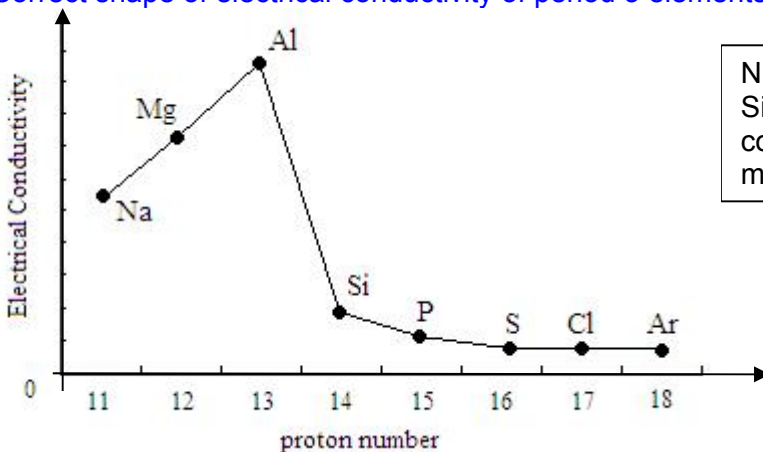
Graph A shows the trends of ionic radius across period 3 elements, not atomic radius. Atomic radius across period should be this.



Correct shape of the melting point of period 3 elements should be this:



Correct shape of electrical conductivity of period 3 elements should be this:



N.B.
Si is a semi-conductor,
conductivity should be lower than
metal.

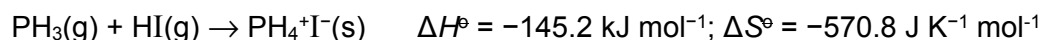
- 9 Compounds of Period 3 elements dissolve in water to form aqueous solutions that are acidic, basic or neutral.

Which of the following sequence shows the order of **increasing** resultant pH when the compounds are added to water?

- A NaCl , MgCl_2 , SiCl_4 C Al_2O_3 , MgO , SO_2
 B AlCl_3 , SiCl_4 , PCl_5 D P_4O_{10} , SiO_2 , MgO

Answer: D. pH 2, pH 7, pH 9

- 10 Phosphine reacts with hydrogen iodide to form phosphonium iodide in the reaction shown below:



Which one of the following statement is true for the above reaction?

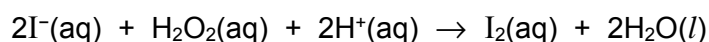
- 1 The products are less disordered than the reactants.
- 2 The reaction is non-spontaneous under standard conditions.
- 3 As temperature increases, the reaction becomes more spontaneous.

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

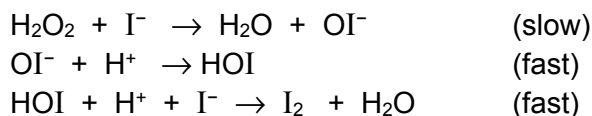
Answer: C

- 1 True. Since $\Delta S^\ominus = -570.8 \text{ J K}^{-1} \text{ mol}^{-1}$ (negative value), disorderness of the system has occurred.
- 2 True.
 At 298K, $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = (-145.2) - (298)(-570.8/1000)$
 $= +24.9 \text{ kJ mol}^{-1} > 0$ (non-spontaneous reaction)
- 3 False. Since both ΔH^\ominus and ΔS^\ominus have negative values, the reaction is only spontaneous at low temperature (so that the magnitude of $-T\Delta S^\ominus$ (+ve) decreases).

- 11 The reaction of acidified aqueous potassium iodide with aqueous hydrogen peroxide:



is thought to involve the following steps:



Which of the following conclusion can be drawn from this information?

- 1 The acid is acting as a catalyst only.
- 2 The reaction is pseudo-first order with respect to H_2O_2 .
- 3 The reaction rate is independent of the pH of the solution.

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

D 1, 2 and 3 only

Answer: B

1 False. H^+ is consumed in Step 2 and 3 and are not regenerated. Hence the acid (H^+) is not acting as a catalyst, it is a reactant in this reaction.

2 False.

Since the first step is the slow step, the rate equation is

$$\text{rate} = k[H_2O_2][I^-]$$

The reaction is first-order with respect to both H_2O_2 and I^- . Statement 2 can only be true if a large concentration of I^- is used so that the rate equation can be simplified to

$$\text{rate} = k'[H_2O_2] \quad \text{where } k' = k[I^-]$$

However, it is not mentioned in the question that a large concentration of I^- is used in the experiment.

3 True. The rate equation does not involve H^+ , hence the pH does not affect the reaction rate.

12 A first-order decomposition reaction is shown below.



The half-life of the reaction was found to be 3.47 s.

What is the time taken for $AB(g)$ to reach one-third of its initial concentration?

A 3.0 s

B 3.5 s

C 5.5 s

D 7.0 s

Answer: C

Using the following formula,

$$\frac{c_t}{c_o} = \left(\frac{1}{2}\right)^n, \quad \text{where } n = \text{no. of half-lives} = \frac{\text{time taken}}{t_{1/2}}$$

If $[AB]$ is $\frac{1}{3}$ of the initial concentration, $\frac{c_t}{c_o} = \left(\frac{1}{3}\right)$

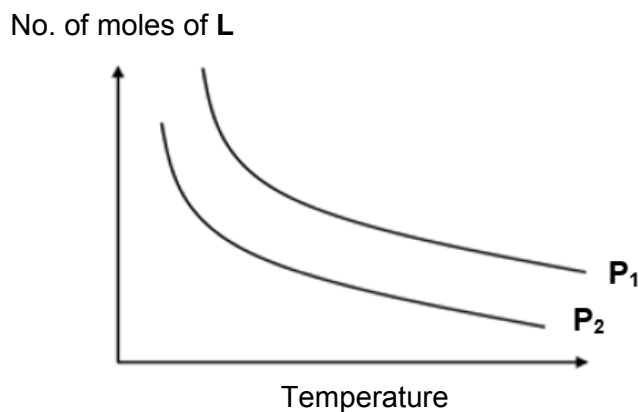
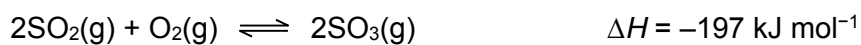
$$\frac{1}{3} = \left(\frac{1}{2}\right)^n$$

$$\lg\left(\frac{0.5}{1.5}\right) = n \lg\left(\frac{1}{2}\right)$$

$$n = 1.585$$

$$\text{time taken} = 1.585 \times 3.47 = 5.5 \text{ s}$$

- 13 The graph below shows how the number of moles of compound **L** varies with temperature at two different pressures of **P₁** and **P₂** respectively. **L** could be any of the following compounds shown in the equation at equilibrium.



What is the correct identity of **L** and the correct magnitude of pressures **P₁** and **P₂**?

	Identity of L	magnitude of pressures P₁ and P₂
A	SO ₂	P₁ > P₂
B	SO ₂	P₁ < P₂
C	SO ₃	P₁ > P₂
D	SO ₃	P₁ < P₂

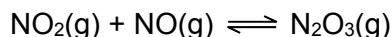
Answer: C

Since forward reaction is exothermic, higher temperatures will favour the backward endothermic reaction. At higher temperature, [SO₂] and [O₂] increases while [SO₃] decreases. Thus the two downward-sloping graphs applies to SO₃.

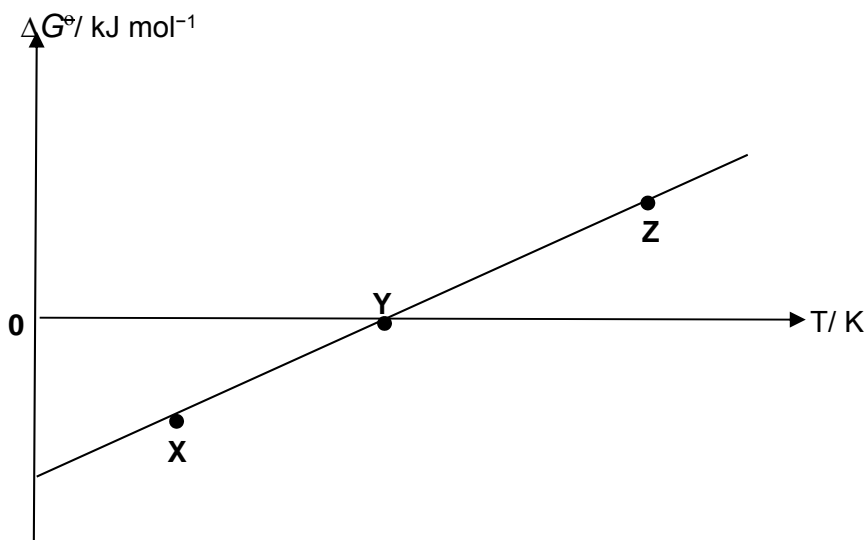
At a higher pressure, forward reaction is favoured since the product has less moles of gaseous particles, therefore [SO₃] increases.

Thus, **P₁ > P₂**.

- 14 When nitrogen dioxide, NO_2 , and nitrogen monoxide, NO , is mixed, the gases react to form dinitrogen trioxide, N_2O_3 . The reaction is shown in the following equilibrium.



The graph below shows how the ΔG^\ominus varies with temperature for the above reaction.



Using the graph above, deduce which of the following statement is true about the reaction at equilibrium?

- A At point X, more NO_2 is present as compared to that at point Y.
- B At point X, the K_c value is likely to be greater than 1.**
- C At point Y, the rate of forward reaction is greater than that of backward reaction.
- D At point Z, more N_2O_3 is present compared to that at point Y.

Answer: B

Since the reaction is at equilibrium, rate of forward reaction = rate of backward reaction for all points X, Y and Z. **(option C is incorrect)**

At point X, $\Delta G^\ominus < 0$, P.O.E lies more to the right and forward reaction occurs more readily compared to backward reaction.

$$\text{Since } K_c = \frac{[\text{N}_2\text{O}_3]}{[\text{NO}_2][\text{NO}]},$$

Therefore K_c value is likely to be greater than 1 at point X. **(option B is correct)**

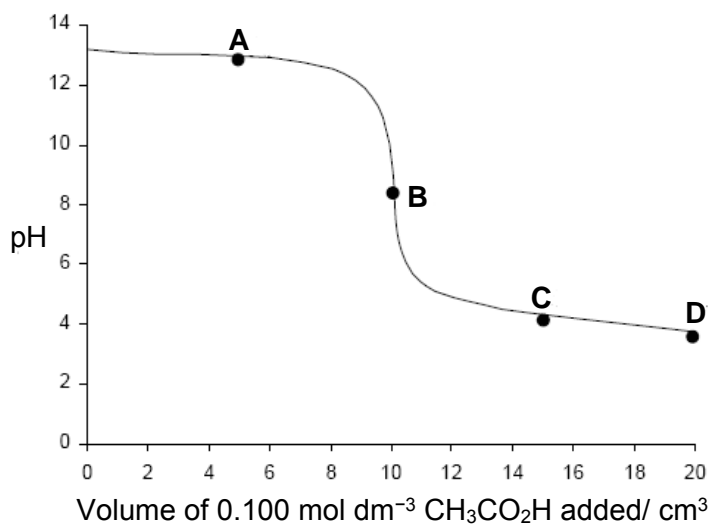
At point Y, $\Delta G^\ominus = 0$.

Comparing point X and Y, less NO_2 gas is present at X since P.O.E lies more to the right at point X compared to point Y. **(option A is wrong)**

At point Z, $\Delta G^\ominus > 0$, P.O.E lies more to the left and backward reaction occurs more readily compared to forward reaction. K_c is lesser than 1. Therefore, at point Z, less N_2O_3 gas is present as compared to that at point Y. **(option D is wrong)**

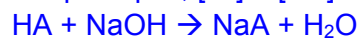
- 15 The pH changes when $0.100 \text{ mol dm}^{-3} \text{ CH}_3\text{CO}_2\text{H}$ is added dropwise to 10.0 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ NaOH(aq)}$ as shown below.

At which point on the graph does $\text{pH} = \text{p}K_a$, where K_a is the acid dissociation constant of the weak acid?



Answer: D

For $\text{pH} = \text{p}K_a$, $[\text{A}^-] = [\text{HA}]$



At A, species present: NaOH and NaA

At equivalence point B, A^- ion hydrolyses in water, $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$

At C, $[\text{A}^-] \neq [\text{HA}]$

At D,

$$\begin{aligned} n_{\text{HA}} &= 20.00/1000 \times 0.100 \\ &= 2 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} n_{\text{OH}^-} &= 10.0/1000 \times 0.100 \\ &= 1 \times 10^{-3} \text{ mol} \end{aligned}$$

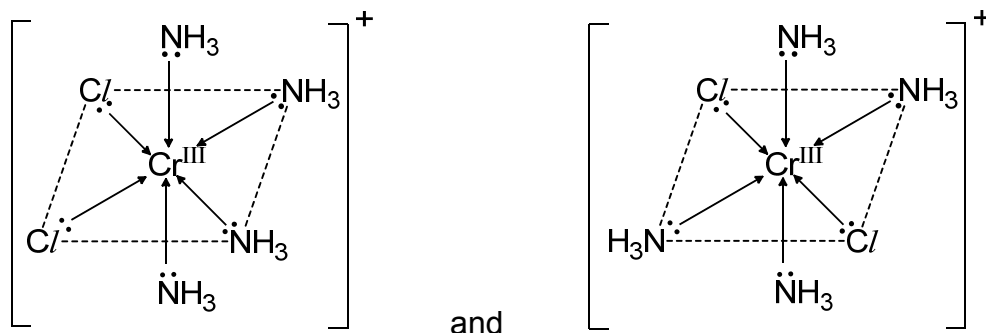
$$n_{\text{A}^- \text{ formed}} = 1 \times 10^{-3} \text{ mol}$$

$$\begin{aligned} n_{\text{HA unreacted}} &= 2 \times 10^{-3} \text{ mol} - 1 \times 10^{-3} \text{ mol} \\ &= 1 \times 10^{-3} \text{ mol} \end{aligned}$$

At D, $[\text{A}^-] = [\text{HA}]$

- 16 Coordination complexes with more than one type of ligand can exist in a number of stereoisomeric forms.

For example, the chromium(III) complex $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ can refer to the two stereoisomers as shown:

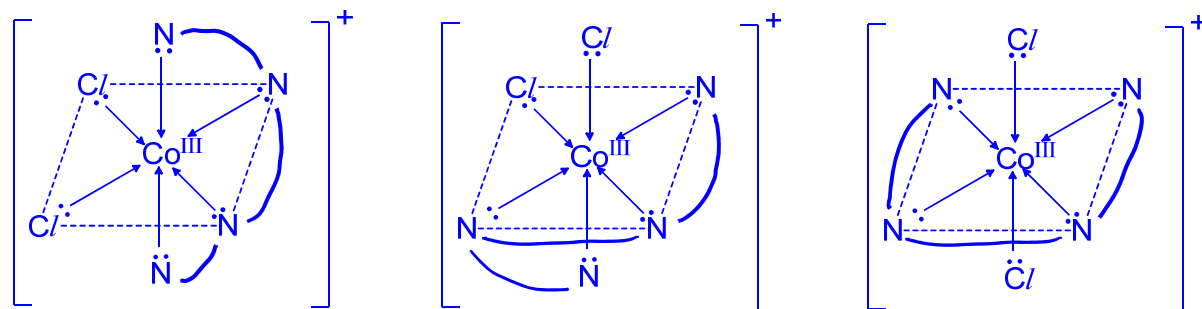


How many stereoisomers can the cobalt(III) complex $[\text{Co}(\text{trien})\text{Cl}_2]^+$ have?
(trien = $(\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2)_2$, a tetradentate ligand)

- A** 1 **B** 2 **C** 3 **D** 4

Answer: C

There are three stereoisomers for $[\text{Co}(\text{trien})\text{Cl}_2]^+$.



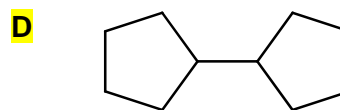
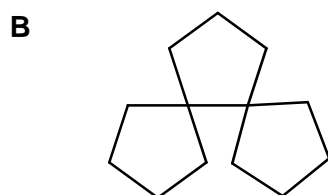
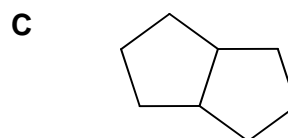
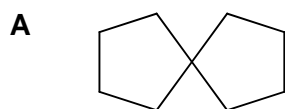
Middle two N in same plane.

Three N in same plane.

All four N in same plane.

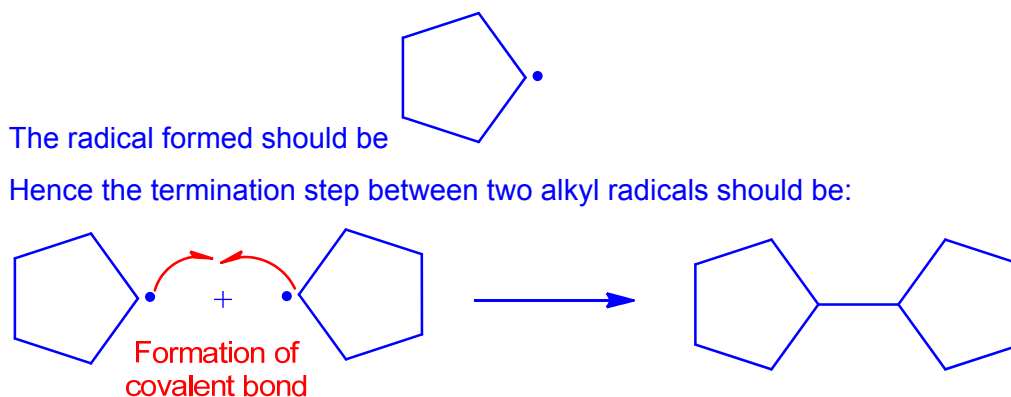
- 17 Cyclopentane undergoes substitution with bromine.

What is a possible by-product of this reaction?

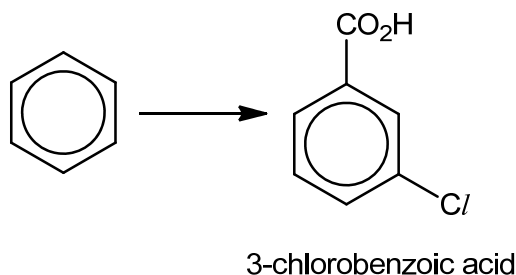


Answer: D

In **A**, **B** and **C**, the cyclopentane units are sharing carbon atoms, whereas in **D**, the carbon atoms of each cyclopentane unit are separate from other cyclopentane units. In free radical substitution, the termination step between two alkyl radicals gives rise to a new C-C bond, and the number of carbon atoms in the product should be the sum of that in the alkyl radicals.



- 18 3-chlorobenzoic acid can be synthesized from benzene in three steps.



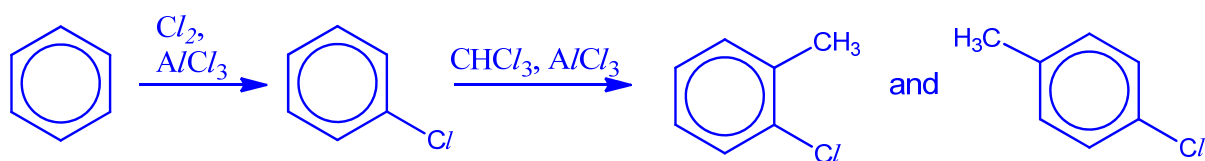
Which of the following is the best method for this synthesis?

	Step 1	Step 2	Step 3
A	$Cl_2, AlCl_3$	$CH_3Cl, AlCl_3$	$KMnO_4, H_2SO_4$
B	$Cl_2, AlCl_3$	$KMnO_4, H_2SO_4$	$CH_3Cl, AlCl_3$
C	$CH_3Cl, AlCl_3$	$KMnO_4, H_2SO_4$	$Cl_2, AlCl_3$
D	$CH_3Cl, AlCl_3$	$Cl_2, AlCl_3$	$KMnO_4, H_2SO_4$

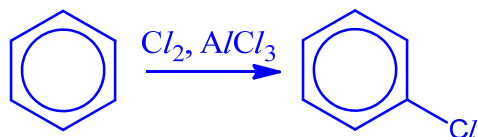
Answer: C

In this synthesis, we need to substitute $-CH_3$ (which is subsequently oxidised to $-CO_2H$) and $-Cl$ onto the benzene ring. Since both $-CH_3$ and $-Cl$ are 2,4-directing, but we want a 1,3-disubstituted product, we need to get $-CH_3$ on the ring first so that we can oxidise it to $-CO_2H$, which is 3-directing.

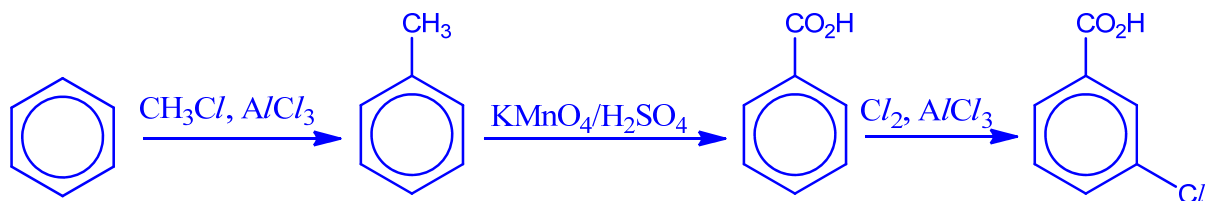
Option **A**: $-CH_3$ is substituted on 2- and 4-positions instead of the 3-position.



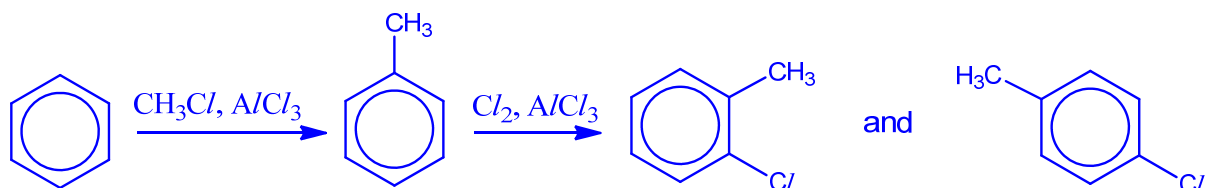
Option B: No alkyl side-chain for KMnO_4 to oxidise in Step 2.



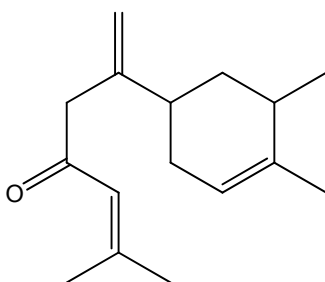
Option C:



Option D: $-\text{Cl}$ is substituted on 2- and 4-positions instead of the 3-position.



19 The structure of a β -atlantone derivative is shown below.



When it is completely reacted with hydrogen in the presence of platinum when heated, how many chiral centres does the product molecule possess?

A 2

B 3

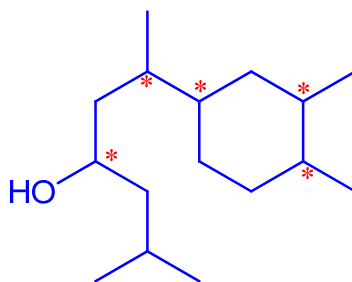
C 4

D 5

Concept: Alkenes, Carbonyl Compounds: Reduction using H_2/Pt

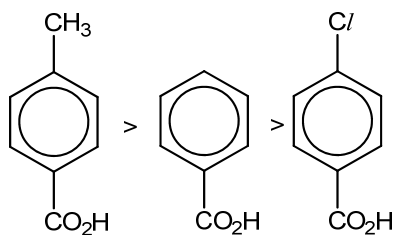
Answer: D

Reduction of $\text{C}=\text{C}$ bonds and the ketone functional group gives the following product, which has 4 chiral centres:

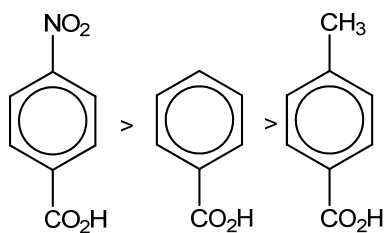


20 Which of the following correctly lists the compounds in order of decreasing acidity in aqueous solution?

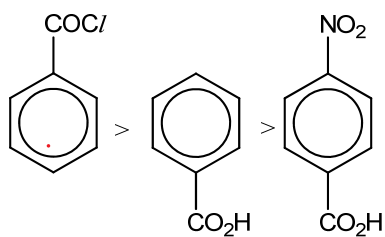
A



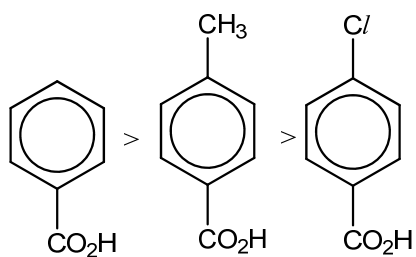
B



C



D



Answer: B

Electron-withdrawing group	$-\text{NO}_2, -\text{Cl}$
Electron-donating group	$-\text{CH}_3$

***Refer to Pg 17 of Data Booklet for the list of electron-donating groups (which activate ring reactivity) and electron-withdrawing groups (which deactivate ring reactivity).

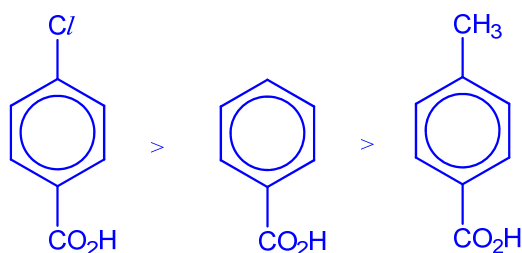
Note that

- electron-withdrawing groups increase acid strength by dispersing the negative charge on O atom and stabilizing the carboxylate ion; while
- electron-donating groups intensify the negative charge on O atom and destabilise the carboxylate ion.

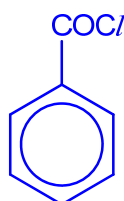
Hence option B is correct.

For the other options,

A & D The correct order should be

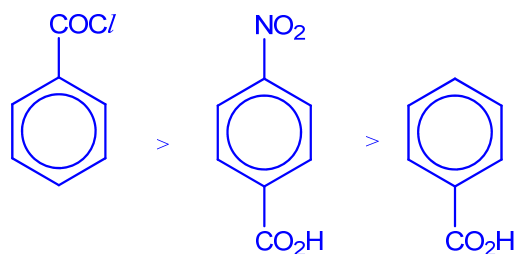


C Note that the following compound

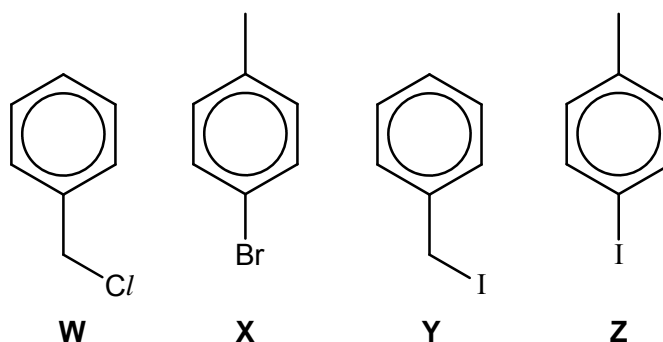


is an acyl chloride and undergoes hydrolysis readily to give HCl which is a strong acid, hence it is the strongest acid.

Hence, the correct order should be



- 21 Equal amounts of compounds **W**, **X**, **Y** and **Z** are added separately to four test-tubes containing equal concentrations of ethanolic silver nitrate solution in a heated water bath. No precipitate forms in two of the tubes. In the other two tubes, precipitates form at different rates.



Which statements are correct?

- 1 The compounds which do not form a precipitate are **X** and **Z**.
- 2 The colour of the precipitate which forms the fastest is white.
- 3 The precipitate which forms the fastest weighs more than the other precipitate.

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

Answer: B

- 1 In both **X** and **Z**, and halogen is directly connected to the benzene ring. This results in a stronger C-X bond, hence **X** and **Z** do not undergo nucleophilic substitution. ✓
- 2 The C-I bond is weaker than the C-Cl bond, hence it will break more readily. The colour of the precipitate should be yellow instead of white (which is the colour of AgCl), since it is AgI that forms the fastest. ✗
- 3 Since equal amounts (i.e., no. of moles) of the compounds **W** to **Z** are used, the same no. of moles of precipitate should form for **X** and **Z**. The M_r of AgI is greater than that of AgCl, so the AgI precipitate should weigh more than the AgCl precipitate. ✓

22 The following reaction gives a mixture of organic products.

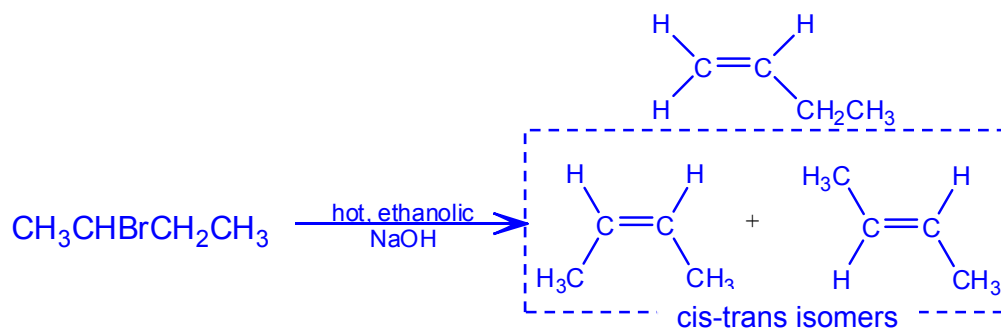
Which of the following statements are true?

- 1 The organic products formed are mainly alcohols.
- 2 The predominant type of reaction occurring is nucleophilic substitution.
- 3 There is a pair of cis-trans isomers among the organic products.

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

Answer: D

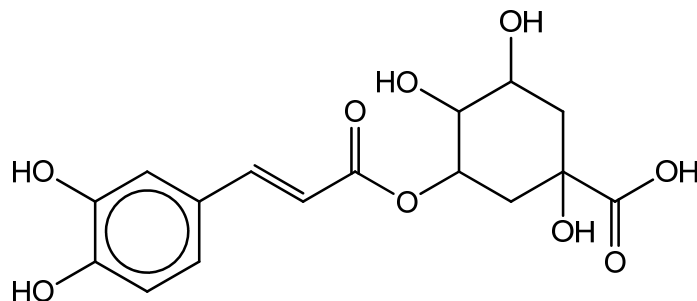
The reaction type is **elimination**. HBr can be eliminated from carbons 1 & 2, or carbons 2 & 3, to give three products, among which there is a pair of cis-trans isomers.



Do not confuse this reaction with the nucleophilic substitution of Br by OH^- , which takes place preferably under aqueous conditions instead of ethanolic conditions.

- 23 Chlorogenic acids account for up to 8% of the composition of unroasted coffee beans. More than 40 different varieties have been identified in green coffee beans, with 5-caffeoylquinic acid being the most prevalent.

The structure of 5-caffeoylquinic acid is shown below.



5-caffeoylquinic acid

How many moles of aqueous sodium hydroxide, sodium hydrogencarbonate and phosphorus(V) chloride will react with one mole of 5-caffeoylquinic acid at room temperature?

	NaOH(aq)	NaHCO ₃ (aq)	PCl ₅ (s)
A	6	3	6
B	5	1	3
C	4	3	4
D	3	1	4

Answer: D

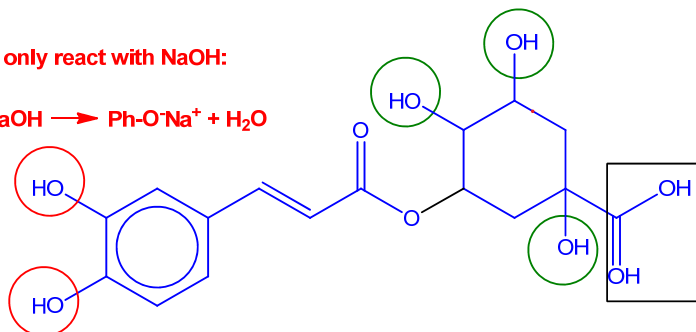
Note:

- NaOH(aq) will react with phenols and carboxylic acids only.
- NaHCO₃(aq) will react with carboxylic acids only.
- PCl₅(s) will react with alcohols and carboxylic acids only.

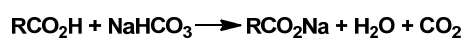
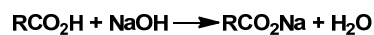
Alcohol, will only react with PCl_5



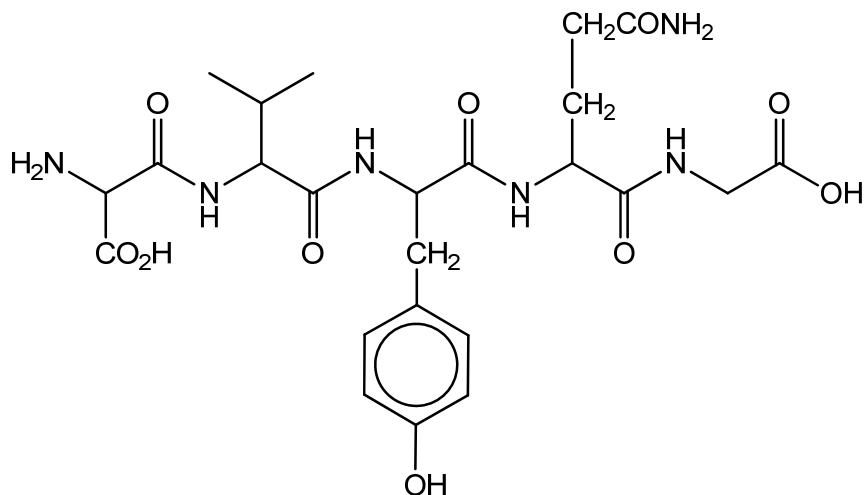
Phenol, will only react with NaOH :



Carboxylic acid, will react with NaOH , NaHCO_3 and PCl_5

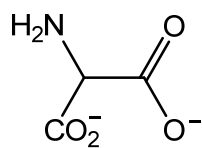


24 The structure of a polypeptide chain is shown below.

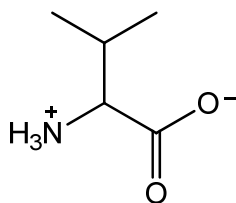


Which of the following will be formed when this polypeptide chain is heated under reflux with 6 mol dm^{-3} of NaOH(aq) ?

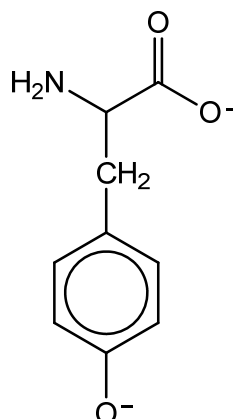
1



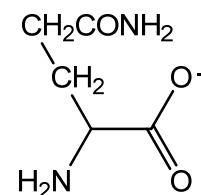
2



3

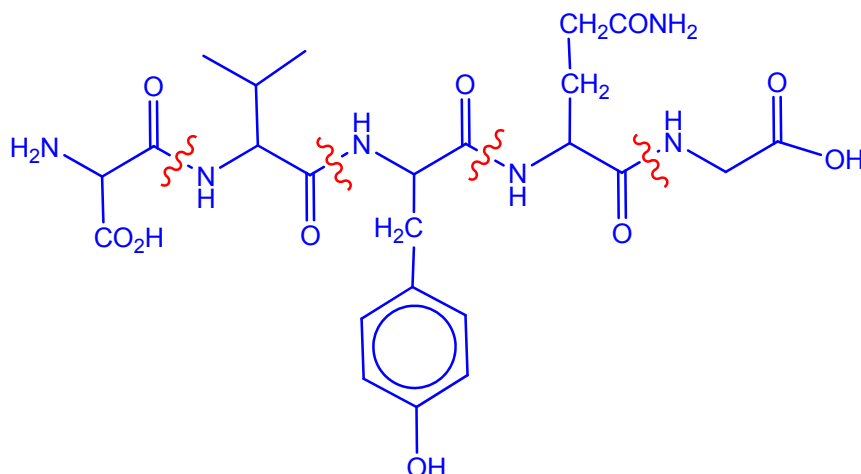


4

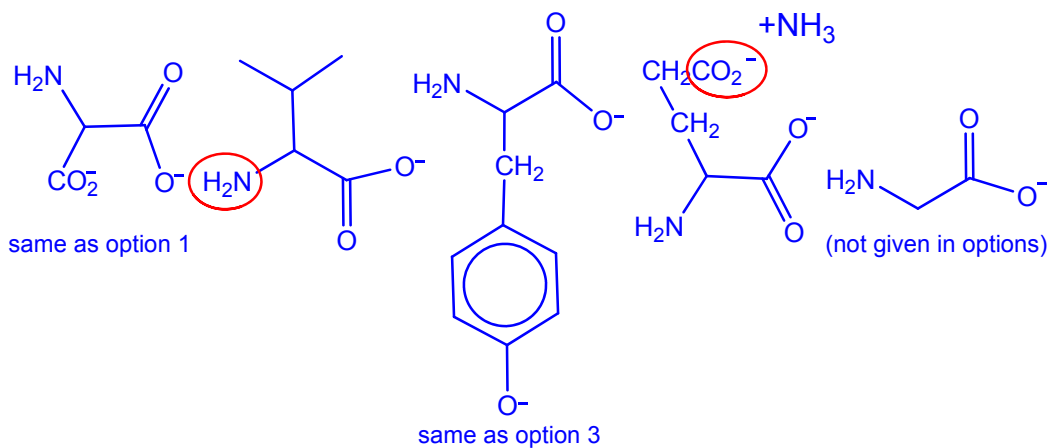


- A** 1 and 3 only
B 2 and 4 only
C 1, 3 and 4 only
D 1, 2, 3 and 4

Answer: A (1 and 3 only)



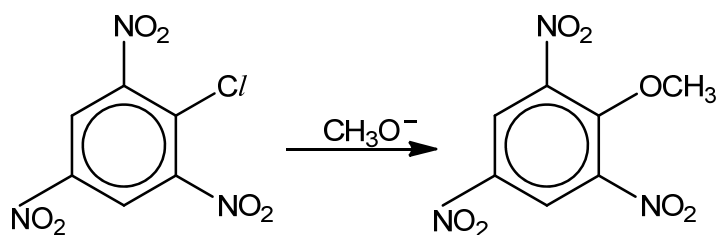
Upon hydrolysis with $\text{NaOH}(\text{aq})$, the correct products should be:



Option 2 is wrong as there should not be $-\text{NH}_3^+$ present when NaOH is used.

Option 4 is wrong as the amide group ($-\text{CONH}_2$) of the R-group should also be hydrolysed

- 25 Methoxide anion, CH_3O^- , can be generated when methanol reacts with sodium metal. The following reaction shows how methoxide anion reacts with an organic compound under suitable conditions.



Which of the following is the correct mechanism for the above reaction?

- A electrophilic addition
- B electrophilic substitution
- C nucleophilic addition
- D nucleophilic substitution**

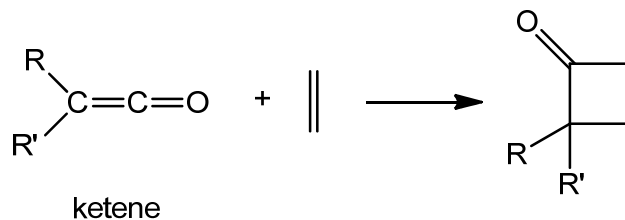
Answer: D

Methoxide anion, CH_3O^- , is a **nucleophile** (lone pair of electrons to be donated) which is attracted to the **electron deficient C** of the benzene ring bonded to Cl . (Due to the presence of 3 electron withdrawing NO_2 groups, the $\text{C}-\text{Cl}$ bond is highly polarised and weakened)

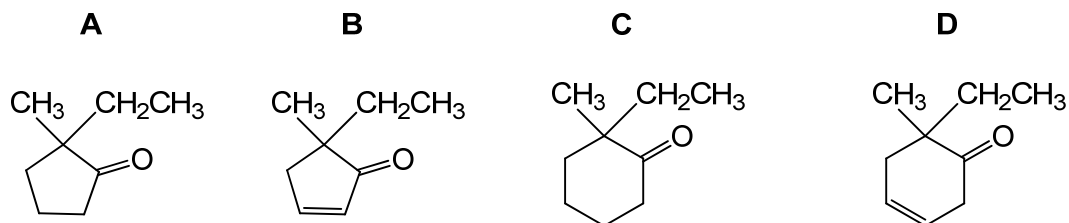
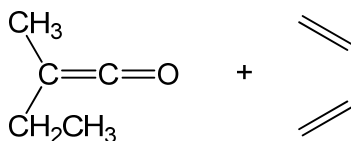
Since the benzene ring is restored at the end of the reaction, this reaction is a **substitution** reaction instead of an addition reaction. Hence, the correct mechanism of this reaction is a nucleophilic substitution.

(Note that under normal conditions, $\text{C}-\text{Cl}$ bond of chlorobenzene does have partial double bond character and will **NOT** be hydrolysed.)

- 26 Ketenes contain a carbon involved in both alkene and ketone functional groups. It is a reactive compound which undergoes cycloaddition reaction readily with unsaturated compounds to form cyclic rings. One example of such a reaction is shown below.



Which of the following is the correct product formed for the following cycloaddition reaction?

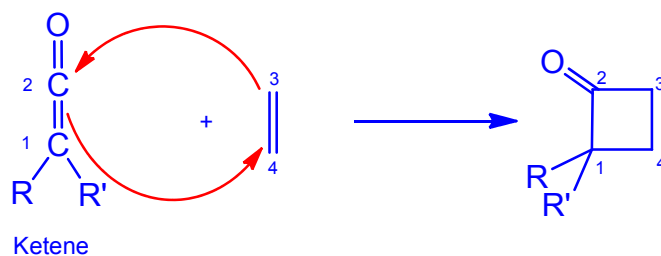


Answer: D

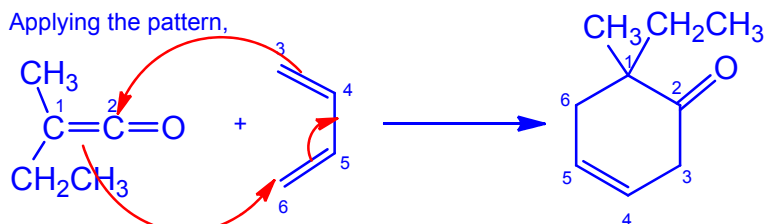
A and B cannot be the correct answer as there would be a loss of 1 C from the reactants to molecules A and B.

C is not the correct answer because there is an addition of 2 H due to a missing C=C. (by comparing the M_r of the reactants and C). In the given reaction, the number of H and C and O should still stay the same after the cycloaddition reaction.

Recognising the pattern,

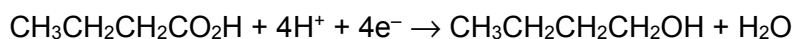


Applying the pattern,



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

When a current is passed through a solution of butanoic acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, the following reaction occurs at the cathode.



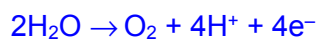
Oxygen is produced at the anode.

Which volume of oxygen, measured at room temperature and pressure, is produced when 0.015 mol of butanoic acid is electrolysed?

- A 90 cm^3 B 180 cm^3 **C 360 cm^3** D 720 cm^3

Answer: C

The half-equation for the oxidation of water to produce oxygen (under acidic conditions) is as follows:

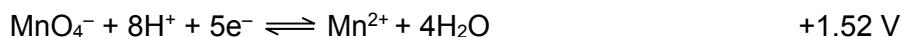
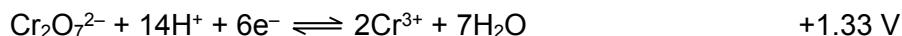


Hence, $\text{O}_2 \equiv 4\text{e}^- \equiv \text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$

No. of moles of O_2 = 0.0150 mol

Volume of O_2 = 0.0150 x 24000 = 360 cm^3

28 Some standard reduction potentials are given below.



Which oxidation is **not** feasible under standard conditions?

- A chloride ions by acidified manganate(VII) ions
- B bromide ions by chlorine
- C manganese(II) ions by acidified dichromate(VI) ions**
- D chromium(III) ions by chlorine

Answer: C

- A chloride ions by acidified manganate(VII) ions
 $E_{\text{cell}}^\ominus = 1.52 - 1.36 > 0 \quad \checkmark$
- B bromide ions by chlorine
 $E_{\text{cell}}^\ominus = 1.36 - 1.07 > 0 \quad \checkmark$
- C manganese(II) ions by acidified dichromate(VI) ions
 $E_{\text{cell}}^\ominus = 1.33 - 1.52 < 0 \quad \times$**
- D chromium(III) ions by chlorine
 $E_{\text{cell}}^\ominus = 1.36 - 1.33 > 0 \quad \checkmark$

29 A compound of chromium with the general formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ forms an aqueous solution. When this solution is treated with an excess of aqueous silver nitrate, only two third of the total chloride present is precipitated as AgCl .

Which of the following represents the structure of the chromium-containing ion present in the original compound?

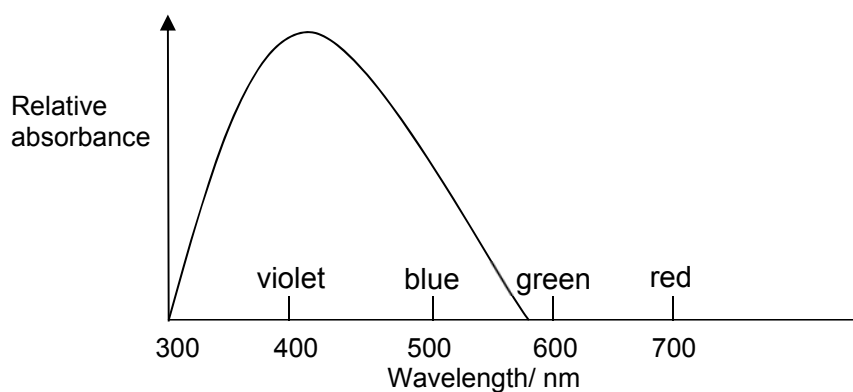
- A Cr^{3+}
- B $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- C $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$
- D $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$

Answer: C

Since only two third of the total chloride present is precipitated as AgCl , the complex of the chromium compound is $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+} \cdot 2\text{Cl}^-$, where 2 Cl^- are free ions and are not bonded to the central metal ion through dative bonding and thus free to react with silver ions to form AgCl ppt.

- 30 The chromium picolinate complex is soluble in water and the visible absorption spectrum of the complex is shown below:

[A visible absorption spectrum is a graph depicting the absorption of radiation by a material over a range of visible light wavelengths.]

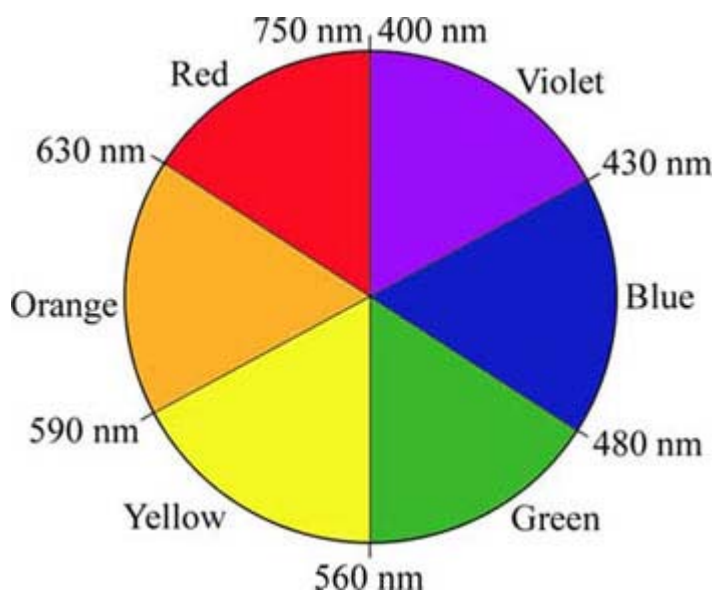


What is the most likely colour of the chromium picolinate complex?

- A violet
B blue
C yellow
D green

Answer: C

In general, the observed colour of an object corresponds to the wavelengths that are not absorbed by the object. The colour observed is complementary of the colour of light (wavelengths) absorbed. Since the complex absorbed light in the violet/blue region, the colour observed will be yellow/orange.





Catholic Junior College

JC2 Preliminary Examination

Higher 2

CANDIDATE
NAME

CLASS

CHEMISTRY

9729/02

Paper 2 Structured Questions

Friday 17 August 2018

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.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of 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			%
Paper 1		30	15
Paper 2	Q 1	15	
	Q 2	15	
	Q 3	15	
	Q 4	15	
	Q 5	15	75
Paper 3	Q 1	20	
	Q 2	20	
	Q 3	20	
	Q 4 / 5	20	80
Paper 4		55	20
Total % and Grade			100

This document consists of **18** printed pages.

Answer **all** the questions in the spaces provided.

- 1 In atmospheric chemistry, NO_x is a generic term for the nitrogen oxides that are most prevalent for air pollution, namely nitric oxide (NO) and nitrogen dioxide (NO_2). These gases contribute to the formation of smog and acid rain, as well as tropospheric ozone. In the atmosphere, dinitrogen pentoxide (N_2O_5) is an important reservoir of the NO_x species that are responsible for ozone depletion.
- (a) In the laboratory, the kinetics involving the decomposition of N_2O_5 into NO_2 and O_2 can be investigated by dissolving it in an organic solvent such as tetrachloromethane, CCl_4 . The decomposition of N_2O_5 was found to be a first-order reaction.



Table 1.1 below shows the variation of $[\text{N}_2\text{O}_5]$ with time.

Time / s	$[\text{N}_2\text{O}_5] / \text{mol dm}^{-3}$	$\ln [\text{N}_2\text{O}_5]$
0	0.910	
300	0.750	
600	0.640	
1200	0.440	
3000	0.160	

Table 1.1

- (i) State the rate equation for the decomposition of N_2O_5 .

..... [1]

- (ii) The rate equation for the decomposition of N_2O_5 can also be expressed as:

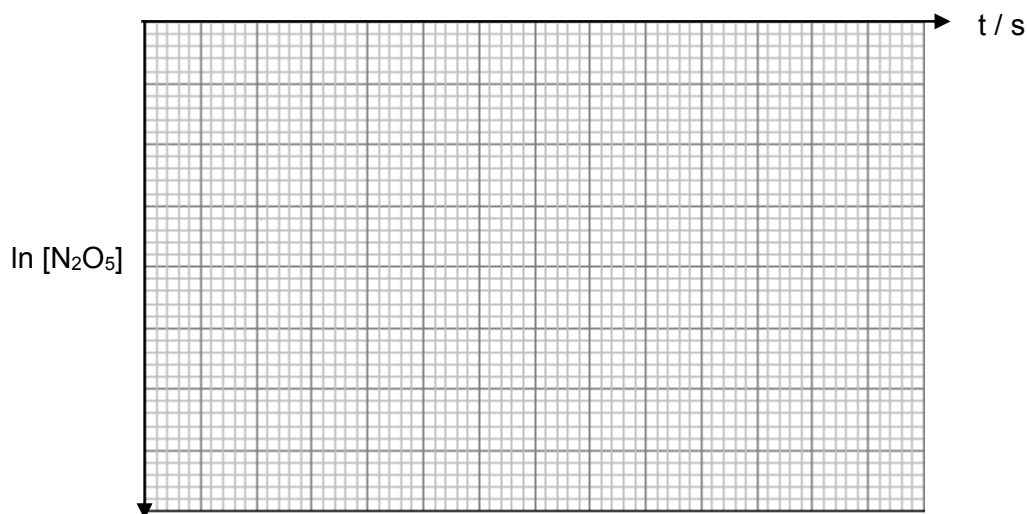
$$\ln [\text{N}_2\text{O}_5]_t = -kt + \ln [\text{N}_2\text{O}_5]_0$$

where $[\text{N}_2\text{O}_5]_0$ is the initial concentration of N_2O_5 and $[\text{N}_2\text{O}_5]_t$ is the concentration of N_2O_5 at time, t .

Using relevant data in Table 1.1, calculate the values for $\ln [\text{N}_2\text{O}_5]$ and complete Table 1.1.

[1]

- (iii) Using the following axes and relevant data in Table 1.1, plot a graph of $\ln [N_2O_5]$ against time (in second), showing how the concentration of N_2O_5 changes with time.



[2]

- (iv) Using your graph, determine a value for the rate constant, k , for the decomposition of N_2O_5 . State the units of k clearly.

[2]

- (v) Hence determine a value for the half-life of the decomposition of N_2O_5 . State the units clearly.

[1]

- (vi) Outline another experiment to determine the rate constant, k , for the decomposition of N_2O_5 in tetrachloromethane.

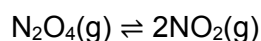
You are provided with the same solution of N_2O_5 used in the experiment described in (a).

No details regarding use of specific glassware are required.

.....

 [2]

- (b) The NO_2 produced in the decomposition reaction in (a) can exist in equilibrium with dinitrogen tetroxide (N_2O_4):



An experiment was conducted at 25 °C by varying initial concentrations of N_2O_4 and NO_2 contained in a closed reaction vessel. The initial and equilibrium concentrations of the two gases are shown in Table 1.2.

Experiment No	Initial concentration / mol dm ⁻³		Equilibrium concentration / mol dm ⁻³	
	[N_2O_4]	[NO_2]	[N_2O_4]	[NO_2]
1	0.000	0.200	0.0898	0.0204
2	0.600	0.040	0.594	0.0523
3	0.500	0.030	0.491	0.0475
4	0.446	0.050	0.448	0.0457
5	0.670	0.000	0.643	0.0547

Table 1.2

- (i) State *Le Chatelier's Principle*.

.....

 [1]

- (ii) State what will be observed when the pressure in the reaction vessel is decreased.

.....
 [1]

- (iii) Identify the experiment that gives the initial concentration of N_2O_4 : NO_2 in the ratio 15:1.

..... [1]

- (iv) Based on the experiment identified in (b)(iii), calculate a value for the equilibrium constant, K_c .

[1]

- (v) For reversible reactions involving gases, the concentrations of the gaseous reactants and products can also be expressed in terms of their partial pressures, and the value of the corresponding K_p can then be determined.

K_p and K_c is related by the following expression:

$$K_p = K_c(0.0821T)^{\Delta n}$$

where Δn = moles of gaseous products – moles of gaseous reactants based on given stoichiometric equation and T is temperature in Kelvin.

Using your answer in (b)(iv) and the above expression, calculate a value for the K_p for the reversible reaction between N_2O_4 and NO_2 .

[2]

[Total: 15]

- 2 (a) Marine organisms such as crabs use peptide signaling molecules such as glycyl-L-histidyl-L-lysine (GHK) to detect predators. In order for this peptide signaling molecule to function in water, it must exist in the form of a zwitterion.

However, due to the increase in carbon dioxide levels in the ocean, the pH of the ocean decreases as shown in Fig. 2. This affects the structure and function of the peptide signaling molecule and thus affecting the survival of these marine organisms.

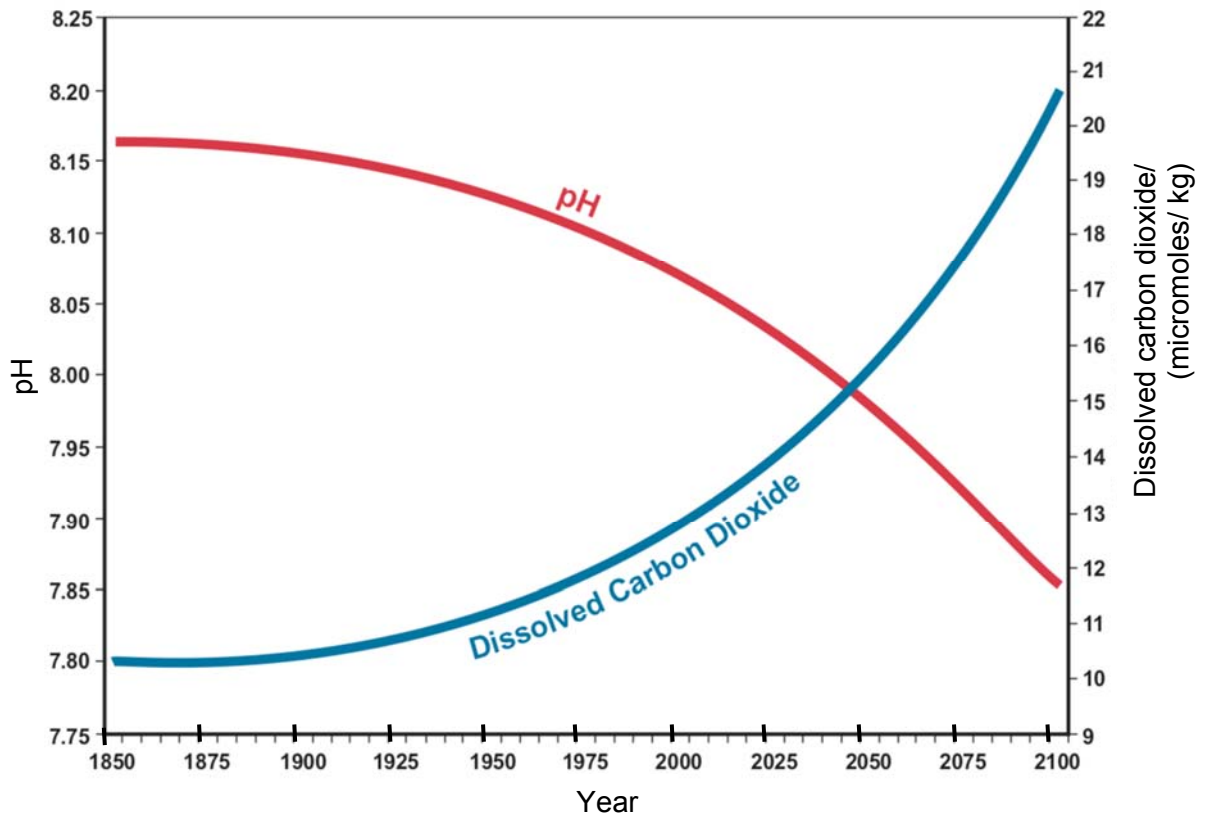


Fig. 2

- (i) State what is meant by a *zwitterion*.

..... [1]

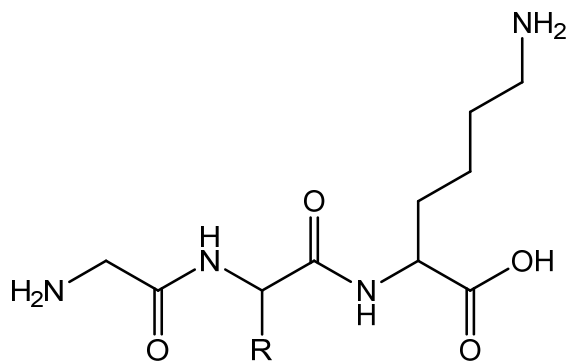
- (ii) Explain briefly why GHK, as a *zwitterion*, is highly soluble in water.

.....
 [1]

- (iii) Write an equation showing how the pH of the ocean decreases due to rising concentration of CO_2 .

..... [1]

The structure of GHK is shown below where R, which is the histidine side chain, need not be considered for this question.



GHK

- (iv) Circle any chiral carbon atom on the above structure, GHK. [1]
- (v) There can be three pK_a values associated with GHK: 2.80, 7.98, 11.44. Make use of these pK_a values to suggest the major species present in solutions of GHK at pH 7.

[2]

- (vi) Use the graph in Fig. 2 to determine from which year onwards, more than 50% of GHK in marine organisms no longer can function as a signaling molecule. Explain why this is so.

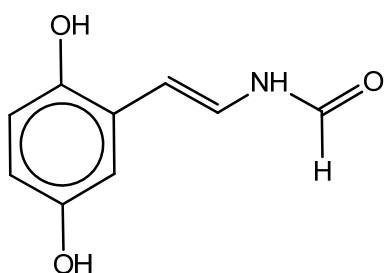
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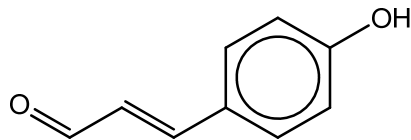
.....

..... [2]

- (b) Bioactive molecules containing dehydrotyrosine derivatives such as erbstatin and 4-hydroxy cinnamaldehyde found in marine organisms are responsible for antibacterial properties.



erbstatin



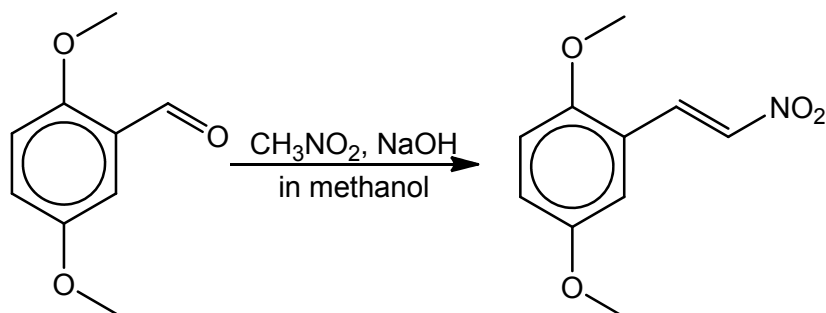
4-hydroxy cinnamaldehyde

- (i) State and explain whether erbstatin or 4-hydroxy cinnamaldehyde has a higher boiling point.

.....

 [3]

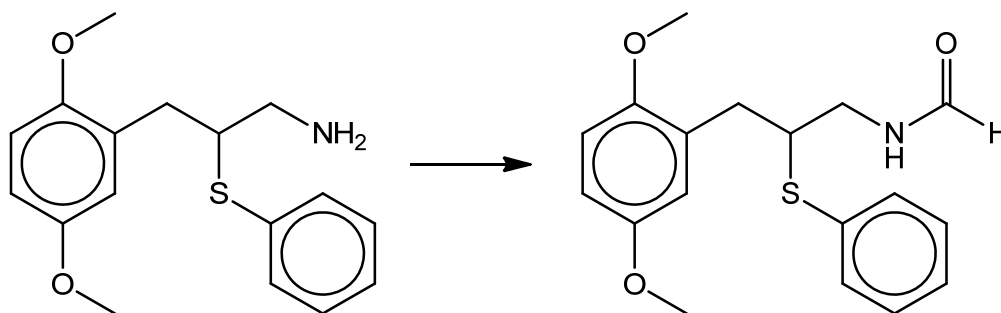
The synthesis of erbstatin involved the following step.



- (ii) Given that NaOH is used as a base to form ${}^{-}\text{CH}_2\text{NO}_2$ as a nucleophile, suggest the type of reaction in the above step.

..... [1]

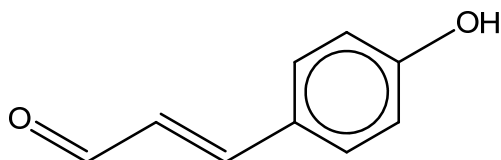
Another step in the synthesis of erbstatin is shown below.



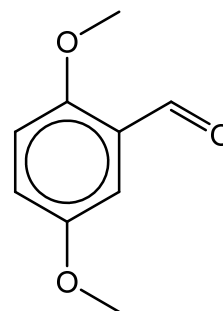
(iii) Suggest suitable reagents for the above step.

..... [1]

(iv) Describe a simple chemical test to distinguish between 4-hydroxy cinnamaldehyde and 2,5-dimethoxybenzaldehyde as shown below.



4-hydroxy cinnamaldehyde



2,5-dimethoxybenzaldehyde

.....

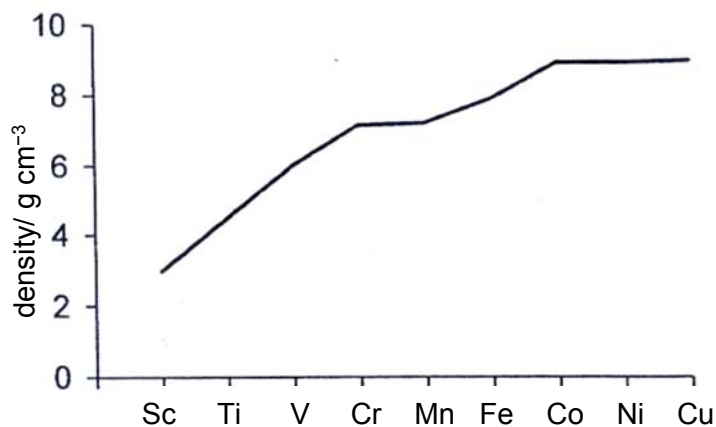
 [2]

[Total: 15]

- 3 (a) d-block elements are remarkably similar to each other in physical properties. In general, they are hard, dense and good conductors of heat and electricity. Transition elements belong to d-block elements in the Periodic Table.

Although all d-block elements are metals, they do show significant physical differences when compared to s-block elements i.e., Group 1 and 2 metals.

The graph below shows the densities of the elements Sc to Cu.

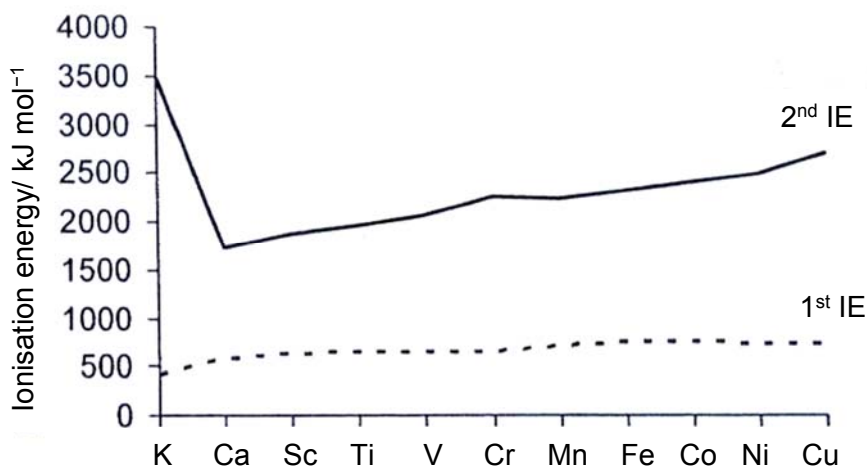


- (i) Suggest why the densities of the elements increase from Sc to Cu.

.....

 [2]

- (ii) The graph below shows the first (dashed line) and second (solid line) ionisation energies (IE) for the element K to Cu inclusive.



Explain why the first ionisation energy remains relatively constant from Sc to Cu.

.....

 [2]

- (iii) Explain briefly why is the second ionisation energy of potassium so much higher than that of the other elements.

.....
 [1]

- (b) Scandium, copper and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

- (i) Define the term *transition element*.

.....
 [1]

- (ii) State the full electronic configuration of Sc^{3+} .

.....[1]

- (iii) Explain why scandium is not classified as a transition element.

.....
 [1]

- (c) **X** and **Y** are period 3 elements.

Element **X** forms a white oxide that is slightly soluble in cold water. Its chloride dissolves in water to form a weakly acidic solution.

Element **Y** forms two oxides. 0.03 moles of one of the two oxides produces 7.00 g of white precipitate when mixed with excess barium chloride solution. The white precipitate is insoluble in dilute strong acid. A solution is obtained when equimolar of the oxide of element **Y** is added to the oxide of element **X** with water.

Identify the elements **X**, **Y**, and the oxide of **Y**.

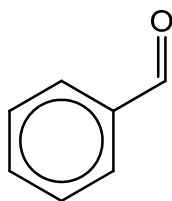
Explain the observations with the aid of relevant equations.

.....

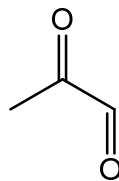
 [7]

[Total: 15]

- 4 (a) Carbonyl compounds occur naturally, giving many signature flavours. For example, benzaldehyde in almonds and 2-oxopropanal in burnt sugar.



benzaldehyde



2-oxopropanal

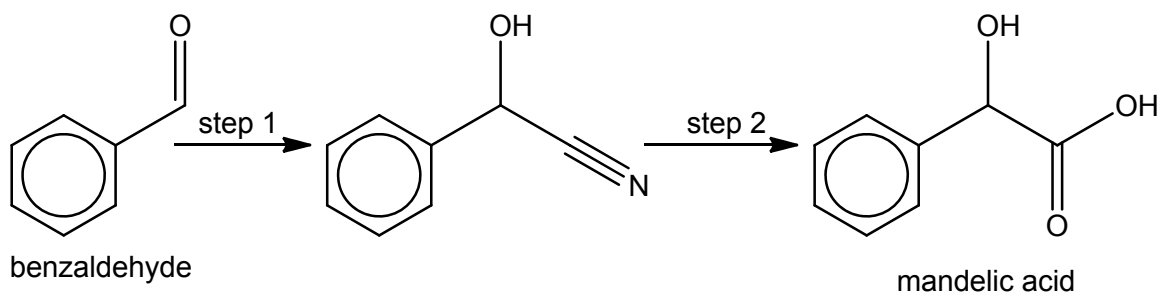
- (i) Suggest a simple chemical test that could distinguish between the two compounds above. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions:

	Observations:	Products:
benzaldehyde		
2-oxopropanal		

[3]

- (ii) Benzaldehyde undergoes a possible reaction sequence as shown below to form mandelic acid, which is used as an antibacterial agent.



State the reagents and conditions for steps 1 and 2.

Step 1:

Step 2:

[2]

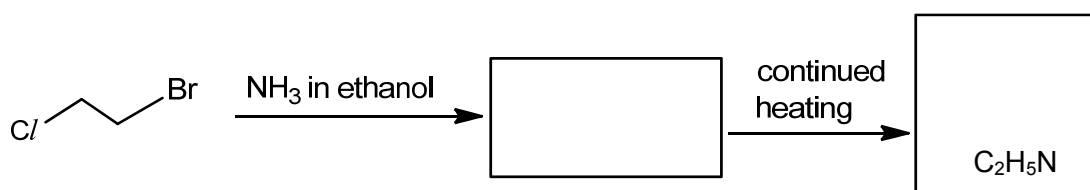
(b) Another class of naturally occurring organic compounds is halogenoalkanes, e.g. bromomethane found in vegetables, chloromethane found in algae and trichloromethane found in termites.

(i) With bromomethane and chloromethane as examples, describe and explain briefly the relative reactivities of bromo- and chloro-compounds with respect to hydrolysis.

.....

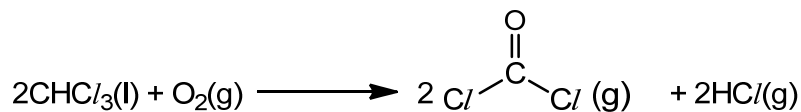
 [1]

(ii) This difference in reactivity can also be observed in organic reactions. Suggest the structural formulae of the compounds formed in the boxes below. The final product is a cyclic compound.



[2]

- (c) Trichloromethane was previously used as an anesthetic, but chronic exposure can harm the liver where it is metabolised to toxic phosgene, COCl_2 . This reaction can also take place slowly in the presence of oxygen and light, as represented below.



- (i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the enthalpy change of the above reaction.

Your cycle should include relevant data from the Data Booklet together with the following data shown below:

The enthalpy change of vaporisation of $\text{CHCl}_3(\text{l})$ is $+31 \text{ kJ mol}^{-1}$.

[3]

- (ii) Predict, with reasons, the sign of the entropy change of the reaction in (c)(i).

.....

 [2]

- (iii) Hence, state the sign of the standard Gibbs free energy change and comment on the spontaneity of the reaction.

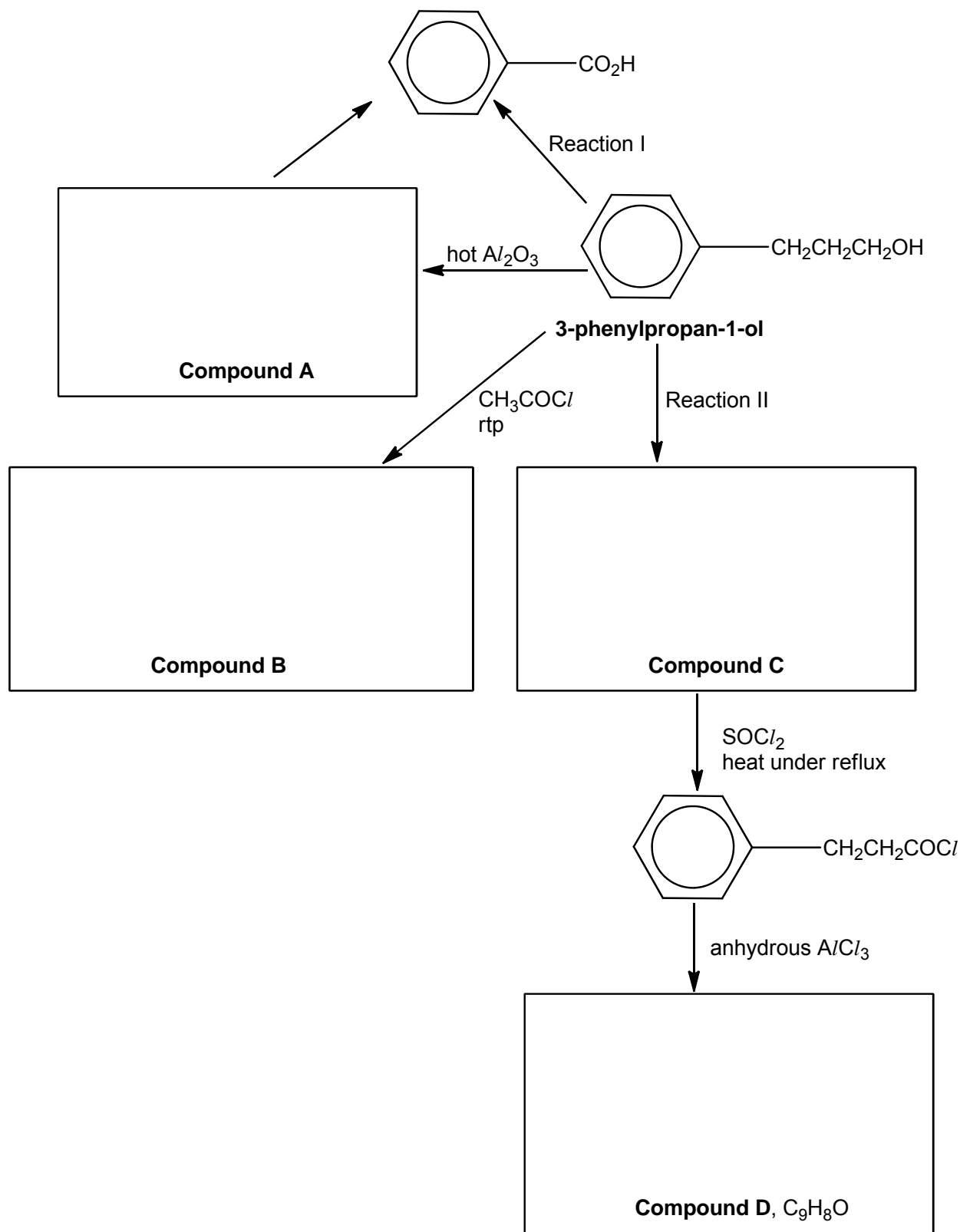
.....

 [2]

[Total: 15]

- 5 (a) Benzene is an important precursor in the production of many chemicals. 3-phenylpropan-1-ol is an example of an organic compound which contains the benzene ring as a substituent.

- (i) The following reaction scheme shows the reactions of 3-phenylpropan-1-ol. Suggest the structural formulae of compounds **A**, **B**, **C** and **D** in the boxes below.



[4]

- (ii) Using the reaction scheme for the reactions of 3-phenylpropan-1-ol, state the reagents and conditions for reactions I and II.

Reaction I

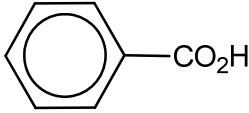
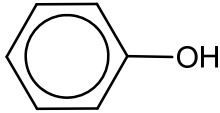
Reaction II

[2]

- (b) There is another form of important organic compounds which are derived from benzene. Benzene derivatives are formed when one of the hydrogens on the ring is replaced with a different functional group.

Benzoic acid and phenol are examples of such benzene derivatives which exhibit acidic character when dissolved in water.

The K_a values of benzoic acid, carbonic acid and phenol are given in the table below.

acid	structural formula	$K_a / \text{mol dm}^{-3}$
benzoic acid		6.3×10^{-5}
carbonic acid	H_2CO_3	4.5×10^{-7}
phenol		1.3×10^{-10}

Both benzoic acid and phenol are reacted with sodium hydroxide to form sodium benzoate and sodium phenoxide respectively.

- (i) Draw the organic product formed when CO_2 is bubbled through a solution of aqueous sodium phenoxide.

[1]

- (ii) However, no reaction occurs when CO_2 is bubbled through a solution of aqueous sodium benzoate. Explain why this is so.

.....

.....

.....

..... [1]

- (c) Cumene, C_9H_{12} , is another benzene derivative that can be used to produce phenol and propanone.

When a sample of cumene is reacted with limited chlorine in the presence of UV light, only two monochlorinated products, **X** and **Y** are formed. Only compound **X** has a chiral carbon. Both **X** and **Y** react with reagent **W** separately under heat to form hydrocarbon **Z**. Hydrocarbon **Z** is able to decolourise aqueous bromine.

- (i) State reagent **W**.

..... [1]

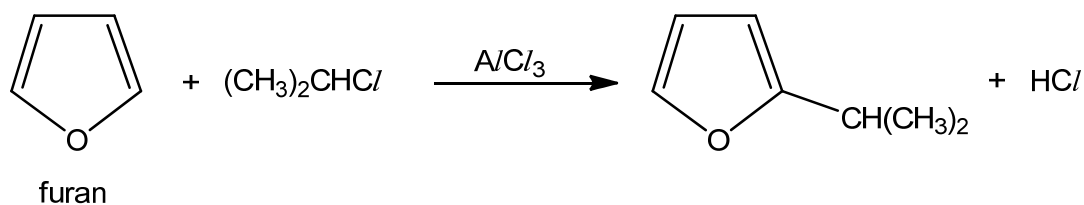
- (ii) In the space below, give the structural formula of compound **X**, **Y** and **Z**.

Compound X	Compound Y	Compound Z

[3]

- (d) As an aromatic compound, benzene undergoes electrophilic substitution reactions. Like benzene, furan, a heterocyclic five-membered aromatic ring with one O atom and four carbon atoms, is also able to undergo electrophilic substitution reactions under suitable conditions.

Outline the mechanism of the reaction below, clearly showing all the steps involved.



[3]

[Total: 15]



Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE
NAME

CLASS

2T

CHEMISTRY

9729/02

Paper 2 Structured Questions

Friday 17 August 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

WORKED SOLUTIONS

This document consists of **19** printed pages.

Answer **all** the questions in the spaces provided.

- 1 In atmospheric chemistry, NO_x is a generic term for the nitrogen oxides that are most prevalent for air pollution, namely nitric oxide (NO) and nitrogen dioxide (NO_2). These gases contribute to the formation of smog and acid rain, as well as tropospheric ozone. In the atmosphere, dinitrogen pentoxide (N_2O_5) is an important reservoir of the NO_x species that are responsible for ozone depletion.
- (a) In the laboratory, the kinetics involving the decomposition of N_2O_5 into NO_2 and O_2 can be investigated by dissolving it in an organic solvent such as tetrachloromethane, CCl_4 . The decomposition of N_2O_5 was found to be a first-order reaction.



Table 1.1 below shows the variation of $[\text{N}_2\text{O}_5]$ with time.

Time / s	$[\text{N}_2\text{O}_5] / \text{mol dm}^{-3}$	$\ln [\text{N}_2\text{O}_5]$
0	0.910	-0.0943
300	0.750	-0.288
600	0.640	-0.446
1200	0.440	-0.821
3000	0.160	-1.83

Table 1.1

- (i) State the rate equation for the decomposition of N_2O_5 .

Rate = $k[\text{N}_2\text{O}_5]$ [1]

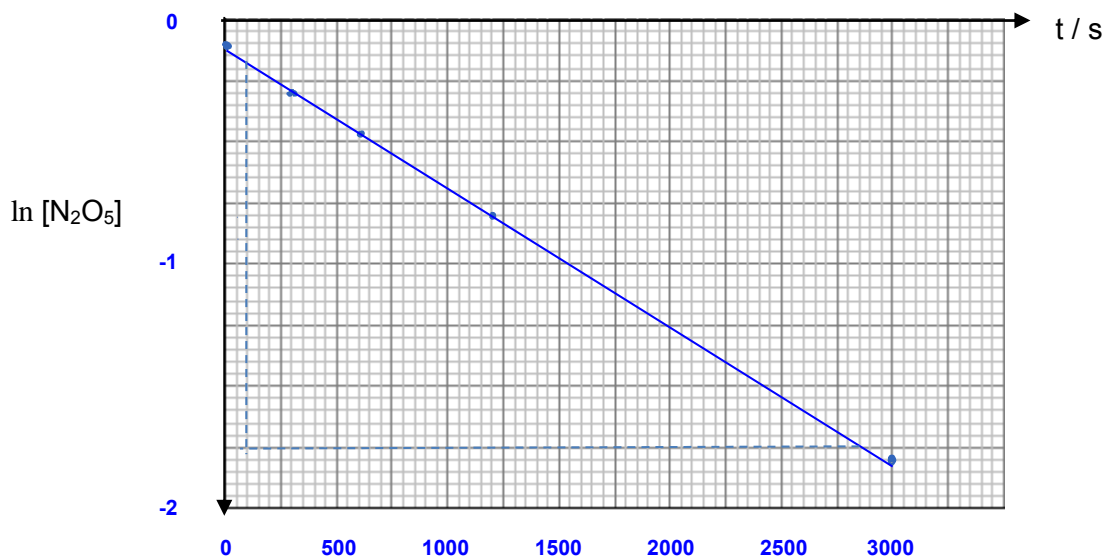
- (ii) The rate equation for the decomposition of N_2O_5 can also be expressed as:

$$\ln [\text{N}_2\text{O}_5]_t = -kt + \ln [\text{N}_2\text{O}_5]_0$$

where $[\text{N}_2\text{O}_5]_0$ is the initial concentration of N_2O_5 and $[\text{N}_2\text{O}_5]_t$ is the concentration of N_2O_5 at time, t .

Using relevant data in Table 1.1, calculate the values for $\ln [\text{N}_2\text{O}_5]$ and complete Table 1.1. [1]

- (iii) Using the following axes and relevant data in Table 1.1, plot a graph of $\ln [N_2O_5]$ against time (in second), showing how the concentration of N_2O_5 changes with time.



[2]

- (iv) Using your graph, determine a value for the rate constant, k , for the decomposition of N_2O_5 . State the units of k clearly. [2]

Using the points (100, -0.155) and (2850, -1.75)

$k = -\text{gradient}$

$$= - \left[\frac{-0.155 - (-1.75)}{100 - 2850} \right]$$

$$= 5.80 \times 10^{-4} \text{ s}^{-1}$$

- (v) Hence determine a value for the half-life of the decomposition of N_2O_5 . State the units clearly. [1]

$$t_{1/2} = \frac{\ln 2}{k}$$

$$= \frac{\ln 2}{5.80 \times 10^{-4}}$$

$$= 1195 \text{ s}$$

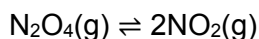
- (vi) Outline another experiment to determine the rate constant, k , for the decomposition of N_2O_5 in tetrachloromethane.

You are provided with the same solution of N_2O_5 used in the experiment described in (a).

No details regarding use of specific glassware are required.

1. Measure the volume of gases (NO_2 and O_2) produced OR the colour intensity of the brown NO_2 gas (using a colorimeter) at regular time intervals from the start of reaction
 2. Plot a graph of "volume of gases produced against time" OR "colour intensity against time" and determine the half-life from the graph.
 3. Use the equation $t_{1/2} = \frac{\ln 2}{k}$ to determine the value of k .
- [2]

- (b) The NO_2 produced in the decomposition reaction in (a) can exist in equilibrium with dinitrogen tetroxide (N_2O_4):



An experiment was conducted at 25 °C by varying initial concentrations of N_2O_4 and NO_2 contained in a closed reaction vessel. The initial and equilibrium concentrations of the two gases are shown in Table 1.2.

Experiment No	Initial concentration / mol dm ⁻³		Equilibrium concentration / mol dm ⁻³	
	[N_2O_4]	[NO_2]	[N_2O_4]	[NO_2]
1	0.000	0.200	0.0898	0.0204
2	0.600	0.040	0.594	0.0523
3	0.500	0.030	0.491	0.0475
4	0.446	0.050	0.448	0.0457
5	0.670	0.000	0.643	0.0547

Table 1.2

- (i) State *Le Chatelier's Principle*.

Le Chatelier's Principle states that if a change (e.g. change in concentration, pressure and temperature) is made to a system in equilibrium, the system reacts in such a way as to tend to oppose the change, and a new equilibrium is formed.

..... [1]

- (ii) State what will be observed when the pressure in the reaction vessel is decreased.

The brown colour of the gas (NO₂) darkens.

..... [1]

- (iii) Identify the experiment that gives the initial concentration of N₂O₄ : NO₂ in the ratio 15:1.

Experiment 2

..... [1]

- (iv) Based on the experiment identified in (b)(iii), calculate a value for the equilibrium constant, K_c . [1]

$$\begin{aligned} K_c &= \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \\ &= \frac{(0.0523)^2}{(0.594)} \\ &= 4.60 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

- (v) For reversible reactions involving gases, the concentrations of the gaseous reactants and products can also be expressed in terms of their partial pressures, and the value of the corresponding K_p can then be determined. K_p and K_c is related by the following expression:

$$K_p = K_c(0.0821T)^{\Delta n}$$

where Δn = moles of gaseous products – moles of gaseous reactants based on given stoichiometric equation and T is temperature in Kelvin.

Using your answer in (b)(iv) and the above expression, calculate a value for the K_p for the reversible reaction between N₂O₄ and NO₂.

$$\begin{aligned} K_p &= K_c(0.0821T)^{\Delta n} \\ &= (4.60 \times 10^{-3})(0.0821)(298)^{(2-1)} \\ &= 0.113 \end{aligned}$$

[2]

[Total: 15]

- 2 (a) Marine organisms such as crabs use peptide signaling molecules such as glycyl-L-histidyl-L-lysine (GHK) to detect predators. In order for this peptide signaling molecule to function in water, it must exist in the form of a zwitterion.

However, due to the increase in carbon dioxide levels in the ocean, the pH of the ocean decreases as shown in Fig. 2. This affects the structure and function of the peptide signaling molecule and thus affecting the survival of these marine organisms.

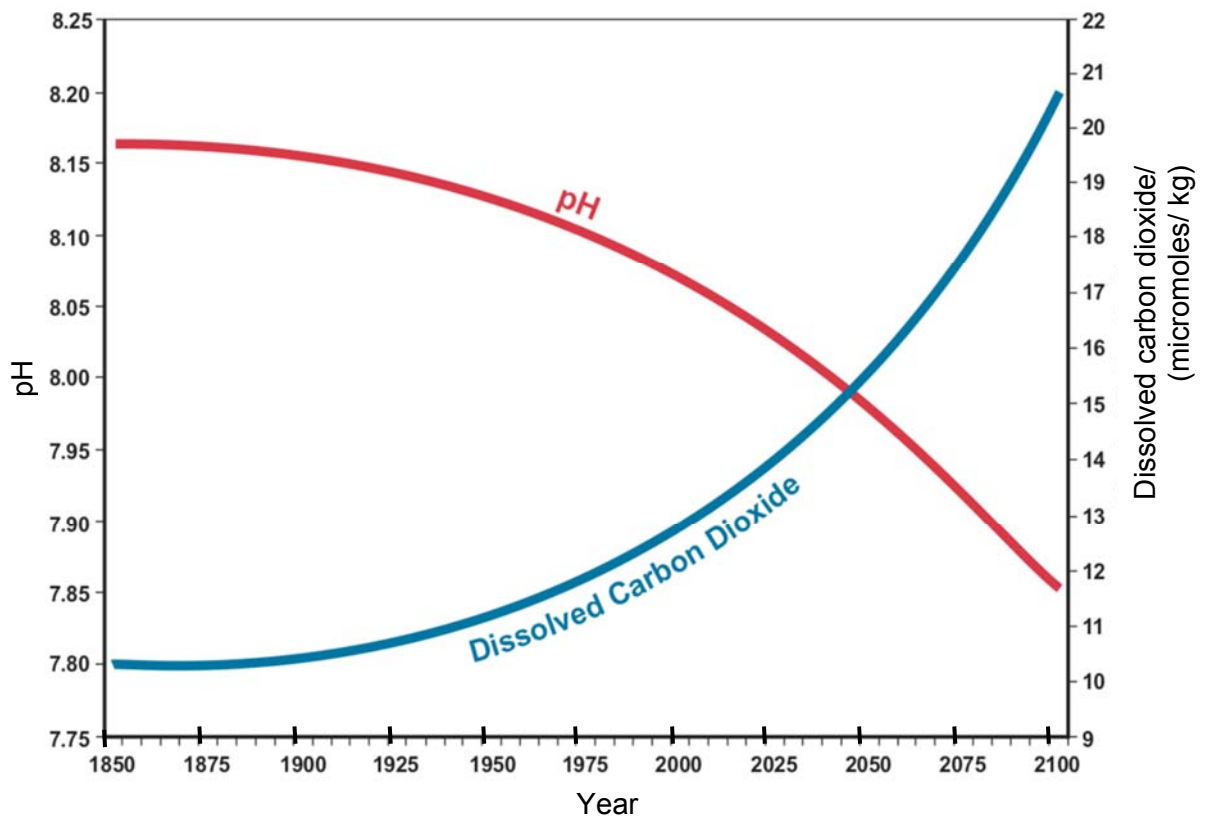


Fig. 2

- (i) State what is meant by a *zwitterion*.

Zwitterion is a species where it is dipolar ion and have no nett charge. [1]

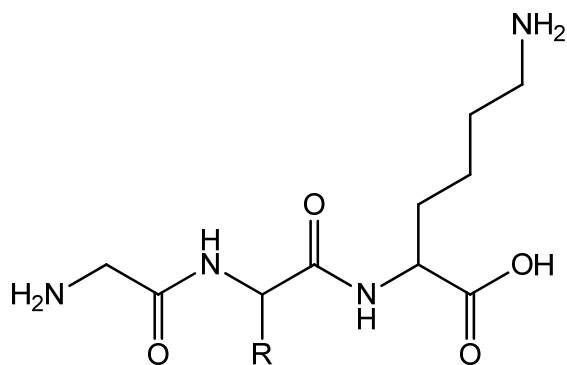
- (ii) Explain briefly why GHK, as a *zwitterion*, is highly soluble in water.

GHK as a zwitterion is able to form ion-dipole attraction with water molecules. [1]

- (iii) Write an equation showing how the pH of the ocean decreases due to rising concentration of CO₂.

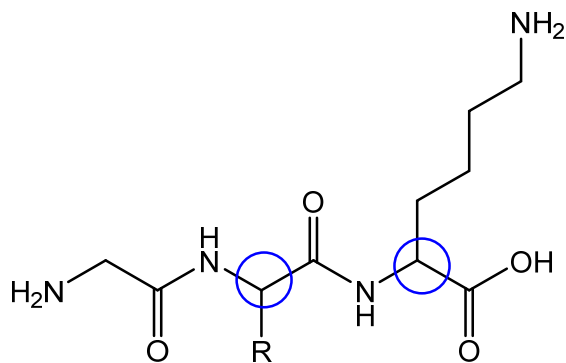
CO₂ + H₂O ⇌ H⁺ + HCO₃⁻ [1]

The structure of GHK is shown below where R, which is the histidine side chain, need not be considered for this question.

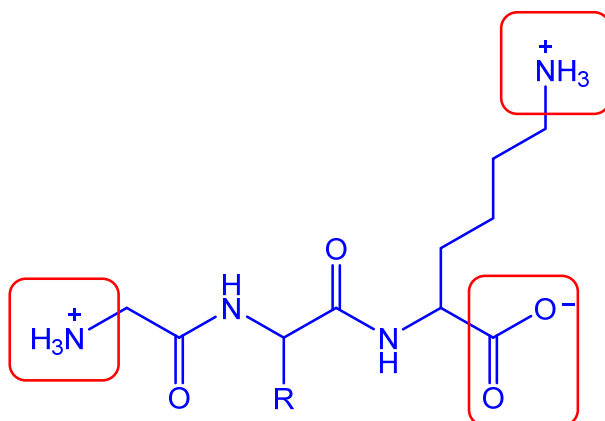


GHK

- (iv) Circle any chiral carbon atom on the above structure, GHK. [1]



- (v) There can be three pK_a values associated with GHK: 2.80, 7.98, 11.44. Make use of these pK_a values to suggest the major species present in solutions of GHK at pH 7.



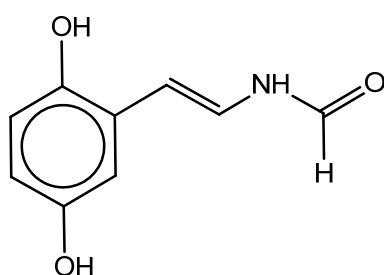
[2]

- (vi) Use the graph in Fig. 2 to determine from which year onwards more than 50% of GHK in marine organisms no longer can function as a signaling molecule. Explain why this is so.

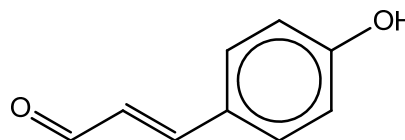
2050. For GHK no longer function as a signaling molecule, it cannot exist as a zwitterion which both the -NH_2 groups are protonated. Since the pKa value of -NH_2 is 7.98, the pH value lower than that will result in -NH_2 to be protonated:

..... [2]

- (b) Bioactive molecules containing dehydrotyrosine derivatives such as erbstatin and 4-hydroxy cinnamaldehyde found in marine organisms are responsible for antibacterial properties.



erbstatin



4-hydroxy cinnamaldehyde

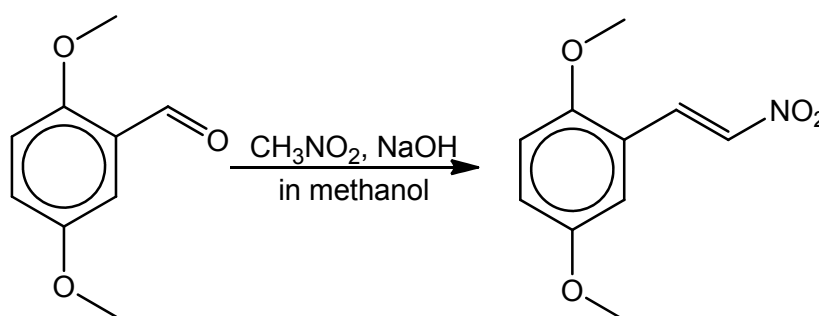
- (i) State and explain whether erbstatin or 4-hydroxy cinnamaldehyde has a higher boiling point.

Erbstatin has a higher boiling point

since it can form more extensive intermolecular hydrogen bonds therefore requires more energy to overcome the intermolecular hydrogen bonds in

Erbstatin compared to 4-hydroxy cinnamaldehyde: [3]

The synthesis of erbstatin involved the following step.

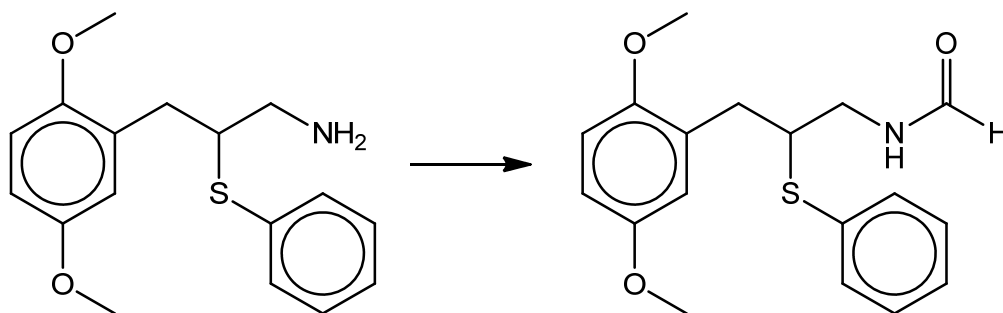


- (ii) Given that NaOH is used as a base to form $\text{^-CH}_2\text{NO}_2$ as a nucleophile, suggest the type of reaction in the above step.

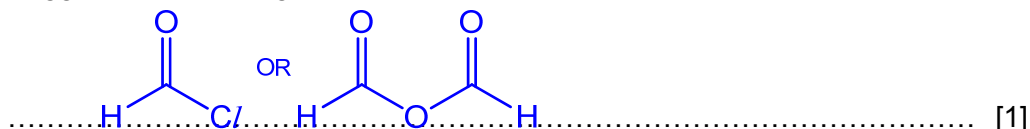
Condensation OR Addition-elimination

..... [1]

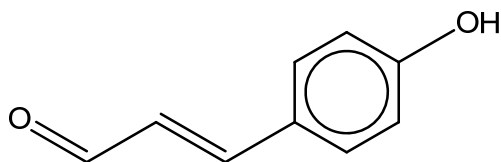
Another step in the synthesis of erbstatin is shown below.



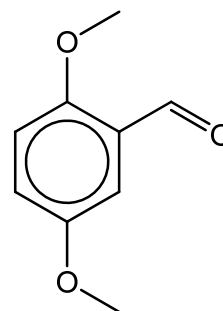
(iii) Suggest suitable reagents for the above step.



(iv) Describe a simple chemical test to distinguish between 4-hydroxy cinnamaldehyde and 2,5-dimethoxybenzaldehyde as shown below.



4-hydroxy cinnamaldehyde



2,5-dimethoxybenzaldehyde

..... Add neutral FeCl_3 to separate test tubes containing each sample.

..... Purple colouration is observed with erbstatin. No purple colouration observed with 2,5-dimethoxybenzaldehyde.

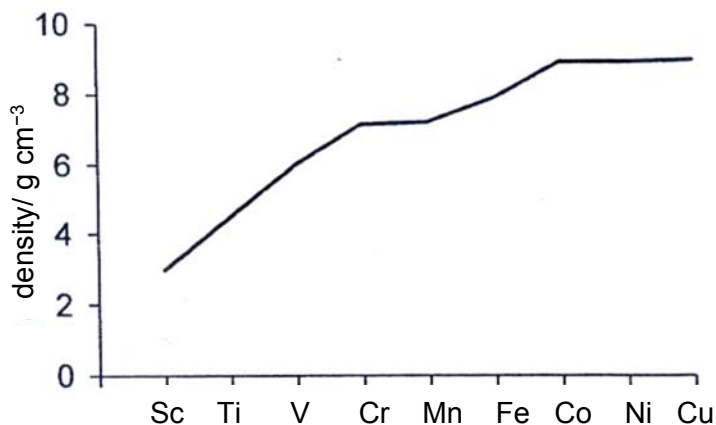
..... [2]

[Total: 15]

- 3 (a) d-block elements are remarkably similar to each other in physical properties. In general, they are hard, dense and good conductors of heat and electricity. Transition elements belong to d-block elements in the Periodic Table.

Although all d-block elements are metals, they do show significant physical differences when compared to s-block elements i.e., Group 1 and 2 metals.

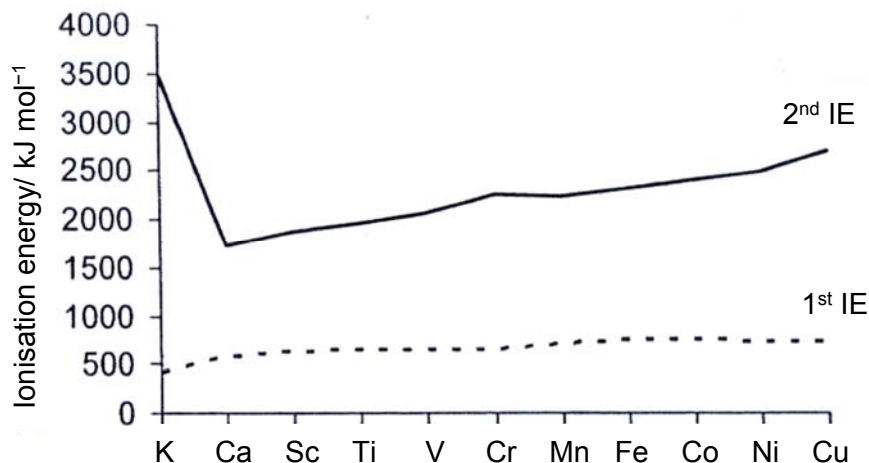
The graph below shows the densities of the elements Sc to Cu.



- (i) Suggest why the densities of the elements increase from Sc to Cu.

From Sc to Cu, relative atomic mass increases and atomic radius decreases slightly(or remain invariant). The elements have a more close-packed structure and thus have a higher mass per unit volume, which is density. [2]

- (ii) The graph below shows the first (dashed line) and second (solid line) ionisation energies (IE) for the element K to Cu inclusive.



Explain why the first ionisation energy remains relatively constant from Sc to Cu.

From Sc to Cu, the number of protons increases, hence the nuclear charge increases. Electrons are added to the inner 3d subshell which provides increased effective shielding between nucleus and valence 4s electron. Therefore, increase in nuclear charge almost cancel out the increase in shielding effect (effective nuclear charge increases slightly). Energy required to remove the outer 4s electrons from Sc to Cu is almost constant. [2]

- (iii) Explain briefly why is the second ionisation energy of potassium so much higher than that of the other elements.

The second electron in K to be removed is from an inner 3p orbital which is more strongly attracted by the nucleus as it experiences less shielding. [1]

- (b) Scandium, copper and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

- (i) Define the term *transition element*.

A transition element is a d-block element which forms one or more stable ions with partially filled d subshells. [1]

- (ii) State the full electronic configuration of Sc³⁺.

1s² 2s² 2p⁶ 3s² 3p⁶ [1]

- (iii) Explain why scandium is not classified as a transition element.

Sc is not a transition element as it only forms stable Sc³⁺ ion which has empty d subshell. [1]

(c) **X** and **Y** are period 3 elements.

Element **X** forms a white oxide that is slightly soluble in cold water. Its chloride dissolves in water to form a weakly acidic solution.

Element **Y** forms two oxides. 0.03 moles of one of the two oxides produces 7.00 g of white precipitate when mixed with excess barium chloride solution. The white precipitate is insoluble in dilute strong acid. A solution is obtained when equimolar of the oxide of element **Y** is added to the oxide of element **X** with water.

Identify the elements **X**, **Y**, and the oxide of **Y**.

Explain the observations with the aid of relevant equations.

Element X: Magnesium Element Y: Sulfur

Formula of the oxide of element Y: SO₃

MgO(s) + H₂O(l) → Mg(OH)₂(aq) when MgO reacts with water, sparingly soluble Mg(OH)₂ is formed

MgCl₂(s) + 6H₂O(l) → [Mg(H₂O)₆]²⁺(aq) + 2Cl⁻(aq)

MgCl₂ hydrolyses slightly to form a weakly acidic solution of pH 6.5

[Mg(H₂O)₆]²⁺(aq) + H₂O(l) ⇌ [Mg(H₂O)₅(OH)]⁺(aq) + H₃O⁺(aq)

Upon addition of excess barium chloride solution, BaSO₄(s) is formed.

7.00 g of white ppt corresponds to the mass of 0.03 mol of BaSO₄.

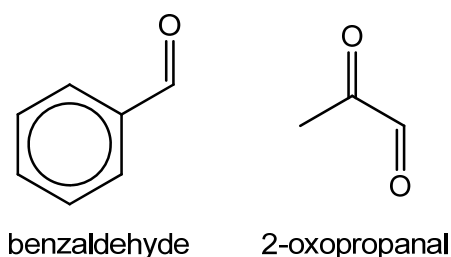
SO₃(g) + H₂O (l) + BaCl₂(aq) → BaSO₄(s) + 2HCl(aq)

OR SO₄²⁻ + Ba²⁺(aq) → BaSO₄(s)

SO₃(g) + MgO(aq) → MgSO₄(aq) [7]

[Total: 15]

- 4 (a) Carbonyl compounds occur naturally, giving many signature flavours. For example, benzaldehyde in almonds and 2-oxopropanal in burnt sugar.



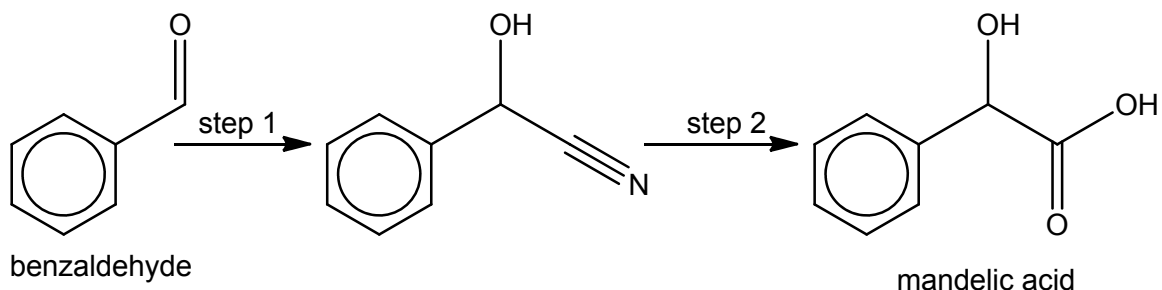
- (i) Suggest a simple chemical test that could distinguish between the two compounds above. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: $\text{I}_2 (\text{aq}), \text{NaOH} (\text{aq}), \text{heat}$ or Fehling's reagent/solution, heat

	Observations:	Products:
benzaldehyde	<u>No Yellow ppt</u> seen. OR <u>No Red ppt</u> seen.	No products
2-oxopropanal	<u>Yellow ppt</u> seen. OR <u>Red ppt</u> seen.	$\text{CHI}_3(\text{s})$ for iodoform $\text{Cu}_2\text{O}(\text{s})$ for Fehling's Reagent used

[3]

- (ii) Benzaldehyde undergoes a possible reaction sequence as shown below to form mandelic acid, which is used as an antibacterial agent.



State the reagents and conditions for steps 1 and 2.

Step 1: $\text{HCN} (\text{aq}), \text{trace amount of NaOH} (\text{aq}), \text{cold } 10\text{-}20\text{ } ^\circ\text{C}$

Step 2: Dilute $\text{H}_2\text{SO}_4 (\text{aq}), \text{heat under reflux}$

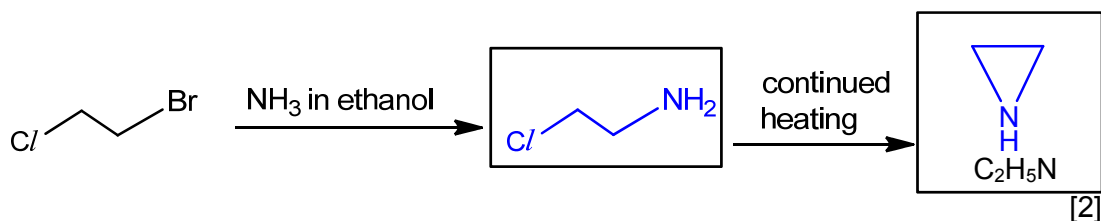
[2]

(b) Another class of naturally occurring organic compounds is halogenoalkanes, e.g. bromomethane found in vegetables, chloromethane found in algae and trichloromethane found in termites.

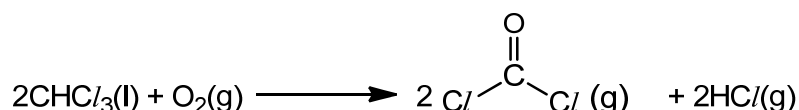
(i) With bromomethane and chloromethane as examples, describe and explain briefly the relative reactivities of bromo- and chloro-compounds with respect to hydrolysis.

CH_3Br would be more reactive towards hydrolysis than CH_3Cl . This is because the C-Br bond is weaker than C-Cl bond and would be more easily broken during hydrolysis. [1]

(ii) This difference in reactivity can also be observed in organic reactions. Suggest the structural formulae of the compounds formed in the boxes below. The final product is a cyclic compound.



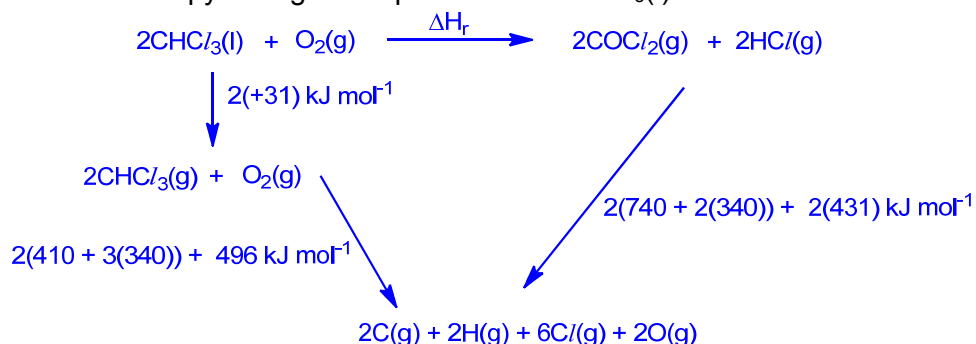
(c) Trichloromethane was previously used as an anesthetic, but chronic exposure can harm the liver where it is metabolised to toxic phosgene, COCl_2 . This reaction can also take place slowly in the presence of oxygen and light, as represented below.



(i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the enthalpy change of the above reaction.

Your cycle should include relevant data from the Data Booklet together with the following data shown below:

The enthalpy change of vaporisation of $\text{CHCl}_3(\text{l})$ is $+31 \text{ kJ mol}^{-1}$.



$$\Delta H_r = 2(31) + 2[410 + 3(340)] + 496 - [2(740 + 2(340)) + 2(431)]$$

$$= -284 \text{ kJ mol}^{-1} \text{ (3 s.f.)}$$

[3]

- (ii) Predict, with reasons, the sign of the entropy change of the reaction in (c)(i).

Entropy change of the reaction should be **positive**, as the number of **moles of gas increases** from 1 mole to 4 moles, there are more ways of arranging the particles, hence the system **increases in disorderness**. [2]

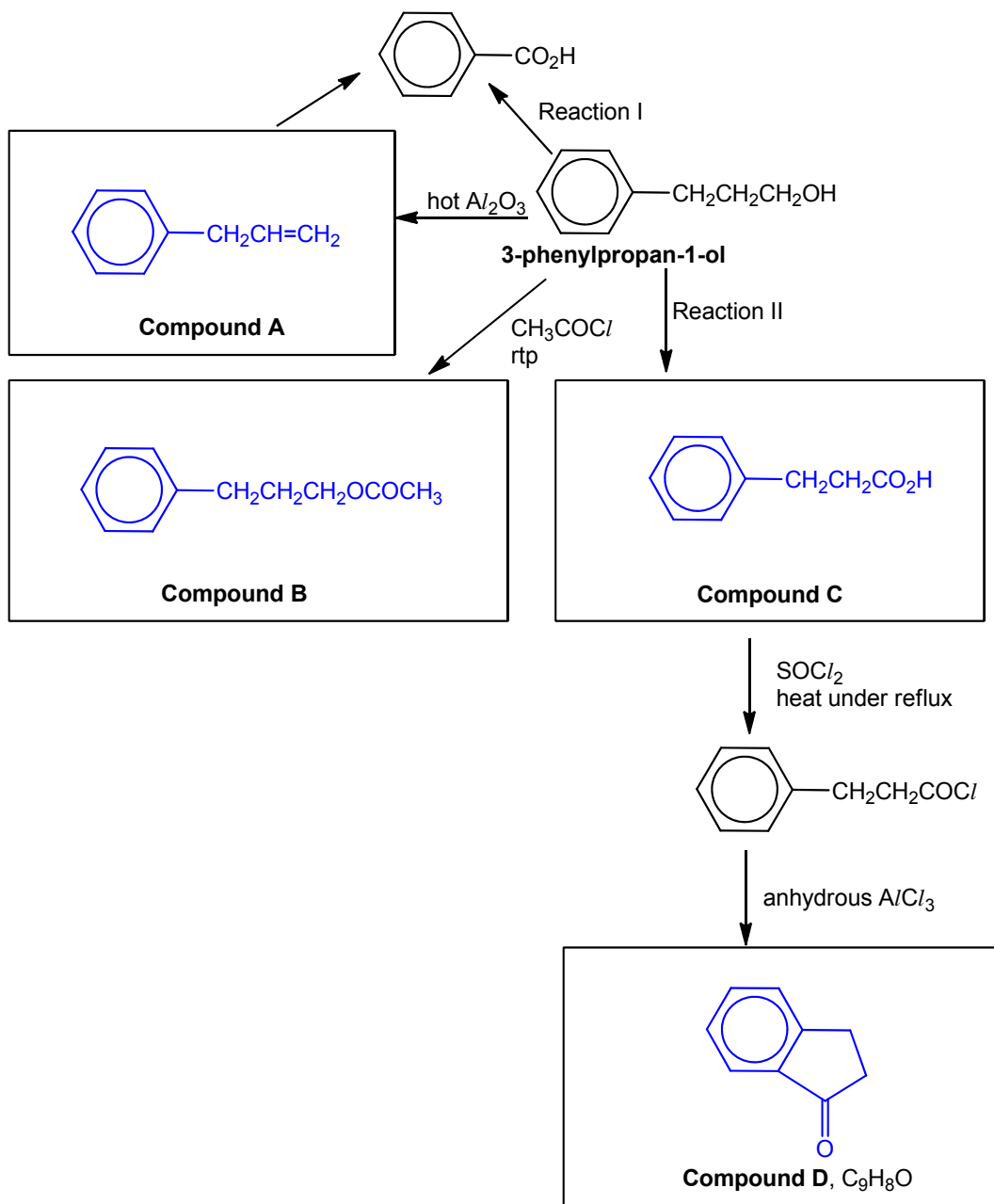
- (iii) Hence, state the sign of the standard Gibbs free energy change and comment on the spontaneity of the reaction.

$\Delta G = \Delta H - T\Delta S$, standard Gibbs free energy change should be **negative**, since the enthalpy change is negative, and entropy change is positive. Thus, the reaction is always **spontaneous** at all temperature. [2]

[Total: 15]

- 5 (a) Benzene is an important precursor in the production of many chemicals. 3-phenylpropan-1-ol is an example of an organic compound which contains the benzene ring as a substituent.

- (i) The following reaction scheme shows the reactions of 3-phenylpropan-1-ol. Suggest the structural formulae of compounds **A**, **B**, **C** and **D** in the boxes below.



[4]

- (ii) Using the reaction scheme for the reactions of 3-phenylpropan-1-ol, state the reagents and conditions for reactions I and II. [2]

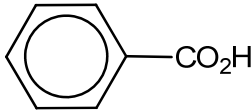
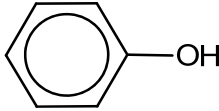
Reaction I KMnO₄, dilute H₂SO₄, heat under reflux

Reaction II K₂Cr₂O₇, dilute H₂SO₄, heat under reflux

- (b) There is another form of important organic compounds which are derived from benzene. Benzene derivatives are formed when one of the hydrogens on the ring is replaced with a different functional group.

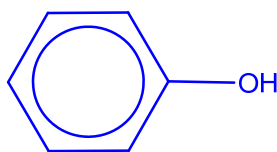
Benzoic acid and phenol are examples of such benzene derivatives which exhibit acidic character when dissolved in water.

The K_a values of benzoic acid, carbonic acid and phenol are given in the table below.

acid	structural formula	$K_a / \text{mol dm}^{-3}$
benzoic acid		6.3×10^{-5}
carbonic acid	H ₂ CO ₃	4.5×10^{-7}
phenol		1.3×10^{-10}

Both benzoic acid and phenol are reacted with sodium hydroxide to form sodium benzoate and sodium phenoxide respectively.

- (i) Draw the organic product formed when CO₂ is bubbled through a solution of aqueous sodium phenoxide. [1]



- (ii) However, no reaction occurs when CO₂ is bubbled through a solution of aqueous sodium benzoate. Explain why this is so. [1]

CO₂ dissolves in water to give carbonic acid, H₂CO₃ which is a weaker acid

($K_a = 4.5 \times 10^{-7}$) compared to benzoic acid ($K_a = 6.3 \times 10^{-5}$) and therefore it

is not able to donate proton to benzoate ion to form benzoic acid.

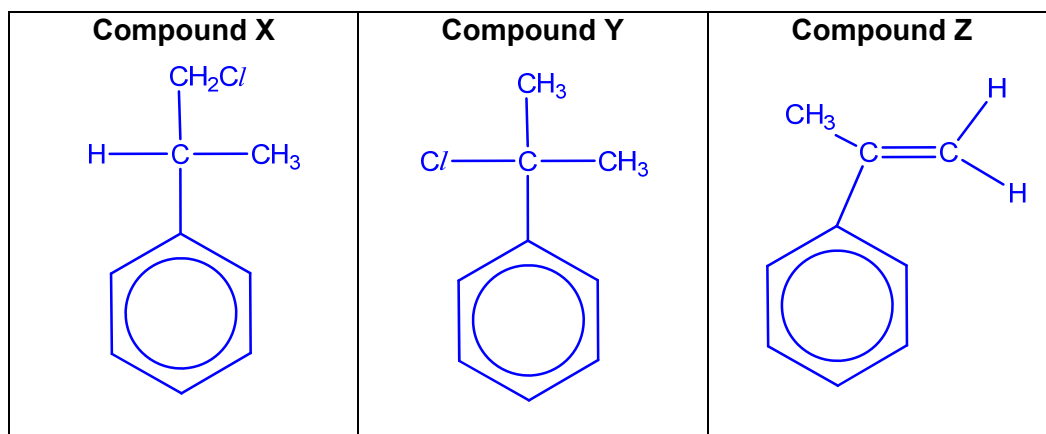
- (c) Cumene, C_9H_{12} , is another benzene derivative that can be used to produce phenol and propanone.

When a sample of cumene is reacted with limited chlorine in the presence of UV light, only two monochlorinated products, **X** and **Y** are formed. Only compound **X** has a chiral carbon. Both **X** and **Y** react with reagent **W** under heat to form hydrocarbon **Z**. Hydrocarbon **Z** is able to decolourise aqueous bromine.

- (i) State reagent **W**. [1]

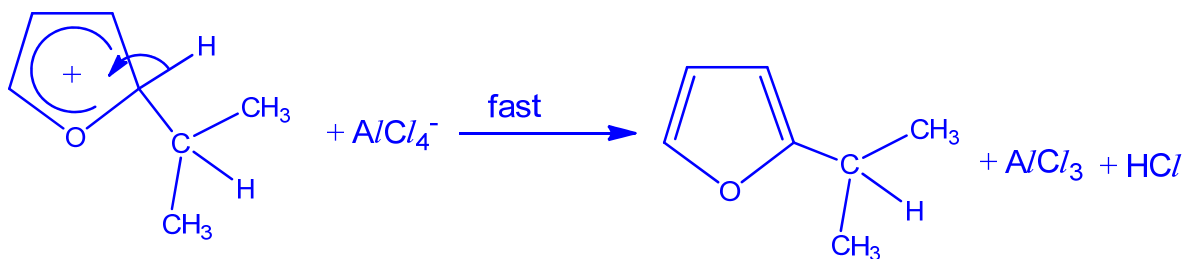
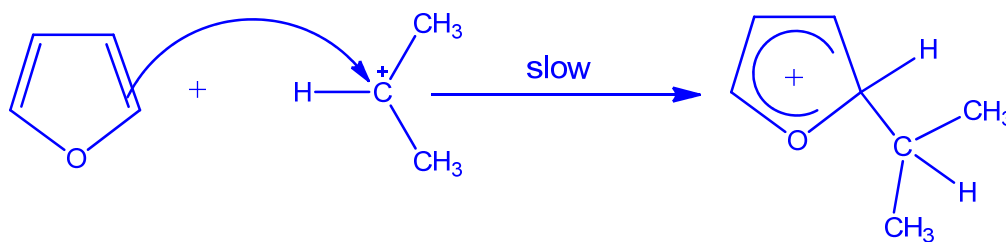
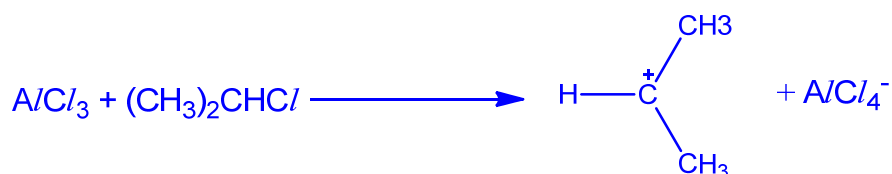
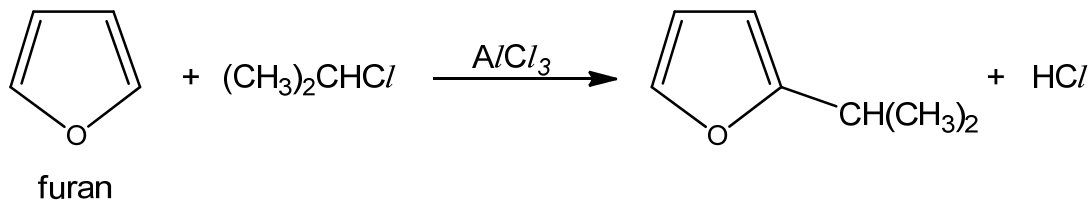
NaOH dissolved in ethanol / alcoholic NaOH/ NaOH (alc).....

- (ii) In the space below, give the structural formula of compound **X**, **Y** and **Z**. [3]



- (d) As an aromatic compound, benzene undergoes electrophilic substitution reactions. Like benzene, furan, a heterocyclic five-membered aromatic ring with one O atom and four carbon atoms, is also able to undergo electrophilic substitution reactions under suitable conditions.

Outline the mechanism of the reaction below, clearly showing all the steps involved.



[3]

[Total: 15]



Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE
NAME

CLASS

CHEMISTRY

9729/03

Paper 3 Free Response

Friday 24 August 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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 examination, fasten all your work securely together.

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

This document consists of **10** printed pages.

Section A

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

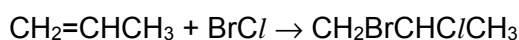
- 1 Propene is a colourless gas that is produced in large quantities by the petrochemical industry. It is used in the production of synthetic rubber and as a propellant in aerosols.

- (a) When propene reacts with HBr, 2-bromopropane is produced as the major product.



- (i) Describe the mechanism of the above reaction, using curly arrows to show the movement of electrons. [4]

- (ii) When propene reacts with BrCl, 1-bromo-2-chloropropane is produced as the major product.



With reference to your answer in (i), explain why the two reactions give major products with bromine in different positions. [2]

- (iii) The product of the reaction in (ii) has a chiral carbon, but it is optically inactive. Explain why this is so. [2]

- (b) 2-bromopropane reacts with hot aqueous sodium hydroxide, whereas 2-bromopropene does not. Suggest reasons for this difference in reactivity. [2]

- (c) Propene can undergo mild oxidation in the presence of cold acidified potassium manganate(VII), to give $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_3$.

- (i) State the IUPAC name of the product of the above reaction. [1]

- (ii) Construct the half-equation for the oxidation of propene as described above. [1]

- (iii) Hence, write the equation for the overall reaction, showing clearly the stoichiometry of reaction between propene and manganate(VII) ions. [1]

- (d) At room temperature and pressure, 28 cm^3 of propene was bubbled into 40.0 cm^3 of $0.0200 \text{ mol dm}^{-3}$ acidified $\text{KMnO}_4(\text{aq})$. The resulting solution was titrated against $\text{Fe}^{2+}(\text{aq})$ of concentration $0.0750 \text{ mol dm}^{-3}$.

- (i) State the colour change at endpoint for this titration. [1]

- (ii) Given that 5 moles of Fe^{2+} react with 1 mole of MnO_4^- , determine the volume of $\text{Fe}^{2+}(\text{aq})$ needed to reach endpoint. [3]

- (e) A mixture of propene ($M_r = 42.0$) and 2-bromopropane ($M_r = 122.9$) kept in a vessel of volume of 3.60 dm^3 maintained at 75°C exerts a pressure of $1.66 \times 10^5 \text{ Pa}$. The mole fraction of propene in the mixture is 0.28.

Find the mass of the mixture of gases. [3]

[Total: 20]

- 2 Copper is a transition metal, and is one of the metals used to make coins, along with silver and gold. Most copper is used in electrical equipment such as wiring and motors. It also has uses in construction and industrial machinery.

- (a) One of the characteristic properties of copper is its ability to form coloured aqueous complexes shown in Fig 2.1.

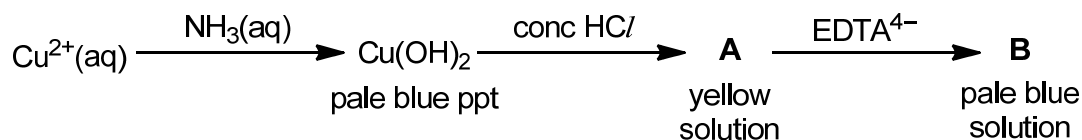


Fig. 2.1

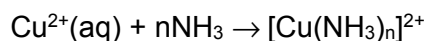
- (i) State the complex ion **A**. [1]
- (ii) Draw the structure of complex ion **A**. [2]
- (iii) EDTA^{4-} is a hexadentate ligand. Deduce the formula of the complex ion **B**. [1]
- (iv) Suggest why complex **B** is readily formed from complex **A**. [1]
- (v) Explain why aqueous Cu^{2+} ions are blue in colour. [3]
- (vi) The numerical value of the solubility product, K_{sp} of $\text{Cu}(\text{OH})_2$ is 2.20×10^{-20} at 25 °C. Write the expression for K_{sp} and state its units. Calculate the solubility of $\text{Cu}(\text{OH})_2$ at 25 °C. [3]

- (b) When an aqueous solution of ammonia is shaken with an organic solvent, trichloromethane, at room temperature, the following equilibrium is set up between the two immiscible liquids.



The equilibrium constant, K_c , for this reaction is 0.04.

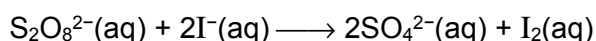
Water that is contaminated with copper(II) sulfate is harmful to crops, animals and humans. Some water that has been contaminated with $0.100 \text{ mol dm}^{-3}$ copper(II) sulfate was allowed to reach dynamic equilibrium at room temperature with an excess of ammonia and trichloromethane. The aqueous layer was found to contain $0.660 \text{ mol dm}^{-3}$ of ammonia, some of which reacted with $\text{Cu}^{2+}(\text{aq})$ according to the following equation



The organic layer contained $0.0104 \text{ mol dm}^{-3}$ of ammonia.

- (i) Define the term *dynamic equilibrium*. [1]
- (ii) Explain the relative solubility of ammonia in water and trichloromethane in terms of the intermolecular forces involved. [2]
- (iii) Hence, in terms of the position of equilibrium, explain why the value of K_c for equilibrium 1 is relatively low. [1]
- (iv) By calculating $[\text{NH}_3(\text{aq})]$ present, show that the value of n in $[\text{Cu}(\text{NH}_3)_n]^{2+}$ is 4. [2]
- (c) Another characteristic property of transition metal ion is its ability to catalyse reactions.

The rate of the reaction between iodide and peroxodisulfate(VI) ions



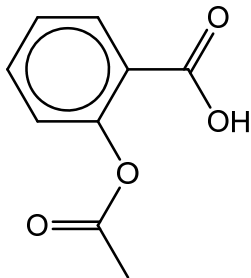
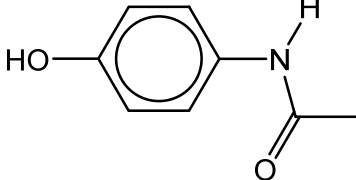
is very slow. If a small amount of aqueous transition metal, cobalt(II) ions is added to the mixture, the rate of reaction increases.

- (i) By considering relevant half equations from the *Data Booklet*, construct chemical equations to show how cobalt(II) ions behave as a catalyst in this reaction. No calculation is required. [2]
- (ii) Suggest another transition metal ion, which will be able to catalyse this reaction. [1]

[Total: 20]

- 3 (a) Analgesics are medicines used to relieve pain. The two most common analgesics in the market are aspirin and paracetamol. Their structures and corresponding pK_a values are shown in Table 3.1.

Table 3.1

Name of analgesic	Structure	pK_a value
Aspirin		3.49
Paracetamol		10.30

- (i) Explain the difference in the pK_a values between aspirin and paracetamol. [2]

Paracetamol can be synthesised from phenol in a 3-step process shown in Fig 3.1.

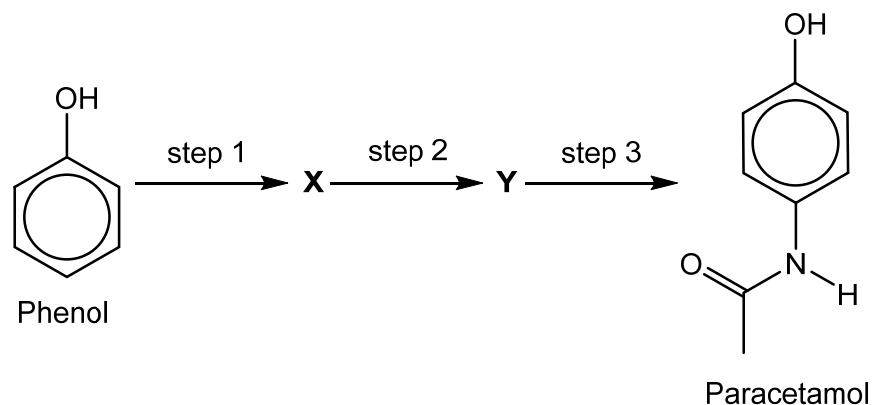


Fig. 3.1

- (ii) Suggest the structures for intermediates X and Y. [2]
- (iii) Suggest the reagents and conditions required for step 1 to 3. [3]

- (b) The use of aspirin has been shown to increase the risk of gastrointestinal bleeding. Hence, buffering agents are added to aspirin to mitigate the problem of gastrointestinal bleeding. These buffering agents work by preventing the aspirin from concentrating in the walls of the stomach. Common buffering agents used include magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and calcium carbonate, CaCO_3 .

Some relevant standard enthalpy change of hydration values and lattice energy of $\text{Mg}(\text{OH})_2$, are shown in Table 3.2.

Table 3.2

Enthalpy term	Value / kJ mol^{-1}
Standard enthalpy change of hydration of $\text{Mg}^{2+}(\text{g})$	-1926
Standard enthalpy change of hydration of $\text{OH}^{-}(\text{g})$	-460
Lattice energy of $\text{Mg}(\text{OH})_2(\text{s})$	-2998

Using relevant data in the table above, construct an energy level diagram to determine the standard enthalpy change of solution, $\Delta H_{\text{sol}}^{\ominus}$, of $\text{Mg}(\text{OH})_2$ in water. [3]

- (c) Compound **A** is an unsaturated ester containing a benzene ring and has a molecular formula of $\text{C}_{16}\text{H}_{22}\text{O}_3$. **A** reacts with neutral FeCl_3 to give violet colouration. **A** reacts with H_2 in the presence of Ni to produce compound **B** ($\text{C}_{16}\text{H}_{24}\text{O}_3$). **B** exhibits enantiomerism whereas **A** does not.

On heating with acidified KMnO_4 , **A** gives three organic products, **C**, $\text{C}_8\text{H}_6\text{O}_5$, **D**, $\text{C}_4\text{H}_{10}\text{O}$ and propanone (CH_3COCH_3). 1 mole of **C** reacts with excess PCl_5 to produce 2 moles of HCl . Effervescence is observed when a small piece of sodium metal is added to **D**.

Suggest the structures for **A** to **D** and explain the reactions described. [10]

[Total: 20]

Section B

Answer **one** question from this section.

- 4 (a) The decomposition of calcium and magnesium carbonates has industrial application as flame retardants due to the endothermic nature of these reactions.

(i) Write an equation showing the thermal decomposition of calcium carbonate. [1]

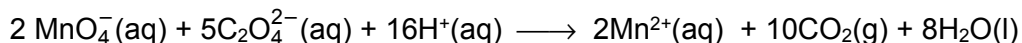
(ii) Compare and explain the decomposition temperature of calcium and magnesium carbonates. [3]

(iii) Separate samples of calcium carbonate and magnesium carbonate of the same mass, were decomposed completely under constant heating and the variation of the masses of the two samples were measured.

Sketch a graph of the mass of solid against time for the two separate samples, indicating clearly the time when decomposition was complete and the final mass for each sample. No calculations are required. [2]

(iv) Besides absorption of heat to slow down the spread of a flame, suggest another reason why CaCO_3 acts as a flame retardant. [1]

- (b) One way to study reaction mechanisms is to deduce the rate equation from kinetics experiments, such as that for the redox reaction between manganate (VII) ions and ethanedioate ions.



A study of the kinetics of this reaction was carried with a suitable catalyst and with $[\text{C}_2\text{O}_4^{2-}]$ at 2.00 mol dm^{-3} and data collected are shown in Table 4.1

Table 4.1

time / min	$[\text{MnO}_4^-] / \text{mol dm}^{-3}$
0	0.0200
3	0.0160
6	0.0128
9	0.0104
12	0.0084
15	0.0068
18	0.0056

(i) Plot the data on suitable axes, using the graph paper provided. [2]

(ii) Use your graph to determine the order of reaction with respect to $[\text{MnO}_4^-]$, showing your working clearly including construction lines on your graph. [2]

(iii) Given that the reaction is first order with respect to $[\text{C}_2\text{O}_4^{2-}]$ and zero order with respect to $[\text{H}^+]$, give the rate equation for the reaction. [1]

- (iv) Determine the initial rate from the graph and use it, together with your rate equation, to calculate the rate constant for the reaction, stating its units. [2]
- (v) Without the initial addition of the catalyst, the reaction is initially slow then speeds up due to autocatalyst, Mn^{2+} , produced, and finally slows down due to low concentration of reactants remaining.

Sketch a graph $[\text{MnO}_4^-]$ against time if the experiment was repeated without the initial addition of catalyst. [1]

- (c) Another way to study reaction mechanisms is to make deductions from the ease of obtaining the products as well as the identity of products formed.

2-bromobutane undergo nucleophilic substitution with nitrile, CN^- , relatively faster, as compared to the reaction of 2-chlorobutane with nitrile, CN^- .

- (i) Under suitable conditions, an initially optically pure (only one enantiomer) sample of 2-bromobutane can undergo reaction with CN^- , and produce a mixture which is almost optically inactive.

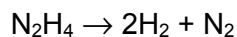
Name the mechanism that has taken place for this, and give the structures of the products formed. [2]

- (ii) A suitable condition that favours the reaction mechanism in (i) can be the use of neutral **polar** solvent (e.g. propanone) instead of non-polar solvents. Suggest why this is the case in consideration of the mechanism stating clearly the interactions involved. [1]

- (iii) Explain why 2-chlorobutane reacts more slowly with nucleophiles, relating to the steps in the mechanism in (i). Quote relevant values from the *Data Booklet* to substantiate your answer. [2]

[Total: 20]

- 5 (a) The decomposition of hydrazine, N_2H_4 , can be used to produce H_2 gas as shown in the following reaction.



- (i) Draw a dot-and-cross diagram showing the bonding in N_2H_4 . [1]
- (ii) Use your diagram to suggest the shape of N_2H_4 about nitrogen atom. [1]
- (iii) Use your diagram to suggest the bond angle about N atom in N_2H_4 . [1]
- (iv) The boiling points of hydrazine, nitrogen and ammonia are shown in Table 5.1

Table 5.1

compound	boiling point/ °C
N_2H_4	114
NH_3	-33
N_2	-196

Suggest an explanation for the difference in boiling points of these three compounds. [4]

- (b) Hydrazine can be used in a fuel cell to generate electricity. At the anode, nitrogen gas is produced from hydrazine in alkaline medium. At the cathode, oxygen gas is being supplied into water.
- (i) Construct half equations for the anode and cathode reactions. [2]
- (ii) Hence, write the overall equation. [1]
- (iii) The cell is capable of producing an e.m.f. of 1.56 V under standard conditions. By using suitable data from the *Data Booklet*, suggest a value of the E^\ominus of the anode. [1]
- (iv) Calculate ΔG for the reaction. [1]
- (v) State one possible advantage of using fuel cell compared to burning hydrocarbons in car engines. [1]

- (c) Local anesthesia is used in surgeries where it is applied to numb the feelings of a specific part of a body. Lidocaine and procaine are examples of local anesthesia shown in Fig 5.1

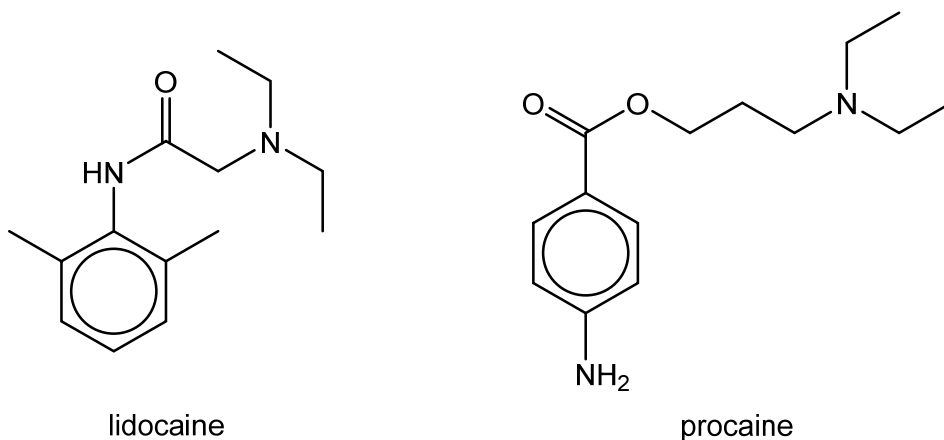


Fig. 5.1

The final step of the synthesis of lidocaine is shown in Fig 5.2.

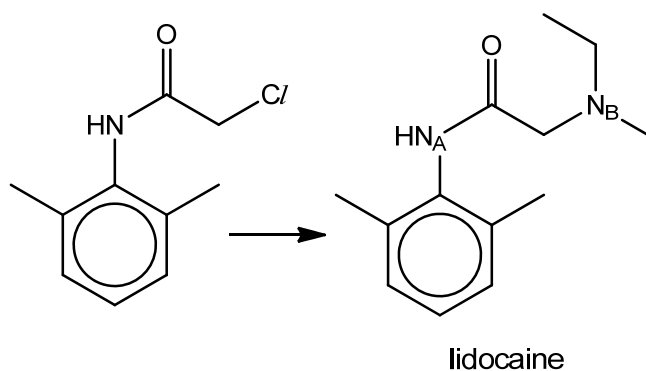


Fig. 5.2

- (i) Suggest a reagent for the above reaction. [1]
- (ii) Suggest how the basicity of N_A might compare to that of N_B . Give reasons for your answers. [2]
- (iii) A possible single chemical test to distinguish procaine and lidocaine involves the use of acidified potassium dichromate. Explain the chemistry involved, including any observation. Draw the structures of the products for the positive test. [3]
- (iv) Suggest another reagent that can also be used to distinguish between lidocaine and procaine. [1]

[Total: 20]



Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE
NAME

CLASS

2T

CHEMISTRY

9729/03

Paper 3 Free Response

Friday 24 August 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

WORKED SOLUTIONS

Section A

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

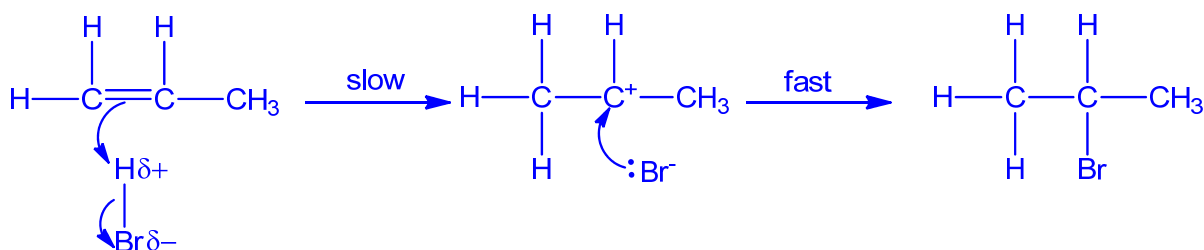
- 1 Propene is a colourless gas that is produced in large quantities by the petrochemical industry. It is used in the production of synthetic rubber and as a propellant in aerosols.

(a) When propene reacts with HBr, 2-bromopropane is produced as the major product.



- (i) Describe the mechanism of the above reaction, using curly arrows to show the movement of electrons. [4]

Electrophilic addition

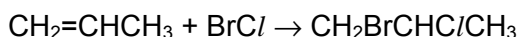


Correct partial charges, lone pair of electrons, slow/fast steps

Correct curly arrows

Correct secondary carbocation intermediate

- (ii) When propene reacts with BrCl, 1-bromo-2-chloropropane is produced as the major product.



With reference to your answer in (i), explain why the two reactions give major products with bromine in different positions. [2]

Br is more electronegative than H but less electronegative than Cl, hence Br acquires a partial positive charge in BrCl. Thus, Br adds first to form the more stable carbocation where the positive charge is on the second carbon

- (iii) The product of the reaction in (ii) has a chiral carbon, but it is optically inactive. Explain why this is so. [2]

There is equal chance of Cl⁻ attacking the trigonal planar carbon in the carbocation intermediate from either side of the plane. Thus, both enantiomers are formed in equal amounts/a racemic mixture is formed.

- (b) 2-bromopropene reacts with hot aqueous sodium hydroxide, whereas 2-bromopropane does not. Suggest reasons for this difference in reactivity. [2]

In 2-bromopropene, p orbitals of Br overlap with π bond (one of the lone pairs of electrons on Br is delocalised into the C=C π bond), hence there is a partial double bond character for the C-Br bond. This makes the C-Br bond stronger and harder to break for nucleophilic substitution to occur.

The carbon of the C-Br bond also has a lower partial positive charge and is less susceptible to nucleophilic attacks.

The electron rich C=C π bond will repel the negatively charged incoming nucleophile, hence the attack of the nucleophile will be less likely to occur.

- (c) Propene can undergo mild oxidation in the presence of cold acidified potassium manganate(VII), to give $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_3$.

- (i) State the IUPAC name of the product of the above reaction. [1]

Propane-1,2-diol

- (ii) Construct the half-equation for the oxidation of propene as described above. [1]



- (iii) Hence, write the equation for the overall reaction, showing clearly the stoichiometry of reaction between propene and manganate(VII) ions. [1]



- (d) At room temperature and pressure, 28 cm^3 of propene was bubbled into 40.0 cm^3 of 0.0200 mol dm^{-3} acidified $\text{KMnO}_4(\text{aq})$. The resulting solution was titrated against $\text{Fe}^{2+}(\text{aq})$ of concentration 0.0750 mol dm^{-3} .

- (i) State the colour change at endpoint for this titration. [1]

Pink/red-brown to colourless/yellow

- (ii) Given that 5 moles of Fe^{2+} react with 1 mole of MnO_4^- , determine the volume of $\text{Fe}^{2+}(\text{aq})$ needed to reach endpoint. [3]

$$\text{No. of moles of propene} = \frac{28}{24000}$$

$$= 1.167 \times 10^{-3} \text{ mol}$$

$$\text{No. of moles of } \text{MnO}_4^- \text{ reacted with propene} = \frac{1.167 \times 10^{-3}}{5} \times 2$$

$$= 4.667 \times 10^{-4} \text{ mol}$$

$$\text{No. of moles of } \text{MnO}_4^- \text{ originally} = \frac{40.0}{1000} \times 0.0200$$

$$= 8.000 \times 10^{-4} \text{ mol}$$

$$\begin{aligned}\text{No. of moles of MnO}_4^- \text{ left} &= 8.000 \times 10^{-4} - 4.667 \times 10^{-4} \\ &= 3.333 \times 10^{-4} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{No. of moles of Fe}^{2+} &= 3.333 \times 10^{-4} \times 5 \\ &= 1.667 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Volume of Fe}^{2+} &= \frac{1.667 \times 10^{-3}}{0.0750} \times 1000 \\ &= 22.2 \text{ cm}^3\end{aligned}$$

- (e) A mixture of propene ($M_r = 42.0$) and 2-bromopropane ($M_r = 122.9$) kept in a vessel of volume of 3.60 dm^3 maintained at $75 \text{ }^\circ\text{C}$ exerts a pressure of $1.66 \times 10^5 \text{ Pa}$. The mole fraction of propene in the mixture is 0.28 .

Find the mass of the mixture of gases.

[3]

[Total: 20]

$$\begin{aligned}\text{Average } M_r &= 0.28 \times 42.0 + (1 - 0.28) \times 122.9 \\ &= 100.2\end{aligned}$$

$$pV = \frac{m}{M_r}RT$$

$$\begin{aligned}m &= \frac{pVM_r}{RT} \\ &= \frac{1.66 \times 10^5 \times 3.60 \times 10^{-3} \times 100.2}{8.31 \times (75 + 273)} \\ &= 20.7 \text{ g}\end{aligned}$$

- 2 Copper is a transition metal, and is one of the metals used to make coins, along with silver and gold. Most copper is used in electrical equipment such as wiring and motors. It also has uses in construction and industrial machinery.

(a) One of the characteristic properties of copper is its ability to form coloured aqueous complexes shown in Fig 2.1.

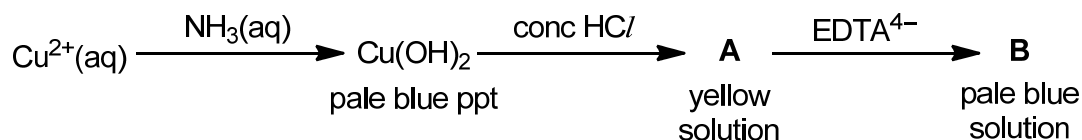
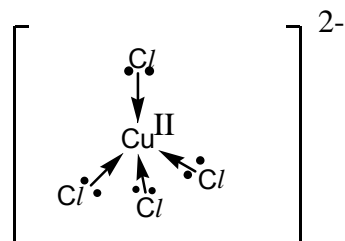


Fig. 2.1

(i) State the complex ion **A**. [1]
 $[\text{CuCl}_4]^{2-}$

(ii) Draw the structure of complex ion **A**. [2]



(iii) EDTA^{4-} is a hexadentate ligand. Deduce the formula of the complex ion **B**. [1]
 $[\text{Cu}(\text{EDTA})]^{2-}$

(iv) Suggest why complex **B** is readily formed from complex **A**. [1]
 $[\text{Cu}(\text{EDTA})]^{2-}$ is more stable as compared to $[\text{CuCl}_4]^{2-}$, therefore Cl^- ligands will be displaced by the stronger EDTA^{4-} ligands. OR EDTA^{4-} is a stronger ligand than Cl^- .

(v) Explain why aqueous Cu^{2+} ions are blue in colour. [3]
When ligands approach/are attached/bonded to the copper ion, they will cause the incompletely/ partially-filled/ $3d^9$ degenerate d-orbitals to split into two slightly different energy levels, d and d^* [OR] two groups of non-degenerate d-orbitals with small energy gap.

When electrons from the lower lying d-orbitals absorbs energy (orange colour) in the visible light region, it will be excited to the higher energy d^* orbital. This is known as $d-d^*$ electronic transition.

The complementary colours, which is not absorbed which is blue is seen/ the colour observed is complementary to the colour that is absorbed.

- (vi) The numerical value of the solubility product, K_{sp} of $\text{Cu}(\text{OH})_2$ is 2.20×10^{-20} at 25°C . Write the expression for K_{sp} and state its units. Calculate the solubility of $\text{Cu}(\text{OH})_2$ at 25°C . [3]



$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^{-}]^2$$

$$\text{Units: mol}^3 \text{ dm}^{-9}$$

Let the solubility of $\text{Cu}(\text{OH})_2$ be $x \text{ mol dm}^{-3}$

$$K_{sp} = [\text{Cu}^{2+}][\text{OH}^{-}]^2 = x(2x)^2$$

$$2.20 \times 10^{-20} = 4x^3$$

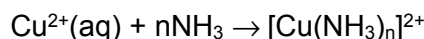
$$x = 1.77 \times 10^{-7} \text{ mol dm}^{-3}$$

- (b) When an aqueous solution of ammonia is shaken with an organic solvent, trichloromethane, at room temperature, the following equilibrium is set up between the two immiscible liquids.



The equilibrium constant, K_c , for this reaction is 0.04.

Water that is contaminated with copper(II) sulfate is harmful to crops, animals and humans. Some water that has been contaminated with $0.100 \text{ mol dm}^{-3}$ copper(II) sulfate was allowed to reach dynamic equilibrium at room temperature with an excess of ammonia and trichloromethane. The aqueous layer was found to contain $0.660 \text{ mol dm}^{-3}$ of ammonia, some of which reacted with $\text{Cu}^{2+}(\text{aq})$ according to the following equation



The organic layer contained $0.0104 \text{ mol dm}^{-3}$ of ammonia.

- (i) Define the term *dynamic equilibrium*. [1]
Dynamic equilibrium refers to a reversible reaction in which the forward rate of reaction is equal to the reverse rate of reaction. There is no net change in the concentrations of the reactants and the products.
- (ii) Explain the relative solubility of ammonia in water and trichloromethane in terms of the intermolecular forces involved. [2]

Ammonia is able to form hydrogen bonding with water, which is much stronger than the permanent dipole-permanent dipole attractions with trichloromethane molecules. Due to the strong forces of attraction between ammonia and water molecules, ammonia is highly soluble in water.

- (iii) Hence, in terms of the position of equilibrium, explain why the value of K_c for equilibrium 1 is relatively low. [1]

Therefore, the position of equilibrium lies largely to the left and K_c for this reaction is relatively low.

- (iv) By calculating $[\text{NH}_3(\text{aq})]$ present, show that the value of n in $[\text{Cu}(\text{NH}_3)_n]^{2+}$ is 4. [2]

$$0.04 = \frac{[\text{NH}_3(\text{organic})]}{[\text{NH}_3(\text{aqueous})]}$$

$$0.04 = \frac{0.0104}{[\text{NH}_3(\text{aqueous})]}$$

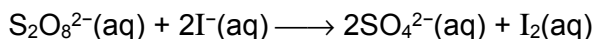
$$[\text{NH}_3(\text{aqueous})] = \frac{0.0104}{0.04} = 0.26 \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{Concentration of NH}_3 \text{ which reacted with Cu}^{2+}(\text{aq}) &= 0.660 - 0.26 \\ &= 0.40 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{Mol ratio of Cu}^{2+} : \text{NH}_3 &= 0.100 : 0.400 = 1 : 4 \\ n \text{ is } &4. \end{aligned}$$

- (c) Another characteristic property of transition metal ion is its ability to catalyse reactions.

The rate of the reaction between iodide and peroxodisulfate(VI) ions

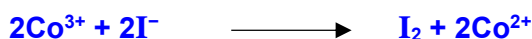


is very slow. If a small amount of aqueous transition metal, cobalt(II) ions is added to the mixture, the rate of reaction increases.

- (i) By considering relevant half equations from the *Data Booklet*, construct chemical equations to show how cobalt(II) ions behave as a catalyst in this reaction. No calculation is required. [2]



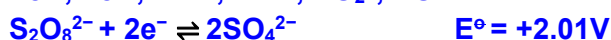
catalyst



catalyst regenerated

- (ii) Suggest another transition metal ion, which will be able to catalyse this reaction. [1]

Fe^{2+} , Fe^{3+} , Mn^{3+} , Mn^{2+} , VO_2^+ , VO^{2+} .

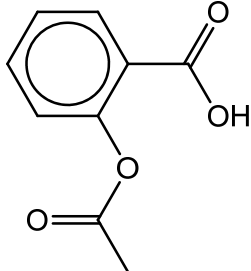
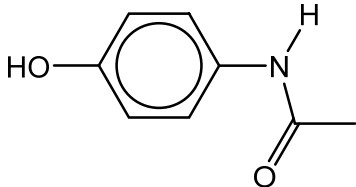


(Transition metal ion redox system requires a E^\ominus of between +0.54V and +2.01V.)

[Total: 20]

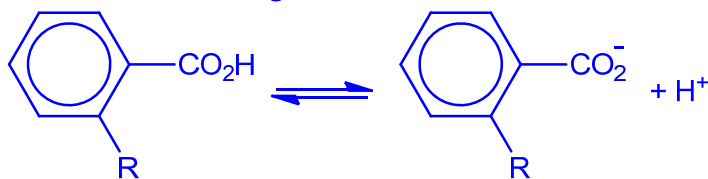
- 3 (a) Analgesics are medicines used to relieve pain. The two most common analgesics in the market are aspirin and paracetamol. Their structures and corresponding pK_a values are shown in Table 3.1.

Table 3.1

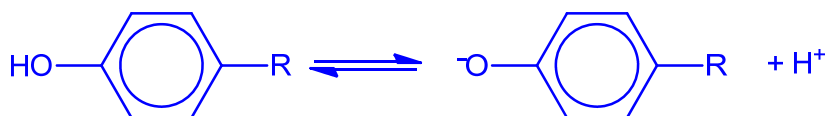
Name of analgesic	Structure	pK_a value
Aspirin		3.49
Paracetamol		10.30

- (i) Explain the difference in the pK_a values between aspirin and paracetamol. [2]

Aspirin is a stronger acid than paracetamol (due to its lower pK_a value) because in the carboxylate ion of aspirin, the negative charge on oxygen atom can be delocalised to a greater extent over the C atom and both O atoms. Hence the carboxylate ion is more resonance-stabilised. Position of equilibrium lies more to the right and aspirin dissociates to a larger extent.



For the phenoxide ion of paracetamol, the negative charge is only delocalised into the benzene ring and hence is less stable. Hence position of equilibrium lies less to the right and paracetamol dissociates to a smaller extent compared to that of Aspirin.



Paracetamol can be synthesised from phenol in a 3-step process shown in Fig 3.1.

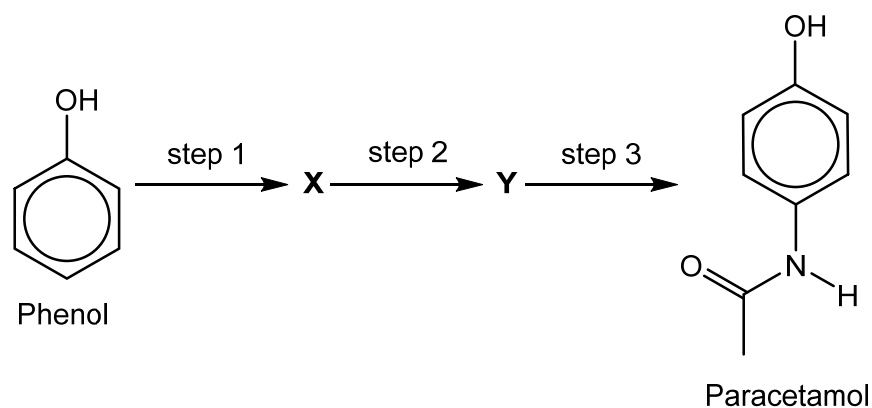
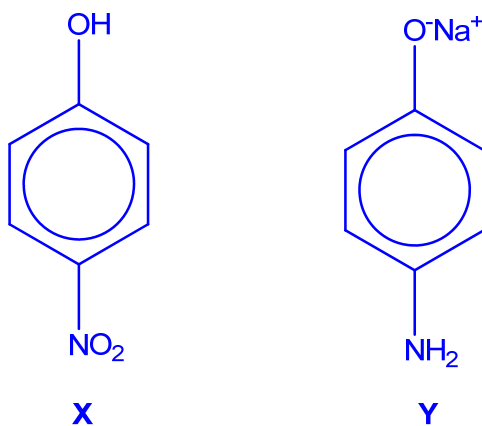


Fig. 3.1

(ii) Suggest the structures for intermediates **X** and **Y**. [2]



(iii) Suggest the reagents and conditions required for step 1 to 3. [3]

Step 1: dilute HNO₃

Step 2: 1. Sn, conc HCl, heat under reflux; 2. NaOH (aq)

Step 3: CH₃COCl

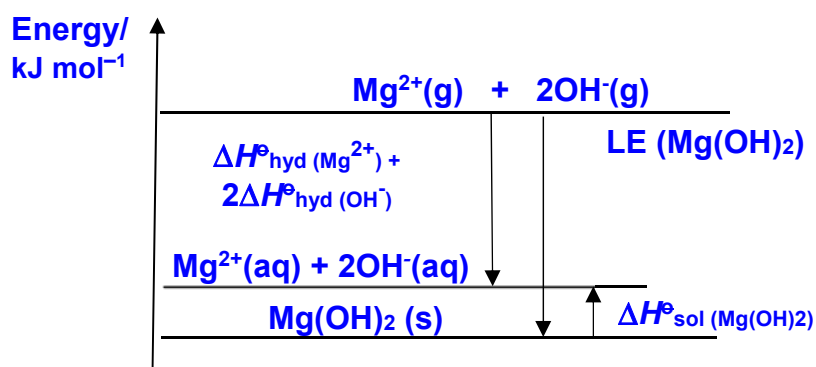
- (b) The use of aspirin has been shown to increase the risk of gastrointestinal bleeding. Hence buffering agents are added to aspirin to mitigate the problem of gastrointestinal bleeding. These buffering agents work by preventing the aspirin from concentrating in the walls of the stomach. Common buffering agents used include magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and calcium carbonate, CaCO_3 .

Some relevant standard enthalpy change of hydration values and lattice energy of $\text{Mg}(\text{OH})_2$, are shown in Table 3.2.

Table 3.2

Enthalpy term	Value / kJ mol^{-1}
Standard enthalpy change of hydration of $\text{Mg}^{2+}(\text{g})$	-1926
Standard enthalpy change of hydration of $\text{OH}^{-}(\text{g})$	-460
Lattice energy of $\text{Mg}(\text{OH})_2(\text{s})$	-2998

Using relevant data in the table above, construct an energy level diagram to determine the standard enthalpy change of solution, $\Delta H_{\text{sol}}^{\ominus}$, of $\text{Mg}(\text{OH})_2$ in water. [3]

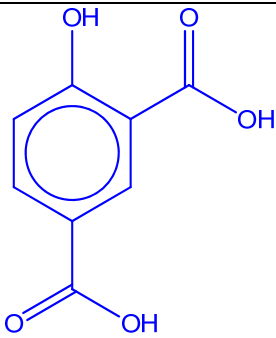


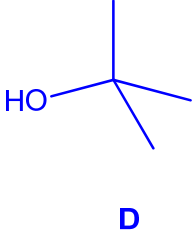
$$\begin{aligned}
 \Delta H_{\text{sol}} &= -\text{lattice energy} + \Sigma \Delta H_{\text{hyd}} \\
 &= -(-2998) + (-1926 - 2 \times 460) \\
 &= +152 \text{ kJ mol}^{-1}
 \end{aligned}$$

- (c) Compound **A** is an unsaturated ester containing a benzene ring and has a molecular formula of $C_{16}H_{22}O_3$. **A** reacts with neutral $FeCl_3$ to give violet colouration. **A** reacts with H_2 in the presence of Ni to produce compound **B** ($C_{16}H_{24}O_3$). **B** exhibits enantiomerism whereas **A** does not.

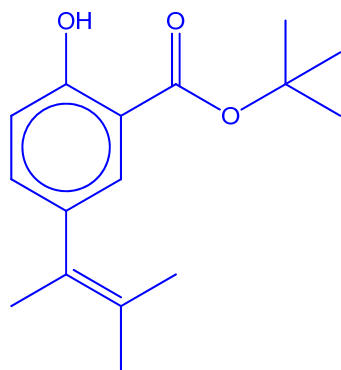
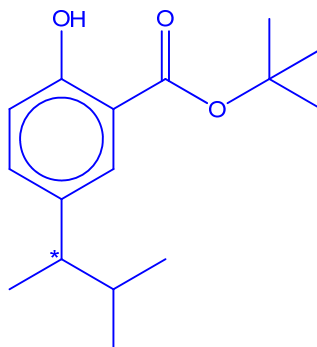
On heating with acidified $KMnO_4$, **A** gives three organic products, **C**, $C_8H_6O_5$, **D**, $C_4H_{10}O$ and propanone (CH_3COCH_3). 1 mole of **C** reacts with excess PCl_5 to produce 2 moles of HCl . Effervescence is observed when a small piece of sodium metal is added to **D**.

Suggest the structures for **A** to **D** and explain the reactions described. [10]

Observation/data	Type of reaction	Deduction	Structure
A reacts with neutral $FeCl_3$ to give violet colouration.	-	A is a phenol/ contains a phenolic group.	-
A reacts with H_2 in the presence of Ni to produce compound B ($C_{16}H_{24}O_3$).	catalytic addition/ reduction of $C=C$ bond	A is likely to contain <u>only one $C=C$ bond</u> since there is an addition of 2 H atoms in B .	-
B exhibits enantiomerism whereas A does not.	-	B contains a <u>chiral carbon</u> whereas A does not.	-
On heating with acidified $KMnO_4$, A gives three organic products, C , $C_8H_6O_5$, D , $C_4H_{10}O$ and propanone (CH_3COCH_3).	Acidic hydrolysis of ester, oxidative cleavage and side-chain oxidation	Hydrolysis of ester occurred to form a <u>carboxylic acid and an alcohol</u> . There is side chain oxidation on the benzene ring since there is <u>loss of 1 C atom</u> (or formation of 1 mol of CO_2).	-
1 mole of C reacts with excess PCl_5 to produce 2 moles of HCl .	Nucleophilic substitution of $-OH$ group	C is likely to contain a benzene ring with <u>2 carboxylic acid groups</u> and 1 phenol group.	 <p style="text-align: center;">C</p>

Effervescence is observed when a small piece of sodium metal is added to D .	Redox reaction	D is likely to be a <u>tertiary alcohol</u> since it is not oxidised by acidic KMnO_4 .	
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Hence structures of **A** and **B** are

**A****B**

[Total: 20]

Section B

Answer **one** question from this section.

- 4 (a) The decomposition of calcium and magnesium carbonates has industrial application as flame retardants due to the endothermic nature of these reactions.

- (i) Write an equation showing the thermal decomposition of calcium carbonate. [1]

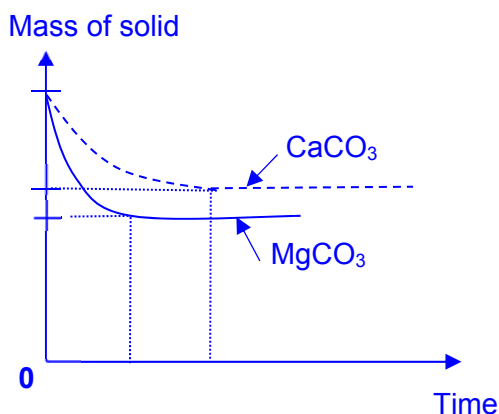


- (ii) Compare and explain the decomposition temperature of calcium and magnesium carbonates. [3]

CaCO₃ decomposes at a higher temperature as compared to MgCO₃. This is because Ca²⁺ has a larger ionic radius than Mg²⁺, and a lower charge density. Thus Ca²⁺ polarises the carbonate ion to a lesser extent hence the C-O bonds are stronger which require higher temperature to break.

- (iii) Separate samples of calcium carbonate and magnesium carbonate of the same mass, were decomposed completely under constant heating and the variation of the masses of the two samples were measured.

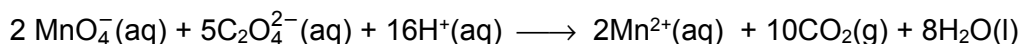
Sketch a graph of the mass of solid against time for the two separate samples, indicating clearly the time when decomposition was complete and the final mass for each sample. No calculations are required. [2]



- (iv) Besides absorption of heat to slow down the spread of a flame, suggest another reason why CaCO₃ acts as a flame retardant. [1]

CO₂ released can displace the oxygen required for a combustion.

- (b) One way to study reaction mechanisms is to deduce the rate equation from kinetics experiments, such as that for the redox reaction between manganate (VII) ions and ethanedioate ions.



A study of the kinetics of this reaction was carried with a suitable catalyst and with $[\text{C}_2\text{O}_4^{2-}]$ at 2.00 mol dm^{-3} and data collected are shown in Table 4.1

Table 4.1

time / min	$[\text{MnO}_4^-] / \text{mol dm}^{-3}$
0	0.0200
3	0.0160
6	0.0128
9	0.0104
12	0.0084
15	0.0068
18	0.0056

- (i) Plot the data on suitable axes, using the graph paper provided. [2]
- (ii) Use your graph to determine the order of reaction with respect to $[\text{MnO}_4^-]$, showing your working clearly including construction lines on your graph. [2]
- (iii) Given that the reaction is first order with respect to $[\text{C}_2\text{O}_4^{2-}]$, give the rate equation for the reaction. [1]
- (iv) Determine the initial rate from the graph and use it, together with your rate equation, to calculate the rate constant for the reaction, stating its units. [2]
- (v) Without the initial addition of the catalyst, the reaction is initially slow then speeds up due to autocatalyst, Mn^{2+} , produced, and finally slows down due to low concentration of reactants remaining.

Sketch a graph $[\text{MnO}_4^-]$ against time if the experiment was repeated without the initial addition of catalyst. [1]

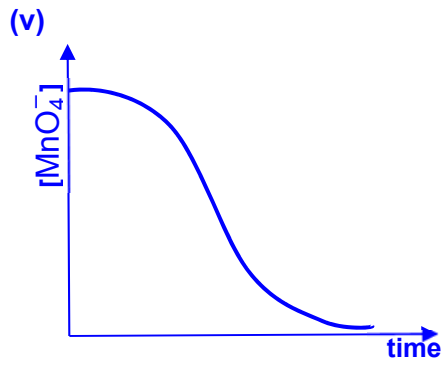
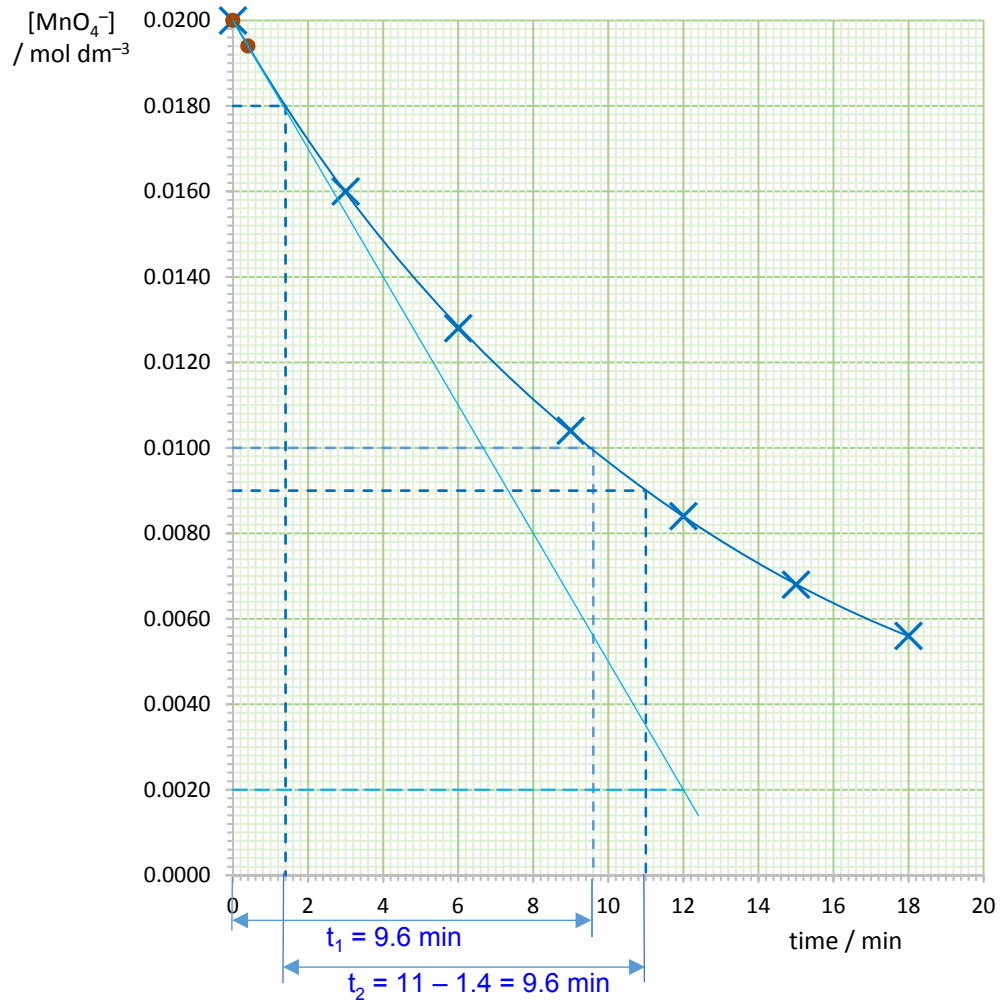
- (ii) **Using half-lives,**
1st half-life = 2nd half-life = 9.6 min

Since both half-lives are constant, the order of reaction with respect to $[\text{MnO}_4^-]$ is 1.

- (iii) **rate = k $[\text{C}_2\text{O}_4^{2-}] [\text{MnO}_4^-]$**

(iv) **rate = $-\frac{0.0200 - 0.0020}{0 - 12}$**
= $0.00150 \text{ mol dm}^{-3} \text{ min}^{-1}$

$$\mathbf{k = \frac{\text{rate}}{[\text{C}_2\text{O}_4^{2-}][\text{MnO}_4^-]} = \frac{0.00150}{2.00 (0.0200)} = 0.0375 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}}$$



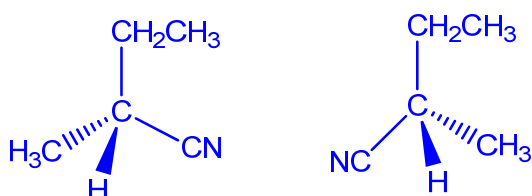
- (c) Another way to study reaction mechanisms is to make deductions from the ease of obtaining the products as well as the identity of products formed.

2-bromobutane undergo nucleophilic substitution with nitrile, CN^- , relatively faster, as compared to the reaction of 2-chlorobutane with nitrile, CN^- .

- (i) Under suitable conditions, an initially optically pure (only one enantiomer) sample of 2-bromobutane can undergo reaction with CN^- , and produce a mixture which is almost optically inactive.

Name the mechanism that has taken place for this, and give the structures of the products formed. [2]

Mechanism: Nucleophilic substitution reaction ($\text{S}_{\text{N}}1$)



- (ii) A suitable condition for the reaction in (i) can be the use of neutral **polar** solvent (e.g. propanone) instead of non-polar solvents. Suggest why this is the case in consideration of the mechanism stating clearly the interactions involved. [1]

Polar solvents can help to stabilise the carbocation formed, due to the ion-dipole interactions between the carbocation and polar solvent molecules, which allows the reaction to proceed via $\text{S}_{\text{N}}1$ mechanism.

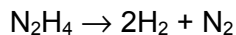
- (iii) Explain why 2-chlorobutane reacts more slowly with nucleophiles, relating to the steps in the mechanism in (i). Quote relevant values from the *Data Booklet* to substantiate your answer. [2]

$\text{BE (C-C)} = 340 \text{ kJ mol}^{-1}$; $\text{BE (C-Br)} = 280 \text{ kJ mol}^{-1}$

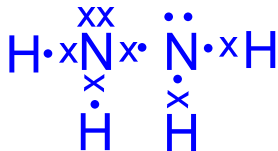
The C-C bond is stronger than C-Br bond, and the breaking of this bond is involved in the slow or rate-determining step (required if $\text{S}_{\text{N}}1$ given in (i)), hence the reaction is slower with 2-chlorobutane

[Total: 20]

- 5 (a) The decomposition of hydrazine, N_2H_4 , can be used to produce H_2 gas as shown in the following reaction.



- (i) Draw a dot-and-cross diagram showing the bonding in N_2H_4 . [1]



- (ii) Use your diagram to suggest the shape of N_2H_4 about nitrogen atom. [1]
Trigonal pyramidal
- (iii) Use your diagram to suggest the bond angle about N atom in N_2H_4 . [1]
 107°

- (i) The boiling points of hydrazine, nitrogen and ammonia are shown in Table 5.1

Table 5.1

compound	boiling point/ $^\circ\text{C}$
N_2H_4	114
NH_3	-33
N_2	-196

Suggest an explanation for the difference in boiling points of these three compounds. [4]

All three compounds have simple molecular structures.

The hydrogen bonding between NH_3 molecules is stronger than the instantaneous dipole-induced dipole (id-id) attraction between N_2 molecules. Greater amount of energy required to overcome the intermolecular H-bonding in NH_3 than the intermolecular id-id in N_2 . Thus, boiling point of NH_3 is higher.

The hydrogen bonding between hydrazine molecules is more extensive (2 hydrogen bonds per molecule) than between NH_3 molecules (1 hydrogen bond per molecule). Greater amount of energy required to overcome the more extensive intermolecular Hydrogen bonding in hydrazine molecules than in NH_3 . Thus, boiling point of hydrazine is higher.

(b) Hydrazine can be used in a fuel cell to generate electricity. At the anode, nitrogen gas is produced from hydrazine in alkaline medium. At the cathode, oxygen gas is being supplied into water.

(i) Construct half equations for the anode and cathode reactions. [2]



(ii) Hence, write the overall equation. [1]



(iii) The cell is capable of producing an e.m.f. of 1.56 V under standard conditions. By using suitable data from the *Data Booklet*, suggest a value of the E^\ominus of the anode. [1]

$E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{oxi}}$

$1.56 = +0.40 - E^\ominus_{\text{oxi}}$

$E^\ominus_{\text{oxi}} = -1.16 \text{ V}$

(iv) Calculate ΔG for the reaction. [1]

$\Delta G = -nFE^\ominus_{\text{cell}}$

$= -\frac{4 \times 96500 \times 1.56}{1000}$

$= -602 \text{ kJ mol}^{-1}$

(v) State one possible advantage of using fuel cell compared to burning hydrocarbons in car engines. [1]

It is pollution free. (only harmless/inert gases are produced, in this case, H_2O and N_2)

It has a high power to mass ratio.

It is highly efficient.

- (c) Local anesthesia is used in surgeries where it is applied to numb the feelings of a specific part of a body. Lidocaine and procaine are examples of local anesthesia shown in Fig 5.1

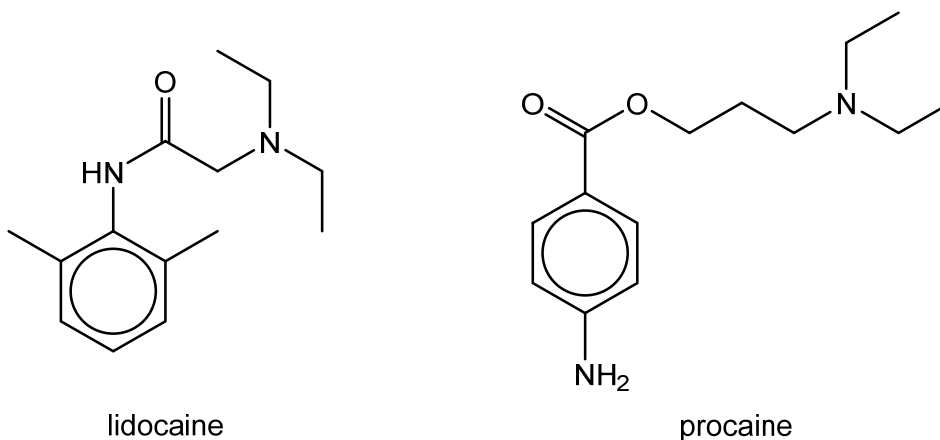


Fig. 5.1

The final step of the synthesis of lidocaine is shown in Fig 5.2.

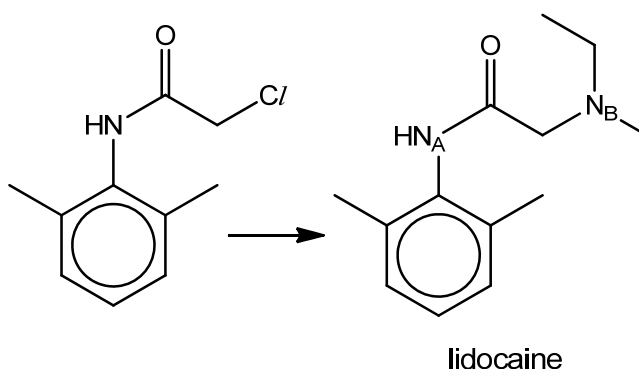
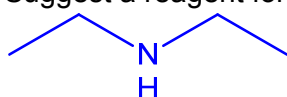


Fig. 5.2

- (i) Suggest a reagent for the above reaction. [1]



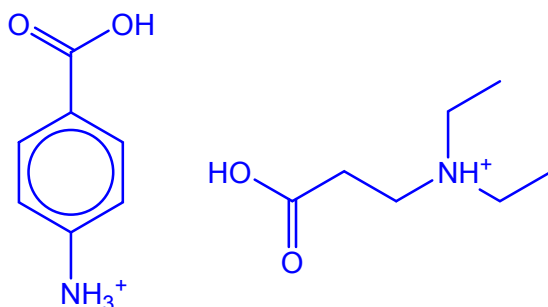
- (ii) Suggest how the basicity of N_A might compare to that of N_B . Give reasons for your answers. [2]

N_A is less basic than N_B due to the lone pair of electrons on nitrogen atom in the amide bond is being delocalised into the C=O group, making it less available to accept a proton.

- (iii) A possible single chemical test to distinguish procaine and lidocaine involves the use of acidified potassium dichromate. Explain the chemistry involved, including any observation. Draw the structures of the products for the positive test. [3]

Hydrolysis of ester or amide bond, followed by oxidation of alcohol formed of procaine.

Orange potassium dichromate turns green with procaine.



- (iv) Suggest another reagent that can also be used to distinguish between lidocaine and procaine. [1]

Aqueous bromine/ bromine in hexane

[Total: 20]