Catholic Junior College

JC 2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	**2T**

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.

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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, $Na_2C_2O_4$, in an acidic medium to produce 144 cm^3 of carbon dioxide gas at room temperature and pressure.

The half equation of $C_2O_4^{2-}$ is shown as follows:

$$2CO_2 + 2e^- \rightleftharpoons C_2O_4^{2-}$$

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, $[PCl_4]^+$ and $[PCl_6]^-$.

Which of the following shows the correct shape for PCl_5, $[PCl_4]^+$ and $[PCl_6]^-$?

	PCl_5	$[PCl_4]^+$	$[PCl_6]^-$
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
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−C*l* to C−I
2 the strength of permanent dipole-permanent dipole attraction increases from C−C*l* 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−C*l* 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.

Reaction 1: $CH_3^+ + Br^- \rightarrow CH_3Br$

Reaction 2: $HPO_4^{2-} + H_2BO_3^- \rightleftharpoons H_2PO_4^- + HBO_3^{2-}$

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

A Both reactions are acid-base reactions.

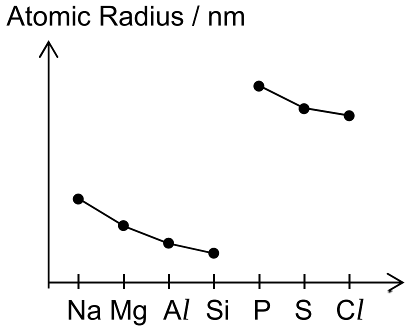
B In reaction 2, HPO_4^{2-} acts as the Brønsted-Lowry base.

C In reaction 2, HBO_3^{2-} is the conjugate acid of $H_2BO_3^-$.

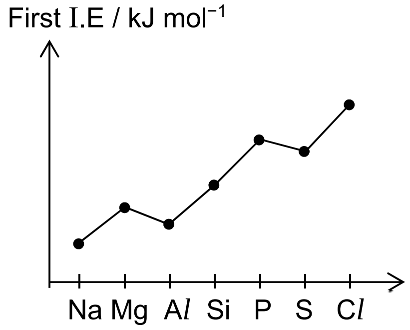
D In reaction 1, a dative covalent bond is formed between CH_3^+ and Br^-.

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?

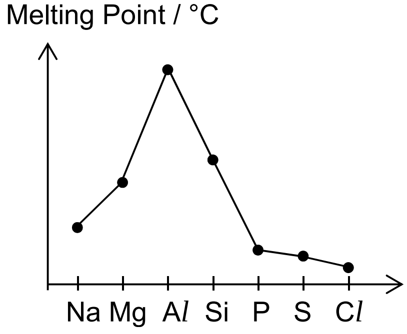
A



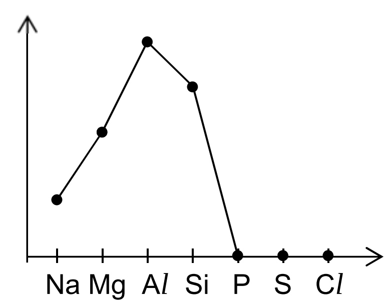
C



B



D



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

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

$$PH_3(g) + HI(g) \rightarrow PH_4^+I^-(s) \qquad \Delta H^\ominus = -145.2 \text{ kJ mol}^{-1}; \Delta S^\ominus = -570.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

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:

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

is thought to involve the following steps:

$H_2O_2 + I^- \rightarrow H_2O + OI^-$ (slow)
$OI^- + H^+ \rightarrow HOI$ (fast)
$HOI + H^+ + I^- \rightarrow I_2 + H_2O$ (fast)

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

12 A first-order decomposition reaction is shown below.

$$AB(g) \rightarrow A(g) + B(g)$$

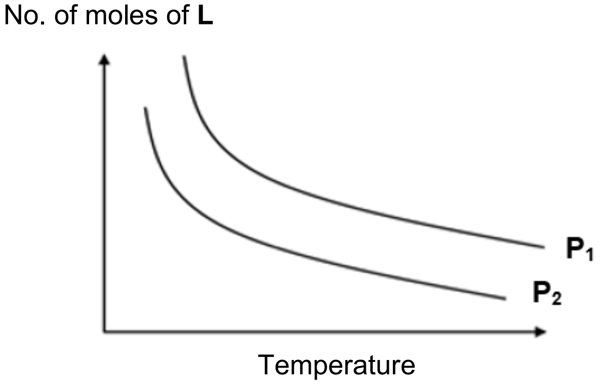
The half-life of the reaction was found to be 3.47 s.

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 $\mathbf{P_1}$ and $\mathbf{P_2}$ respectively.
L could be any of the following compounds shown in the equation at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197 \text{ kJ mol}^{-1}$$



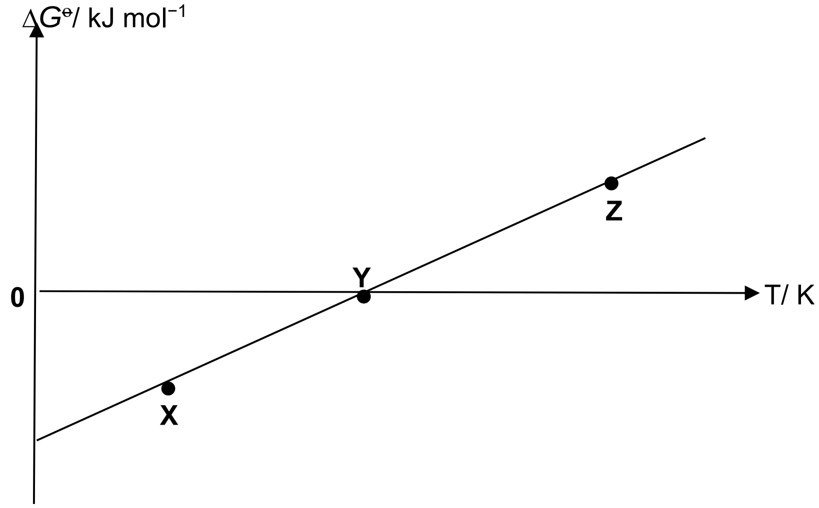
What is the correct identity of **L** and the correct magnitude of pressures $\mathbf{P_1}$ and $\mathbf{P_2}$?

	Identity of **L**	magnitude of pressures $\mathbf{P_1}$ and $\mathbf{P_2}$
A	SO_2	$\mathbf{P_1} > \mathbf{P_2}$
B	SO_2	$\mathbf{P_1} < \mathbf{P_2}$
C	SO_3	$\mathbf{P_1} > \mathbf{P_2}$
D	SO_3	$\mathbf{P_1} < \mathbf{P_2}$

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.

$$NO_2(g) + NO(g) \rightleftharpoons N_2O_3(g)$$

The graph below shows how the $\Delta G^{\ominus}$ 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**.

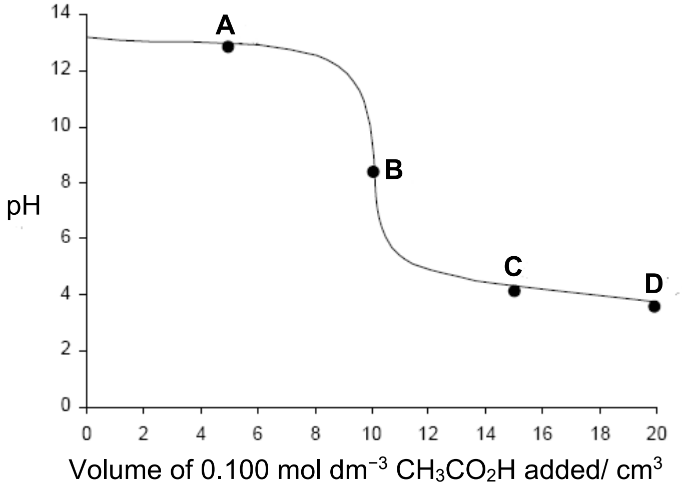
B At point **X**, the K_c value is likely to be greater than 1.

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**.

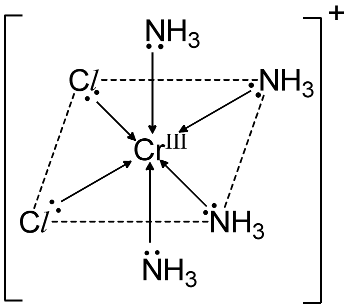
15 The pH changes when 0.100 mol dm^{-3} CH_3CO_2H is added dropwise to 10.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq) as shown below.

At which point on the graph does pH = pK_a, where K_a is the acid dissociation constant of the weak acid?

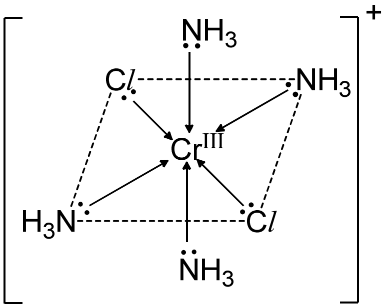


16 Coordination complexes with more than one type of ligand can exist in a number of stereoisomeric forms.

For example, the chromium(III) complex $[Cr(NH_3)_4Cl_2]^+$ can refer to the two stereoisomers as shown:



and



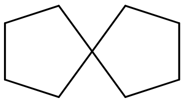
How many stereoisomers can the cobalt(III) complex $[Co(trien)Cl_2]^+$ have?
(trien = $(NH_2CH_2CH_2NHCH_2)_2$, a tetradentate ligand)

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

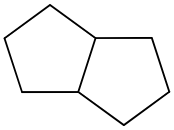
17 Cyclopentane undergoes substitution with bromine.

What is a possible by-product of this reaction?

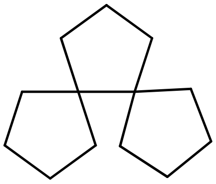
A



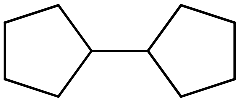
C



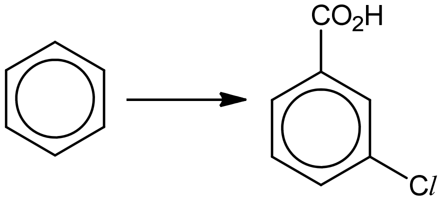
B



D



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

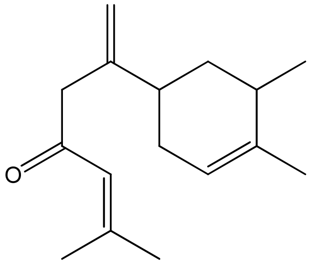


3-chlorobenzoic acid

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.

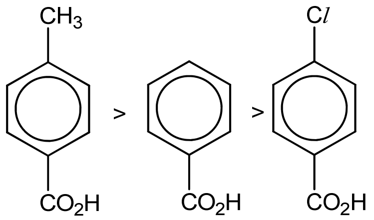


When it is completely reacted with hydrogen in the presence of platinum when heated, how many chiral centres does the product molecule possess?

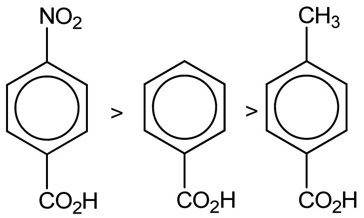
A 2 **B** 3 **C** 4 **D** 5

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

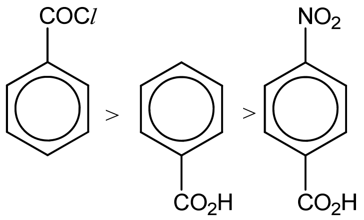
A



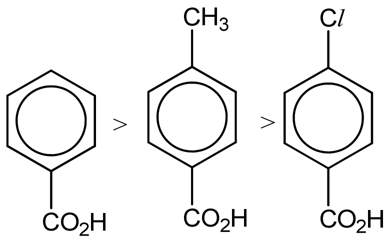
B



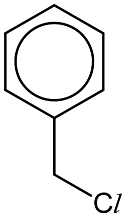
C



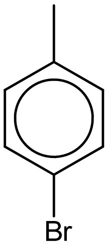
D



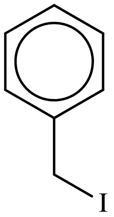
21 Equal amounts of compounds **W**, **X**, **Y** and **Z** are added separately to four test-tubes containing equal concentrations of ethanolic silver nitrate solution in a heated water bath. No precipitate forms in two of the tubes. In the other two tubes, precipitates form at different rates.



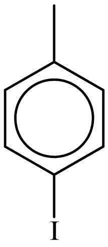
W



X



Y



Z

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.

$$CH_3CHBrCH_2CH_3 \xrightarrow[\text{NaOH}]{\text{hot, ethanolic}}$$

Which of the following statements are true?

1 The organic products formed are mainly alcohols.

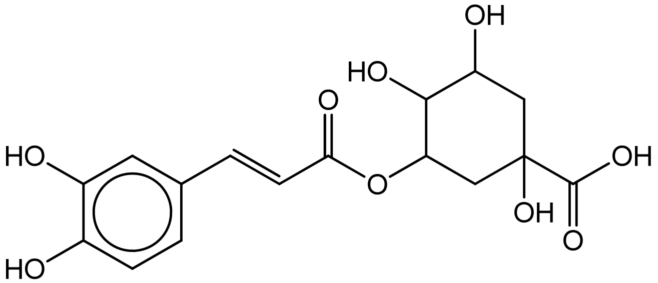
2 The predominant type of reaction occurring is nucleophilic substitution.

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.

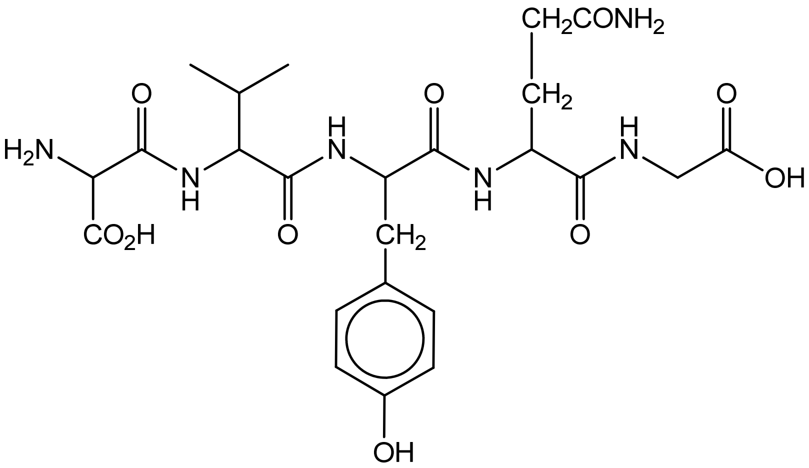


5-caffeoylquinic acid

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?

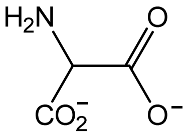
	NaOH(aq)	$NaHCO_3$(aq)	PCl_5(s)
A	6	3	6
B	5	1	3
C	4	3	4
D	3	1	4

24 The structure of a polypeptide chain is shown below.

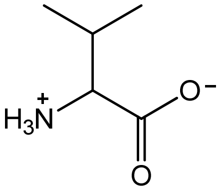


Which of the following will be formed when this polypeptide chain is heated under reflux with 6 mol dm^{-3} of NaOH(aq)?

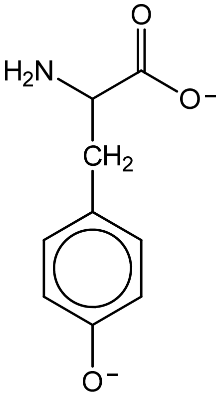
1



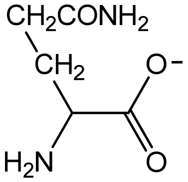
2



3



4



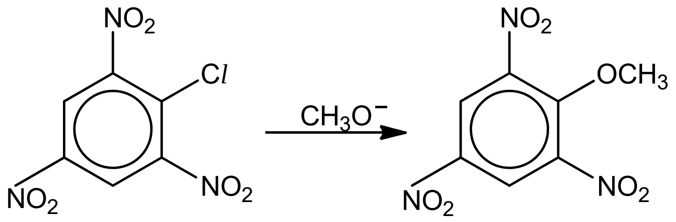
A 1 and 3 only

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?

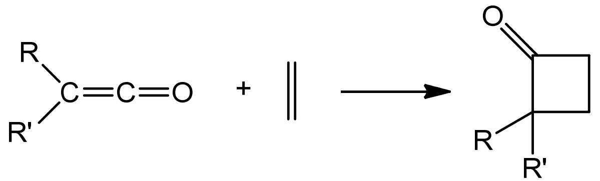
A electrophilic addition

B electrophilic substitution

C nucleophilic addition

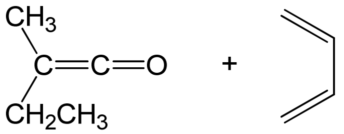
D nucleophilic substitution

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.

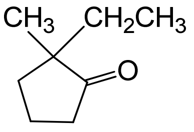


ketene

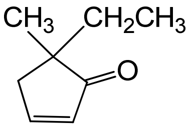
Which of the following is the correct product formed for the following cycloaddition reaction?



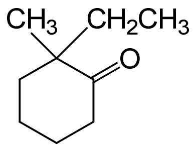
A



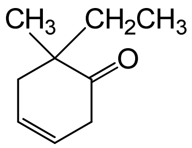
B



C



D



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

When a current is passed through a solution of butanoic acid, $CH_3CH_2CH_2CO_2H$, the following reaction occurs at the cathode.

$$CH_3CH_2CH_2CO_2H + 4H^+ + 4e^- \rightarrow CH_3CH_2CH_2CH_2OH + H_2O$$

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

28 Some standard reduction potentials are given below.

$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07 V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33 V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36 V
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52 V

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 $CrCl_3.6H_2O$ 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 AgC*l*.

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

A Cr^{3+}

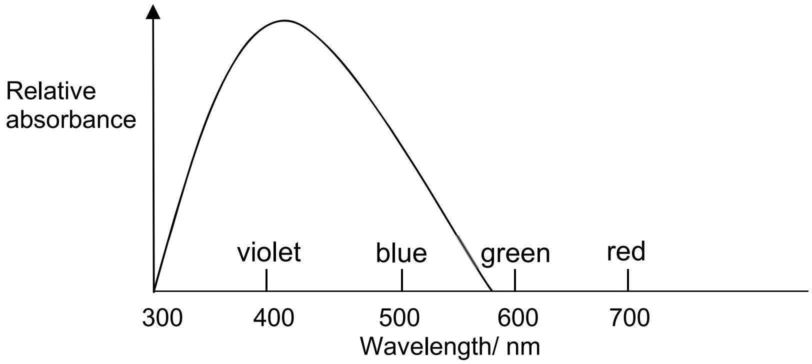
B $[Cr(H_2O)_6]^{3+}$

C $[Cr(H_2O)_5Cl]^{2+}$

D $[Cr(H_2O)_4Cl_2]^+$

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

Catholic Junior College
JC 2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
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CHEMISTRY

9729/01

Paper 1 Multiple Choice

Wednesday 29 August 2018

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

WORKED SOLUTIONS

This document consists of **29** printed pages.

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

B 14.4

C 26.4

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 cm^3 of 0.100 mol dm^{-3} of potassium ferrate(VI), K_2FeO_4, reacts with sodium ethanedioate, $Na_2C_2O_4$, in an acidic medium to produce 144 cm^3 of carbon dioxide gas at room temperature and pressure.

The half equation of $C_2O_4^{2-}$ is shown as follows:

$$2CO_2 + 2e^- \rightleftharpoons C_2O_4^{2-}$$

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 K_2FeO_4 = +6

Amt of FeO_4^{2-} reacted = $\frac{20}{1000} \times 0.100 = 0.002$ mol

Amt of CO_2 formed = $144 \div 24\,000 = 0.006$ mol

Amt of $C_2O_4^{2-}$ reacted = $\frac{1}{2} \times 0.006 = 0.003$ mol

Ratio of FeO_4^{2-} : $C_2O_4^{2-}$ = 0.002 : 0.003

$2\ FeO_4^{2-} \equiv 3\ C_2O_4^{2-}$

3 mol of $C_2O_4^{2-}$ 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, $[PCl_4]^+$ and $[PCl_6]^-$.

Which of the following shows the correct shape for PCl_5, $[PCl_4]^+$ and $[PCl_6]^-$?

	PCl_5	$[PCl_4]^+$	$[PCl_6]^-$
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

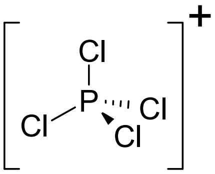
Answer: D

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

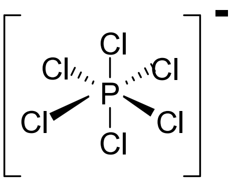
$[PCl_4]^+$: 4 bond pairs 0 lone pairs of electrons; shape is tetrahedral

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

tetrahedral



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 CH_3CH_2Cl to CH_3CH_2I.

3 the strength of instantaneous dipole-induced dipole attraction increases from CH_3CH_2Cl to CH_3CH_2I
Statement is **correct** as the total number of electrons increases from CH_3CH_2Cl to CH_3CH_2I and due to the increase in id-id attraction, the boiling point increases from CH_3CH_2Cl to CH_3CH_2I.

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 CH_3CH_2Cl to CH_3CH_2I.

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

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

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.

Reaction 1: $CH_3^+ + Br^- \rightarrow CH_3Br$

Reaction 2: $HPO_4^{2-} + H_2BO_3^- \rightleftharpoons H_2PO_4^- + HBO_3^{2-}$

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

A Both reactions are acid-base reactions.

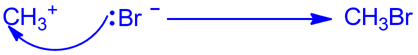
B In reaction 2, HPO_4^{2-} acts as the Brønsted-Lowry base.

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:

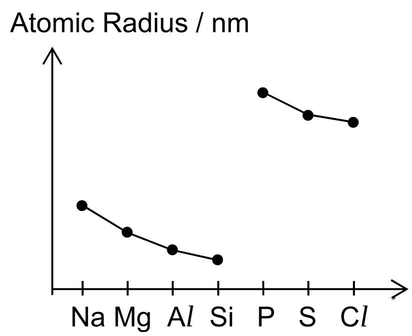
$HPO_4^{2-} + H_2BO_3^- \rightleftharpoons H_2PO_4^- + HBO_3^{2-}$

$H_2BO_3^-$ 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)

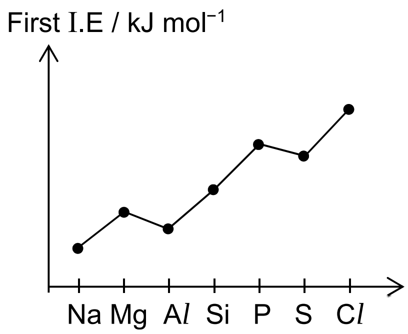
HBO_3^{2-} is the conjugate **base** of $H_2BO_3^-$ (option C is not true)

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?

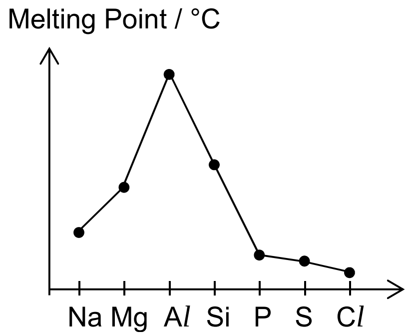
A



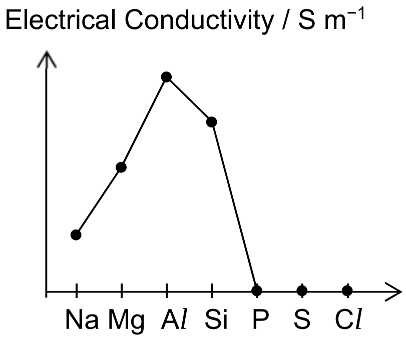
C



B

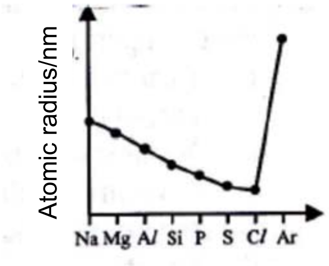


D

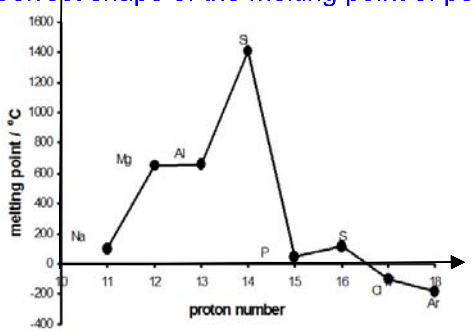


Answer: C

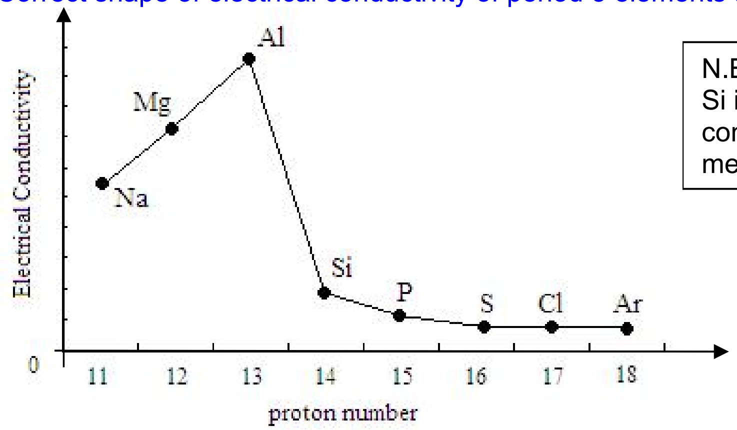
Graph A shows the trends of ionic radius across period 3 elements, not atomic radius. Atomic radius across period should be this.



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, $MgCl_2$, $SiCl_4$

B $AlCl_3$, $SiCl_4$, PCl_5

C Al_2O_3, MgO, SO_2

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:

$$PH_3(g) + HI(g) \rightarrow PH_4^+I^-(s) \qquad \Delta H^\ominus = -145.2 \text{ kJ mol}^{-1}; \Delta S^\ominus = -570.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

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 $\Delta S^\theta = -570.8$ J K^{-1} mol^{-1} (negative value), disorderness of the system has occurred.

2 True.
At 298K, $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta = (-145.2) - (298)(-570.8/1000)$
$= +24.9$ kJ mol^{-1} > 0 (non-spontaneous reaction)

3 False. Since both ΔH^θ and ΔS^θ 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:

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

is thought to involve the following steps:

$H_2O_2 + I^- \rightarrow H_2O + OI^-$ (slow)
$OI^- + H^+ \rightarrow HOI$ (fast)
$HOI + H^+ + I^- \rightarrow I_2 + H_2O$ (fast)

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

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

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.

$$AB(g) \rightarrow A(g) + B(g)$$

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,

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

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

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

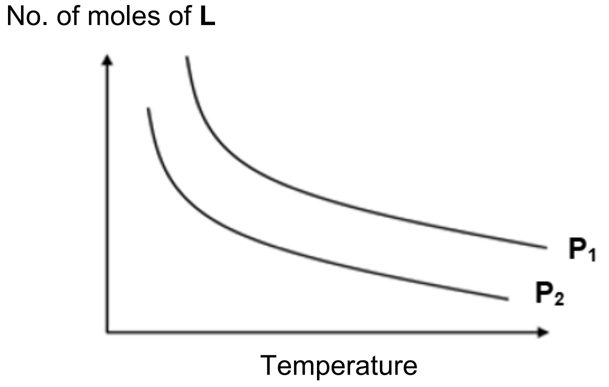
$$\lg\left(\frac{0.5}{1.5}\right) = n \lg\left(\frac{1}{2}\right)$$

n = 1.585

time taken = 1.585 x 3.47 = 5.5 s

13 The graph below shows how the number of moles of compound **L** varies with temperature at two different pressures of $\mathbf{P_1}$ and $\mathbf{P_2}$ respectively.
L could be any of the following compounds shown in the equation at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197\ \text{kJ mol}^{-1}$$



What is the correct identity of **L** and the correct magnitude of pressures $\mathbf{P_1}$ and $\mathbf{P_2}$?

	Identity of **L**	magnitude of pressures $\mathbf{P_1}$ and $\mathbf{P_2}$
A	SO_2	$\mathbf{P_1 > P_2}$
B	SO_2	$\mathbf{P_1 < P_2}$
C	SO_3	$\mathbf{P_1 > P_2}$
D	SO_3	$\mathbf{P_1 < P_2}$

Answer: C

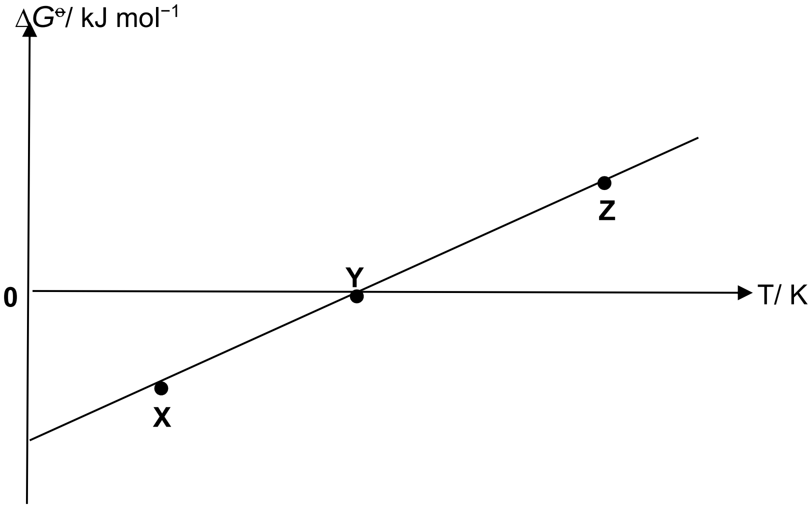
Since forward reaction is exothermic, higher temperatures will favour the backward endothermic reaction. At higher temperature, $[SO_2]$ and $[O_2]$ increases while $[SO_3]$ decreases. Thus the two downward–sloping graphs applies to SO_3.

At a higher pressure, forward reaction is favoured since the product has less moles of gaseous particles, therefore $[SO_3]$ increases.
Thus, $\mathbf{P_1 > P_2}$.

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.

$$NO_2(g) + NO(g) \rightleftharpoons N_2O_3(g)$$

The graph below shows how the $\Delta G^\ominus$ 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)**

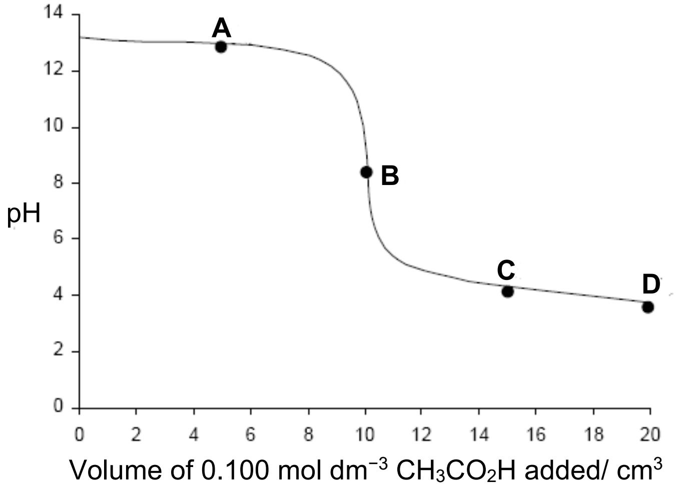
At point **X**, $\underline{\Delta G^\theta < 0}$, P.O.E lies <u>more to the right</u> and forward reaction occurs more readily compared to backward reaction.
Since $K_c = \frac{[N_2O_3]}{[NO_2][NO]}$,
Therefore K_c value is likely to be greater than 1 at point **X**. **(option B is correct)**

At point **Y**, $\Delta G^\theta = 0$.
Comparing point **X** and **Y**, <u>**less**</u> NO_2 gas is present at **X** since P.O.E lies <u>more to the right at point **X**</u> compared to point **Y**. **(option A is wrong)**

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

15 The pH changes when 0.100 mol dm^{-3} CH_3CO_2H is added dropwise to 10.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq) as shown below.

At which point on the graph does pH = pK_a, where K_a is the acid dissociation constant of the weak acid?



Answer: D

For pH = pK_a, $[A^-] = [HA]$

$HA + NaOH \rightarrow NaA + H_2O$

At A, species present: NaOH and NaA

At equivalence point B, A^- ion hydrolyses in water, $A^- + H_2O \rightleftharpoons HA + OH^-$

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

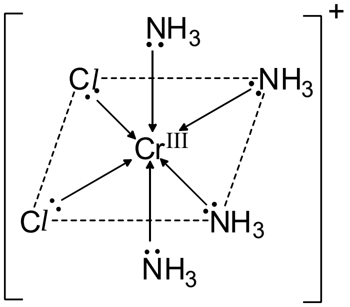
At D,

n_{HA} = 20.00/1000 x 0.100
= 2 x 10^{-3} mol
n_{OH^-} = 10.0/1000 x 0.100
= 1 x 10^{-3} mol
n_{A^-} formed = 1 x 10^{-3} mol
n_{HA} unreacted = 2 x 10^{-3} mol − 1 x 10^{-3} mol
= 1 x 10^{-3} mol

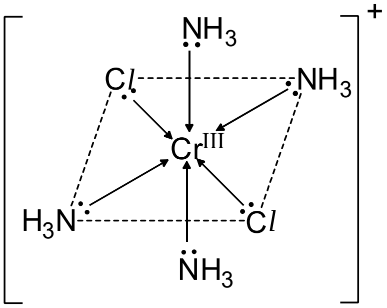
At D, $[A^-] = [HA]$

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

For example, the chromium(III) complex $[Cr(NH_3)_4Cl_2]^+$ can refer to the two stereoisomers as shown:



and

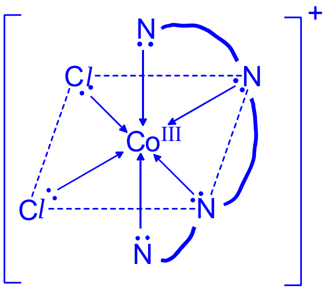


How many stereoisomers can the cobalt(III) complex $[Co(trien)Cl_2]^+$ have?
(trien = $(NH_2CH_2CH_2NHCH_2)_2$, a tetradentate ligand)

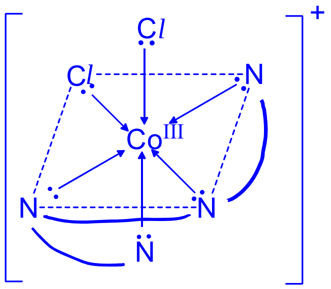
A 1 **B** 2 **C** 3 **D** 4

Answer: C

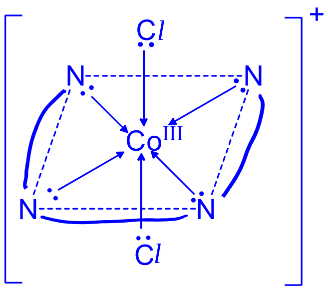
There are three stereoisomers for $[Co(trien)Cl_2]^+$.



Middle two N in same plane.



Three N in same plane.

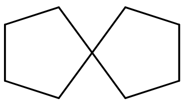


All four N in same plane.

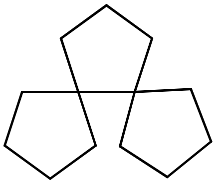
17 Cyclopentane undergoes substitution with bromine.

What is a possible by-product of this reaction?

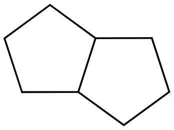
A



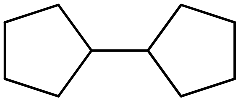
B



C

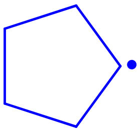


D

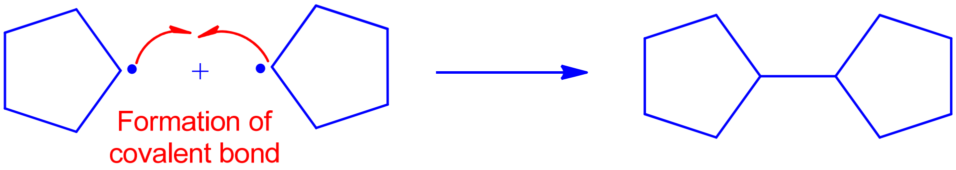


Answer: D

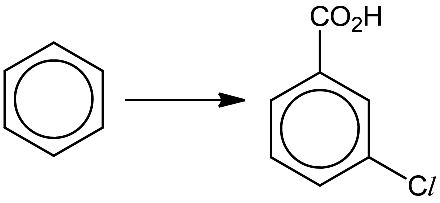
In **A**, **B** and **C**, the cyclopentane units are sharing carbon atoms, whereas in **D**, the carbon atoms of each cyclopentane unit are separate from other cyclopentane units. In free radical substitution, the termination step between two alkyl radicals gives rise to a new C-C bond, and the number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

The radical formed should be 

Hence the termination step between two alkyl radicals should be:



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



3-chlorobenzoic acid

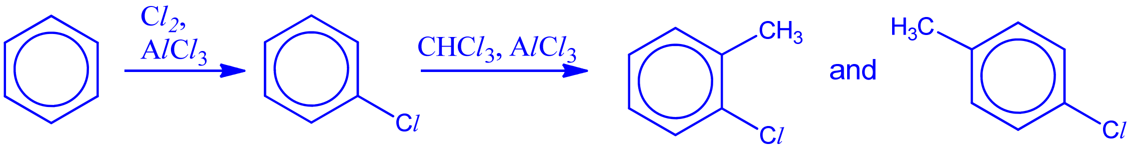
Which of the following is the best method for this synthesis?

	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

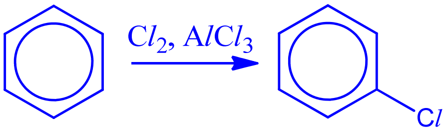
Answer: C

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.

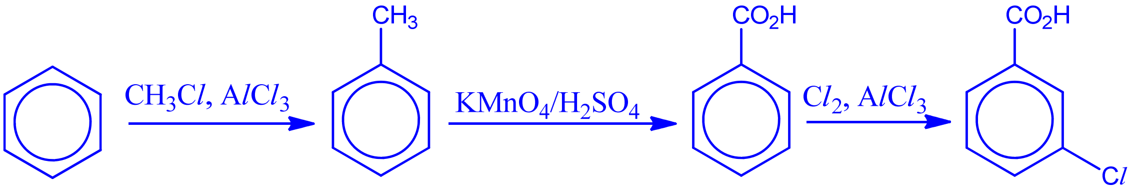
Option **A:** $–CH_3$ is substituted on 2- and 4-positions instead of the 3-position.



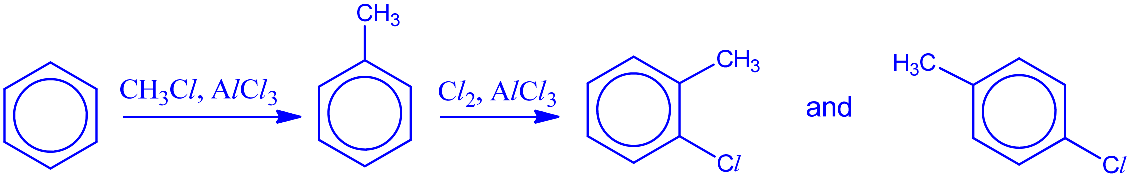
Option **B**: No alkyl side-chain for $KMnO_4$ to oxidise in Step 2.



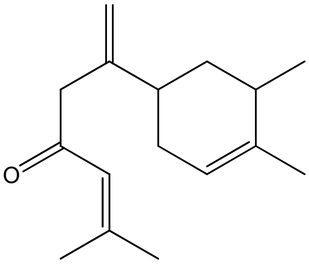
Option **C**:



Option **D**: –C*l* is substituted on 2- and 4-positions instead of the 3-position.



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



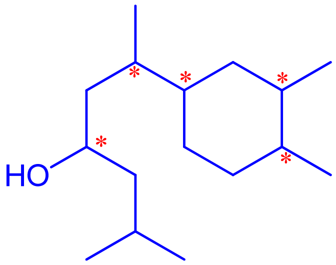
When it is completely reacted with hydrogen in the presence of platinum when heated, how many chiral centres does the product molecule possess?

A 2
B 3
C 4
D 5

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

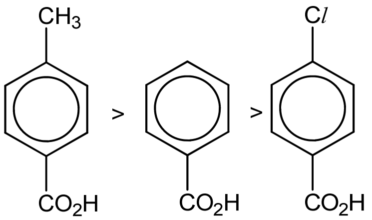
Answer: D

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

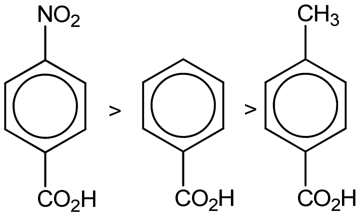


20 Which of the following correctly lists the compounds in order of decreasing acidity in aqueous solution?

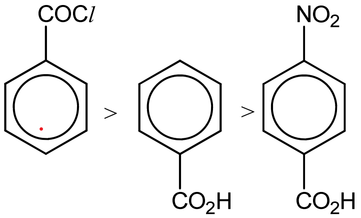
A



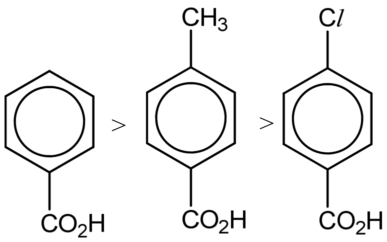
B



C



D



Answer: B

Electron-withdrawing group	$-NO_2$, $-Cl$
Electron-donating group	$-CH_3$

***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).

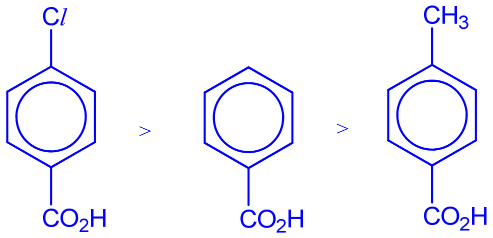
Note that

- 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.

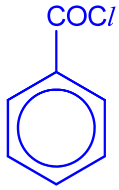
Hence option B is correct.

For the other options,

A & D The correct order should be

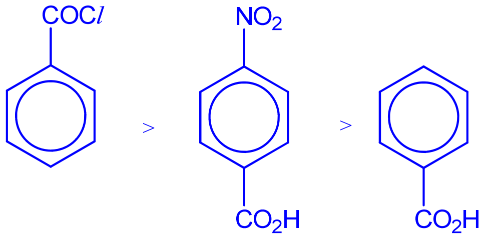


C Note that the following compound

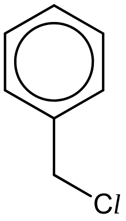


is an acyl chloride and undergoes hydrolysis readily to give HCl which is a strong acid, hence it is the strongest acid.

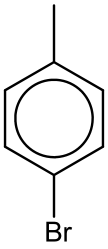
Hence, the correct order should be



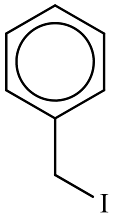
21 Equal amounts of compounds **W**, **X**, **Y** and **Z** are added separately to four test-tubes containing equal concentrations of ethanolic silver nitrate solution in a heated water bath. No precipitate forms in two of the tubes. In the other two tubes, precipitates form at different rates.



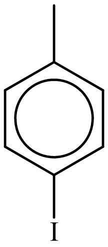
W



X



Y



Z

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−C*l* bond, hence it will break more readily. The colour of the precipitate should be yellow instead of white (which is the colour of AgC*l*), 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 AgC*l*, so the AgI precipitate should weigh more than the AgC*l* 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.

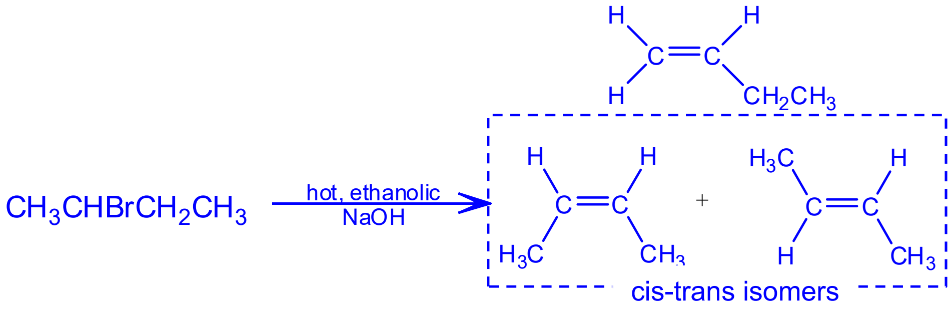
2 The predominant type of reaction occurring is nucleophilic substitution.

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

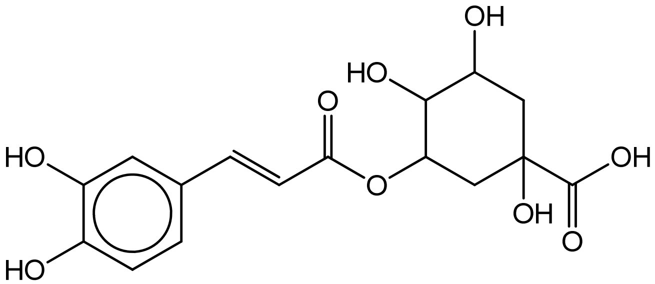
The reaction type is **elimination**. HBr can be eliminated from carbons 1 & 2, or carbons 2 & 3, to give three products, among which there is a pair of cis-trans isomers.



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:

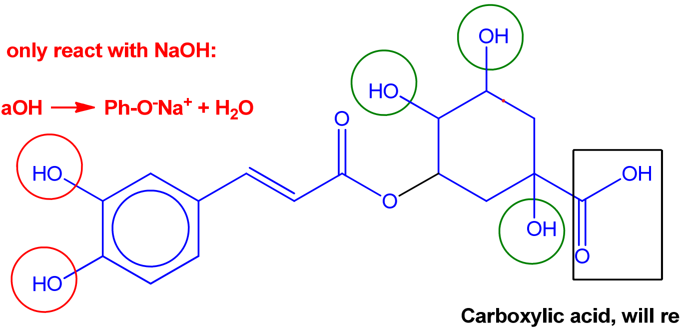
- NaOH(aq) will react with phenols and carboxylic acids only.
- $NaHCO_3$(aq) will react with carboxylic acids only.
- PCl_5(s) will react with alcohols and carboxylic acids only.

Alcohol, will only react with PCl_5

$R\text{-}OH + PCl_5 \longrightarrow R\text{-}Cl + POCl_3 + HCl$

Phenol, will only react with NaOH:

$Ph\text{-}OH + NaOH \longrightarrow Ph\text{-}O^-Na^+ + H_2O$



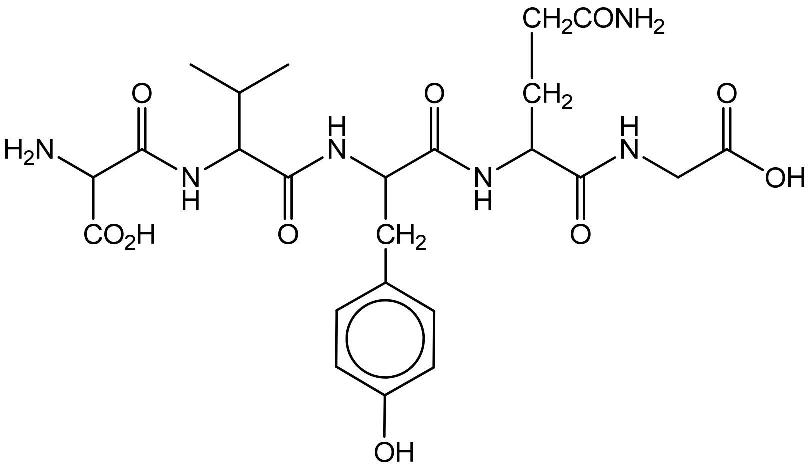
Carboxylic acid, will react with NaOH, $NaHCO_3$ and PCl_5

$RCO_2H + NaOH \longrightarrow RCO_2Na + H_2O$

$RCO_2H + NaHCO_3 \longrightarrow RCO_2Na + H_2O + CO_2$

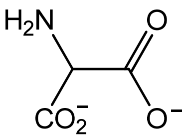
$RCO_2H + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

24 The structure of a polypeptide chain is shown below.

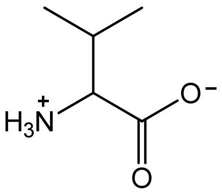


Which of the following will be formed when this polypeptide chain is heated under reflux with 6 mol dm^{-3} of NaOH(aq)?

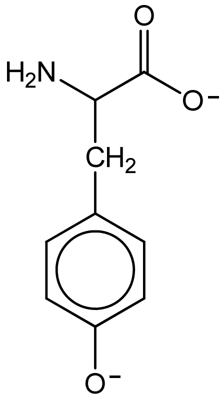
1



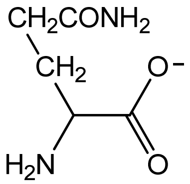
2



3



4



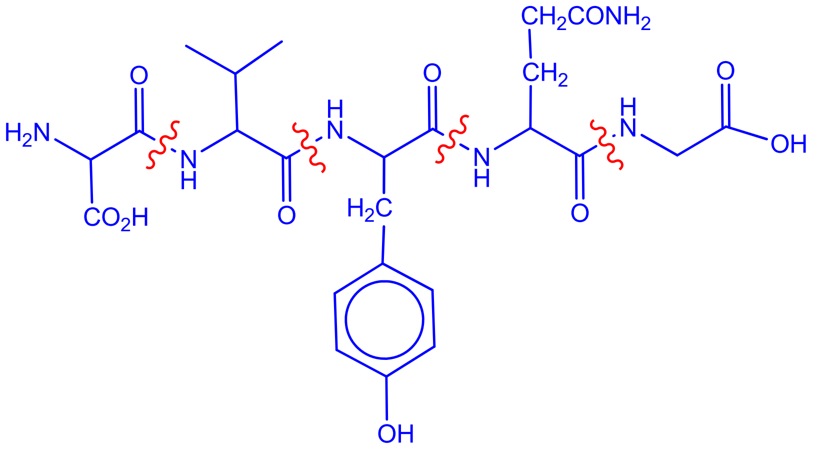
A 1 and 3 only

B 2 and 4 only

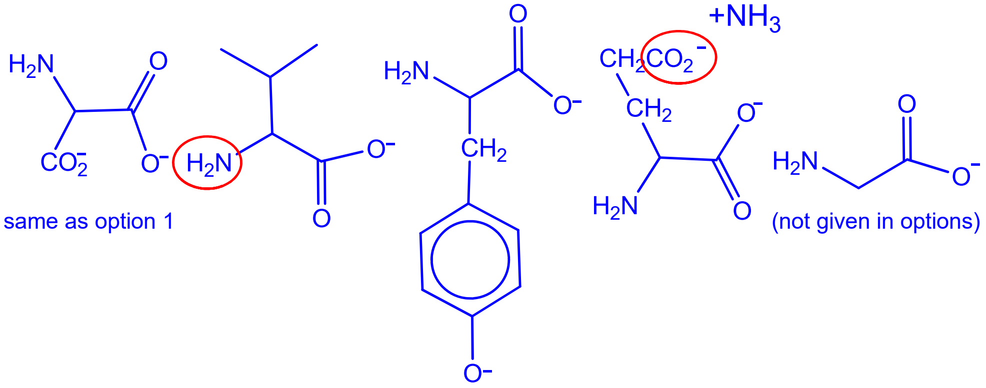
C 1, 3 and 4 only

D 1, 2, 3 and 4

Answer: A (1 and 3 only)



Upon hydrolysis with NaOH(aq), the correct products should be:



same as option 1

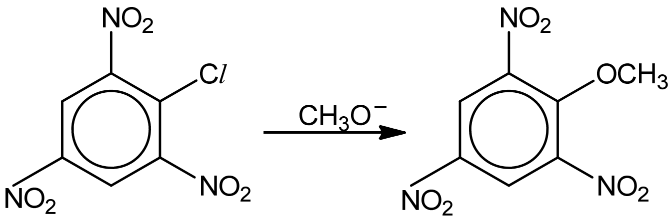
(not given in options)

same as option 3

Option 2 is wrong as there should not be $-NH_3^+$ present when NaOH is used.

Option 4 is wrong as the amide group ($-CONH_2$) 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

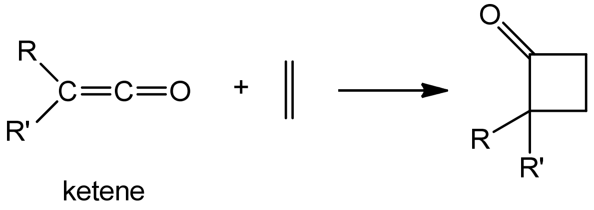
D nucleophilic substitution

Answer: D

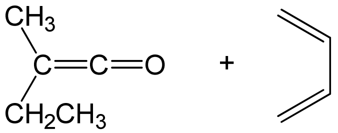
Methoxide anion, CH_3O^-, is a **nucleophile** (lone pair of electrons to be donated) which is attracted to the **electron deficient C** of the benzene ring bonded to C*l*. (Due to the presence of 3 electron withdrawing NO_2 groups, the C–C*l* bond is highly polarised and weakened)
Since the benzene 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, C–C*l* bond of chlorobenzene does have partial double bond character and will **NOT** be hydrolysed.)

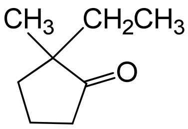
26 Ketenes contain a carbon involved in both alkene and ketone functional groups. It is a reactive compound which undergoes cycloaddition reaction readily with unsaturated compounds to form cyclic rings. One example of such a reaction is shown below.



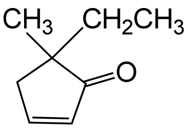
Which of the following is the correct product formed for the following cycloaddition reaction?



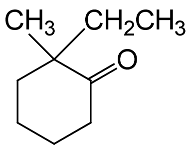
A



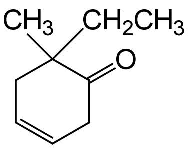
B



C



D

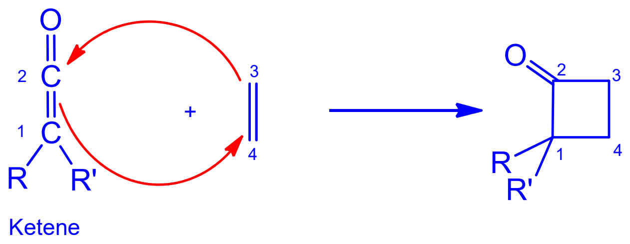


Answer: D

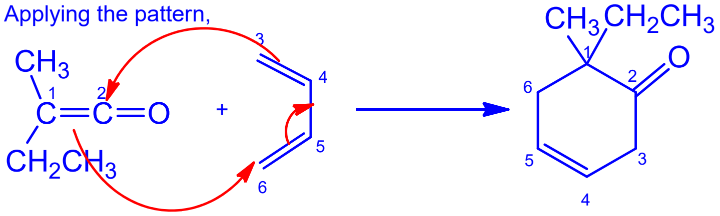
A and B cannot be the correct answer as there would be a loss of 1 C from the reactants to molecules A and B.

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, $CH_3CH_2CH_2CO_2H$, the following reaction occurs at the cathode.

$$CH_3CH_2CH_2CO_2H + 4H^+ + 4e^- \rightarrow CH_3CH_2CH_2CH_2OH + H_2O$$

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:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Hence, $O_2 \equiv 4e^- \equiv CH_3CH_2CH_2CO_2H$

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.

$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07 V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33 V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36 V
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52 V

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
$E_{cell}^{\ominus} = 1.52 - 1.36 > 0$ ✓
B bromide ions by chlorine
$E_{cell}^{\ominus} = 1.36 - 1.07 > 0$ ✓
C manganese(II) ions by acidified dichromate(VI) ions
$E_{cell}^{\ominus} = 1.33 - 1.52 < 0$ ✗
D chromium(III) ions by chlorine
$E_{cell}^{\ominus} = 1.36 - 1.33 > 0$ ✓

29 A compound of chromium with the general formula $CrCl_3.6H_2O$ 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?

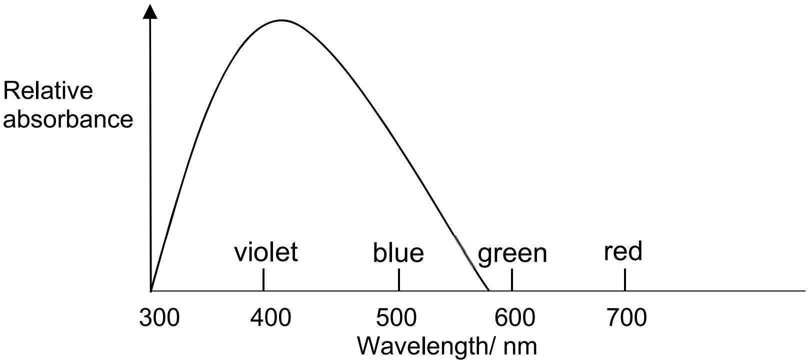
A Cr^{3+}
B $[Cr(H_2O)_6]^{3+}$
C $[Cr(H_2O)_5Cl]^{2+}$
D $[Cr(H_2O)_4Cl_2]^+$

Answer: C

Since only two third of the total chloride present is precipitated as $AgCl$, the complex of the chromium compound is $[Cr(H_2O)_5Cl]^{2+} \bullet 2Cl^-$, 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

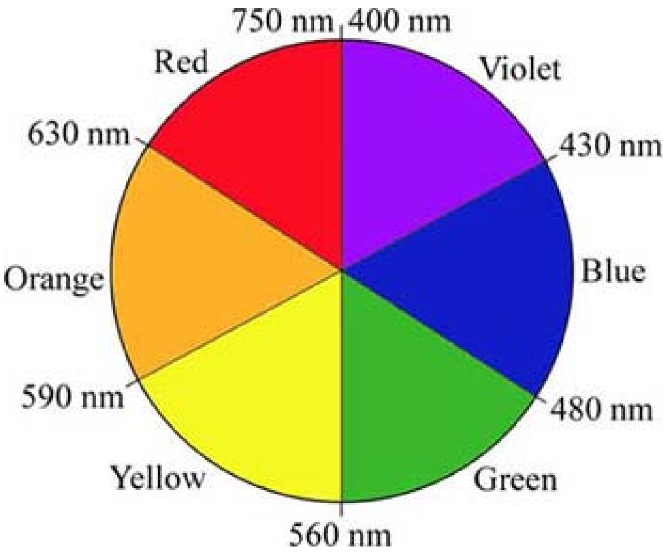
B blue

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	2T

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	30
Paper 3	**Q 1**	20	80	35
	Q 2	20		
	Q 3	20		
	Q 4 / 5	20		
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.

$$2N_2O_5 \rightarrow 4NO_2(g) + O_2(g)$$

Table 1.1 below shows the variation of $[N_2O_5]$ with time.

Time / s	$[N_2O_5]$ / mol dm^{-3}	ln $[N_2O_5]$
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:

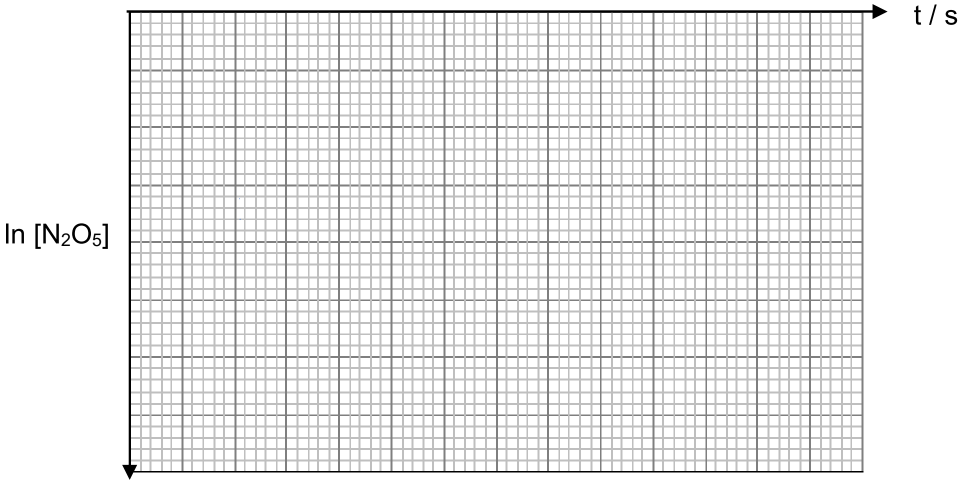
$$\ln [N_2O_5]_t = -kt + \ln [N_2O_5]_o$$

where $[N_2O_5]_o$ is the initial concentration of N_2O_5 and $[N_2O_5]_t$ is the concentration of N_2O_5 at time, *t*.

Using relevant data in Table 1.1, calculate the values for ln $[N_2O_5]$ 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):

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

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.

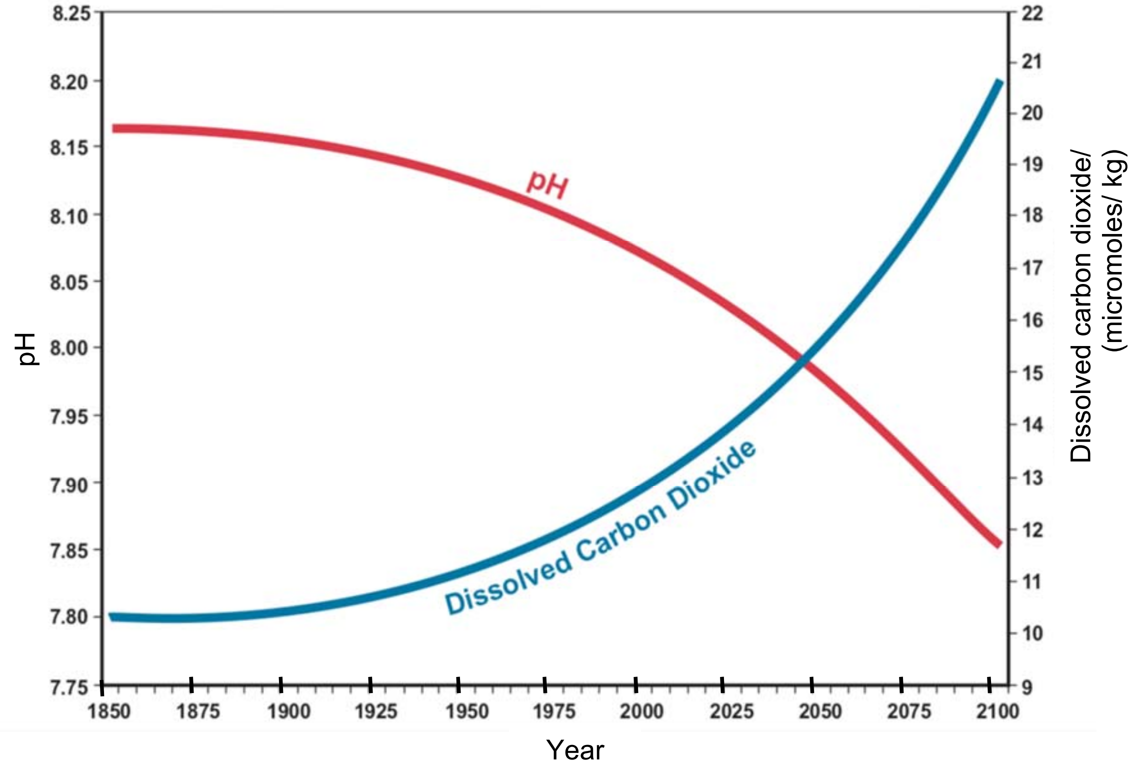


Fig. 2

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

.... [1]

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

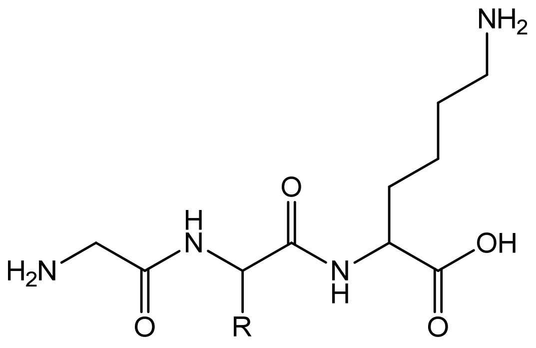
....

.... [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.

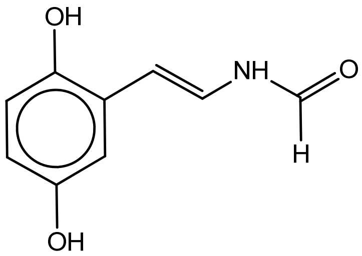
…………………………………………………………………………………………..

…………………………………………………………………………………………..

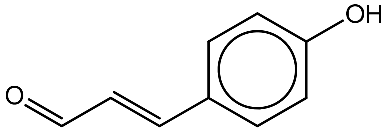
…………………………………………………………………………………………..

……………………………………………………………………………………… [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

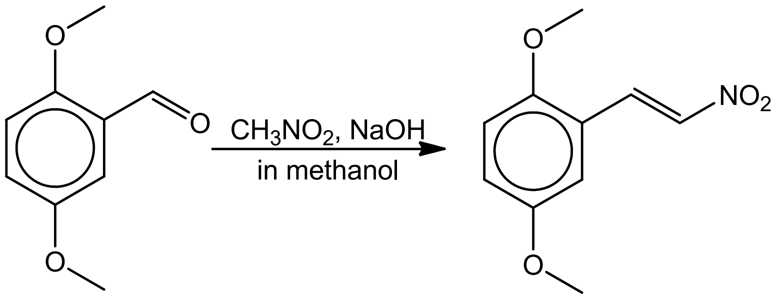
(i) State and explain whether erbstatin or 4-hydroxy cinnamaldehyde has a higher boiling point.

………………………………………………………………………………………..

………………………………………………………………………………………..

……………………………………………………………………………………… [3]

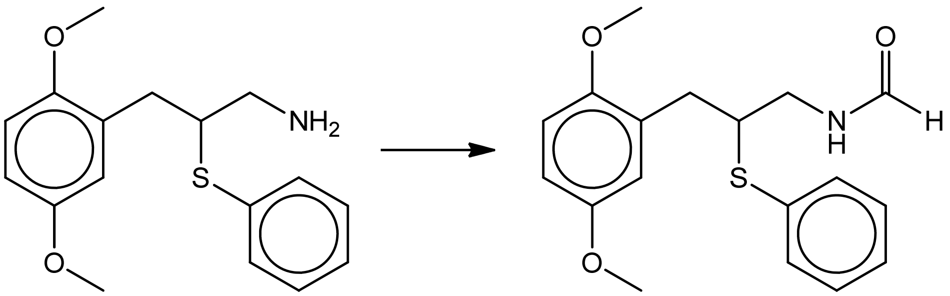
The synthesis of erbstatin involved the following step.



(ii) Given that NaOH is used as a base to form $^{-}CH_2NO_2$ as a nucleophile, suggest the type of reaction in the above step.

……………………………………………………………………………………… [1]

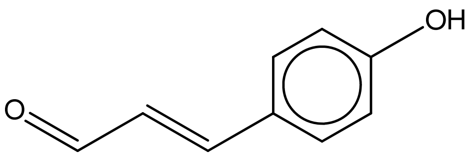
Another step in the synthesis of erbstatin is shown below.



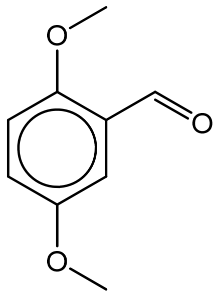
(iii) Suggest suitable reagents for the above step.

…………………………………………………………………………………… [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

……………………………………………………………………………………………

……………………………………………………………………………………………

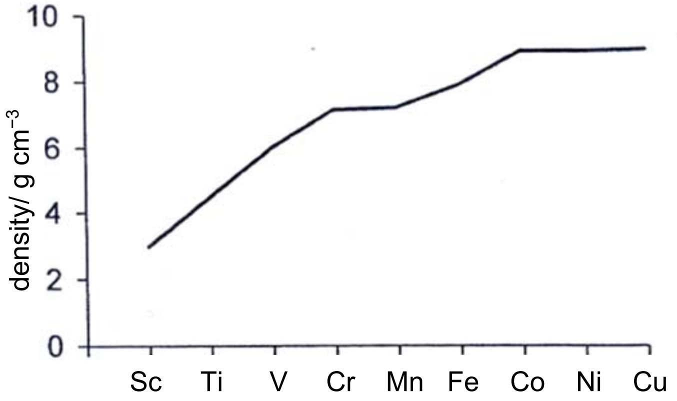
…………………………………………………………………………………… [2]

[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.



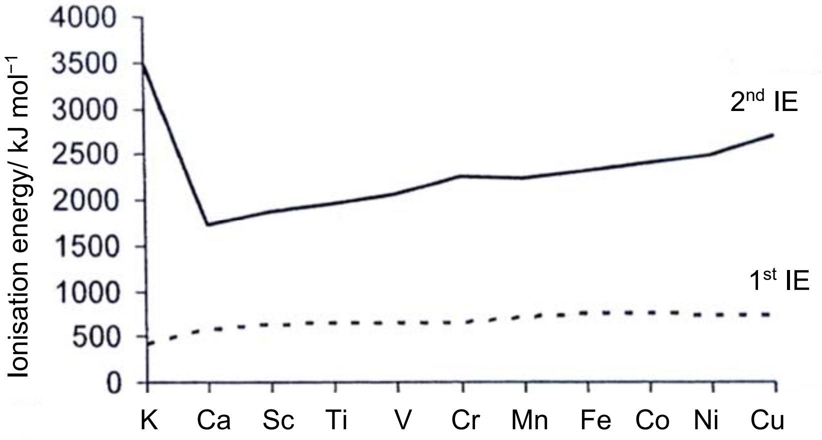
(i) Suggest why the densities of the elements increase from Sc to Cu.

....

....

.... [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.

…...

....

....

....

....

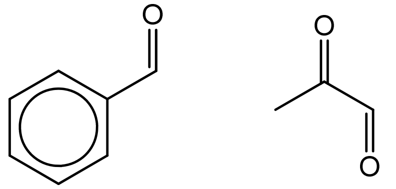
....

....

.... [7]

[Total: 15]

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



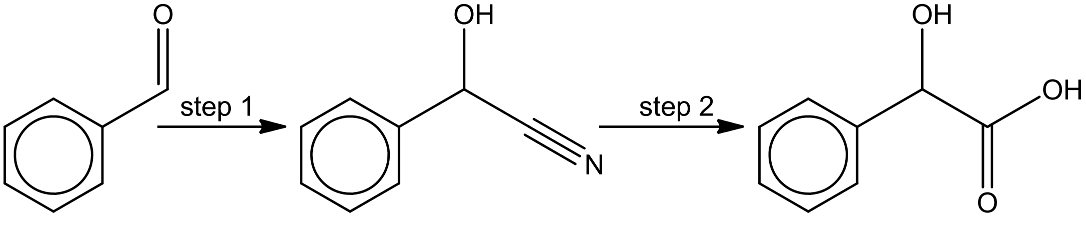
(i) Suggest a simple chemical test that could distinguish between the two compounds above. State the observations expected for each compound and the products (if any) that gives the observations.

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.

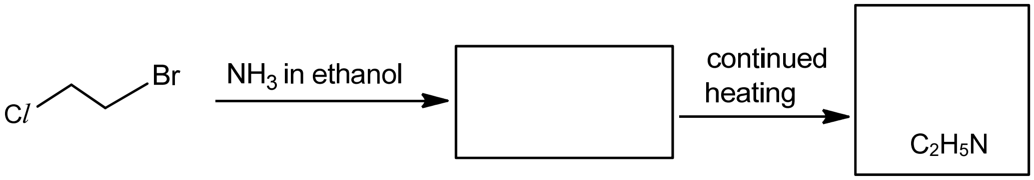
(i) With bromomethane and chloromethane as examples, describe and explain briefly the relative reactivities of bromo- and chloro-compounds with respect to hydrolysis.

....

....

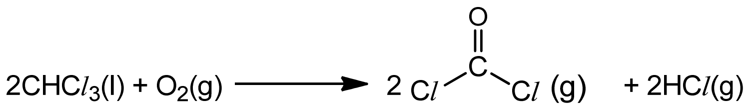
.... [1]

(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.



$$2CHCl_3(l) + O_2(g) \longrightarrow 2\,Cl{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl\,(g) + 2HCl(g)$$

(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 $CHCl_3(l)$ is $+31\ kJ\ mol^{-1}$.

[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.

....

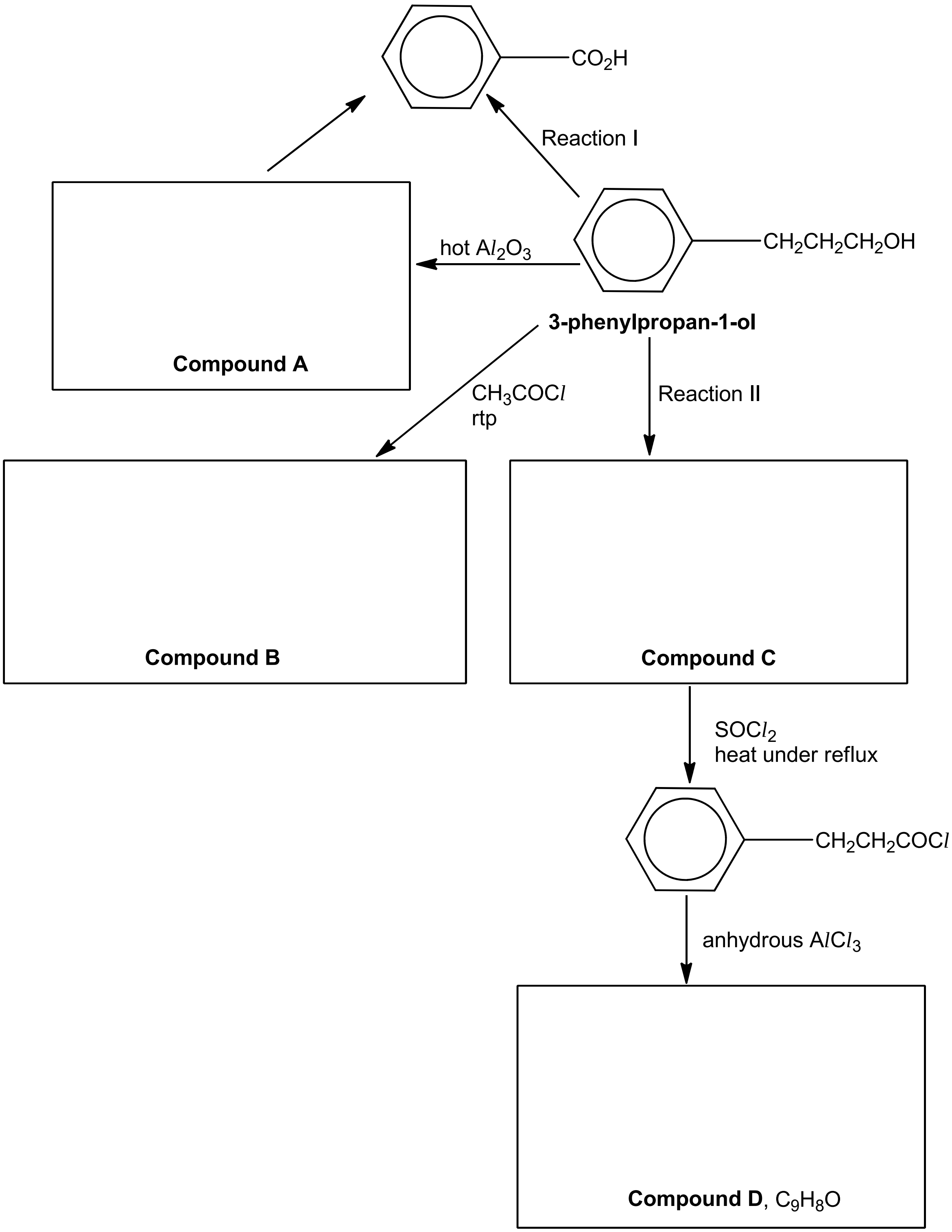
....

.... [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 ……………………………………………………………

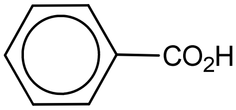
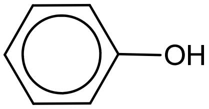
Reaction II ……………………………………………………………

[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 / 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]

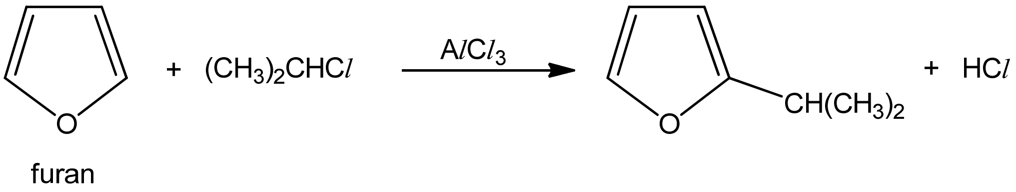
(ii) In the space below, give the structural formula of compound **X**, **Y** and **Z**.

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.

$$2N_2O_5 \rightarrow 4NO_2(g) + O_2(g)$$

Table 1.1 below shows the variation of $[N_2O_5]$ with time.

Time / s	$[N_2O_5]$ / mol dm^{-3}	ln $[N_2O_5]$
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$[N_2O_5]$ .... [1]

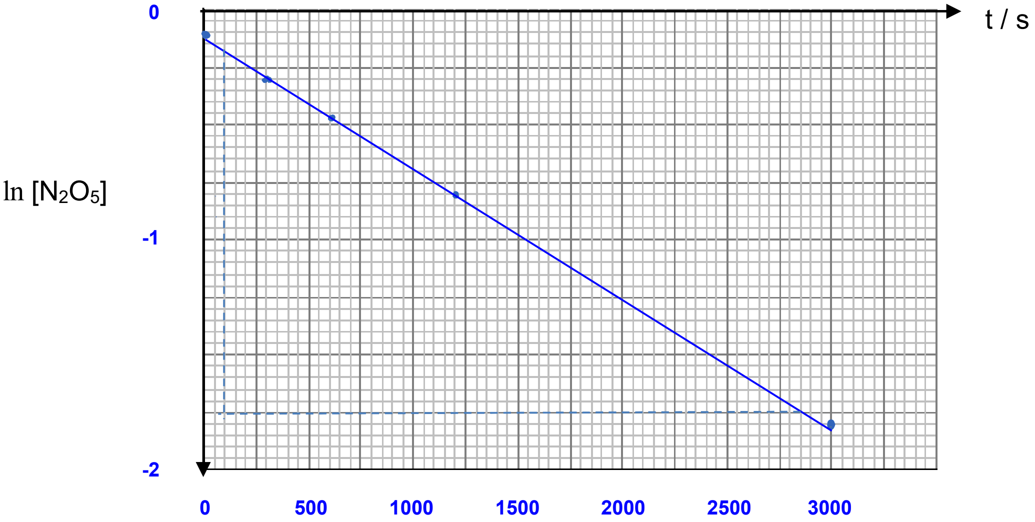
(ii) The rate equation for the decomposition of N_2O_5 can also be expressed as:

$$\ln [N_2O_5]_t = -kt + \ln [N_2O_5]_o$$

where $[N_2O_5]_o$ is the initial concentration of N_2O_5 and $[N_2O_5]_t$ is the concentration of N_2O_5 at time, *t*.

Using relevant data in Table 1.1, calculate the values for ln $[N_2O_5]$ 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 = – gradient

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

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

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

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

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

$$= 1195\ s$$

(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 $t_{1/2} = \frac{In2}{k}$ 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):

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

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 (NO_2) darkens.

.... [1]

(iii) Identify the experiment that gives the initial concentration of $N_2O_4 : NO_2$ 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]

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$= \frac{(0.0523)^2}{(0.594)}$$

$$= 4.60 \times 10^{-3} \text{ mol dm}^{-3}$$

(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.

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

$$= (4.60\times10^{-3})(0.0821)(298)^{(2-1)}$$

$$= 0.113$$

[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.

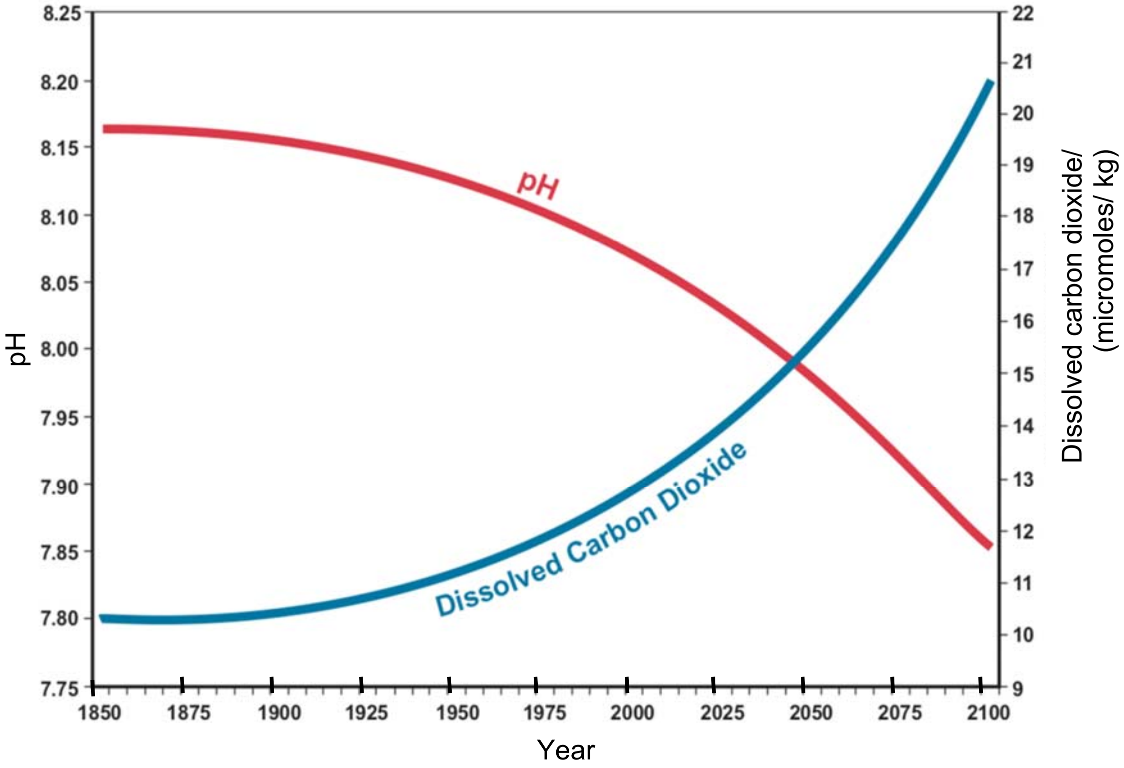


Fig. 2

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

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

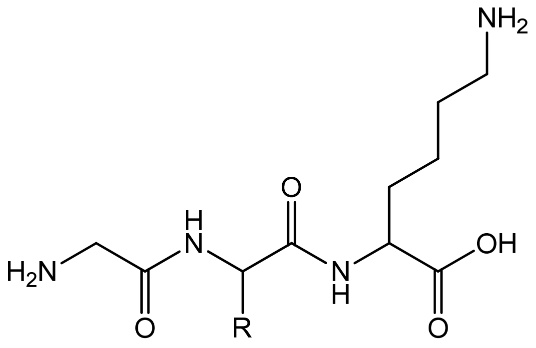
(ii) Explain briefly why GHK, as a *zwitterion*, is highly soluble in water.

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 CO_2.

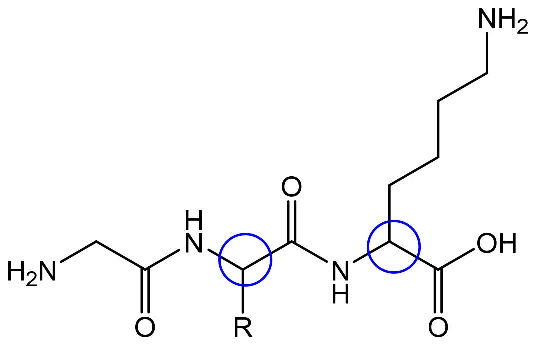
$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$ [1]

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

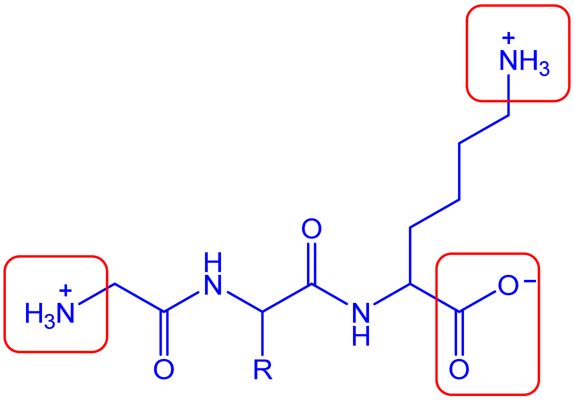


GHK

(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.



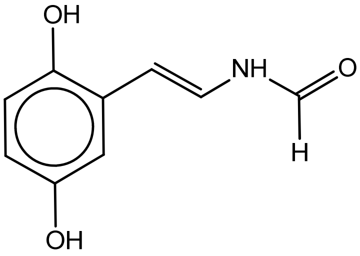
[2]

(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.

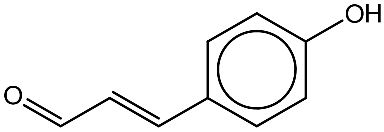
2050. For GHK no longer function as a signaling molecule, it cannot exist as a zwitterion which both the –NH_2 groups are protonated. Since the pKa value of –NH_2 is 7.98, the pH value lower than that will result in –NH_2 to be protonated .

[2]

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



erbstatin

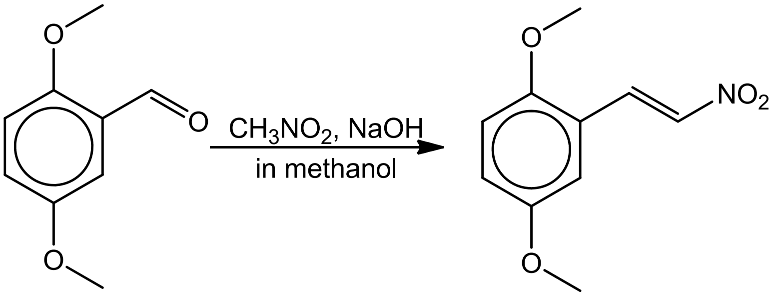


4-hydroxy cinnamaldehyde

(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.

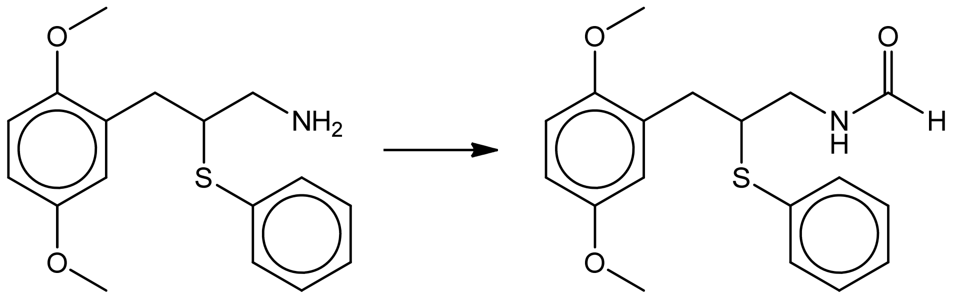


(ii) Given that NaOH is used as a base to form $^{-}CH_2NO_2$ as a nucleophile, suggest the type of reaction in the above step.

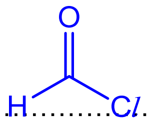
Condensation OR Addition-elimination

[1]

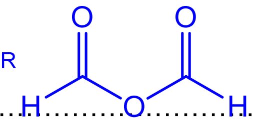
Another step in the synthesis of erbstatin is shown below.



(iii) Suggest suitable reagents for the above step.

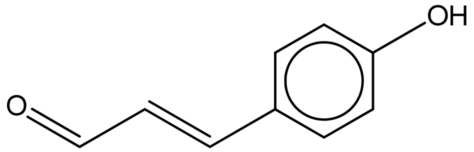


OR

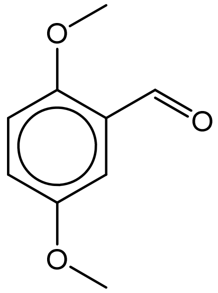


[1]

(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

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

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

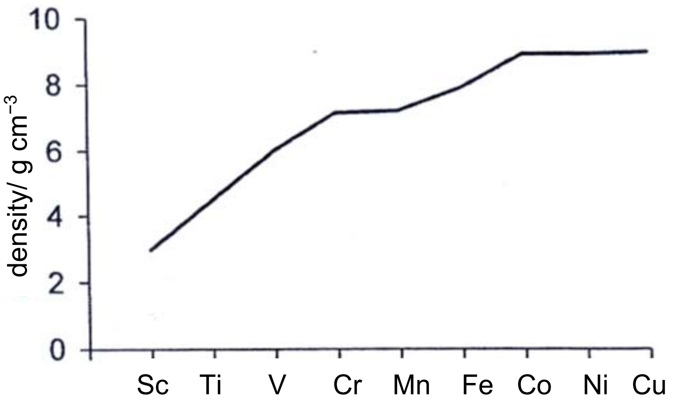
[2]

[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.

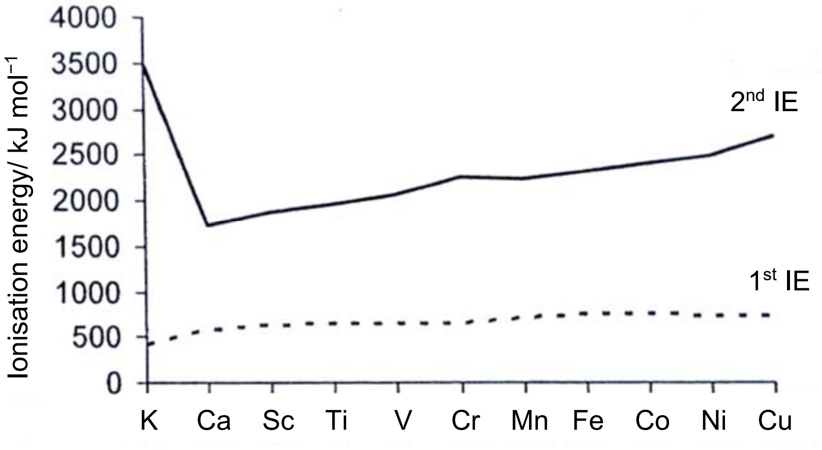
The graph below shows the densities of the elements Sc to Cu.



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

From Sc to Cu, relative <u>atomic mass increases</u> and <u>atomic radius</u> decreases slightly(or remain invariant). The elements have a more close-packed structure and thus have a <u>higher mass per unit volume</u>, 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 Sc^{3+}.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

[1]

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

Sc is not a transition element as it only forms stable Sc^{3+} 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: SO_3

$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$ when MgO reacts with water, sparingly soluble $Mg(OH)_2$ is formed

$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$

$MgCl_2$ hydrolyses slightly to form a weakly acidic solution of pH 6.5

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$

Upon addition of excess barium chloride solution, $BaSO_4(s)$ is formed.

7.00 g of white ppt corresponds to the mass of 0.03 mol of $BaSO_4$.

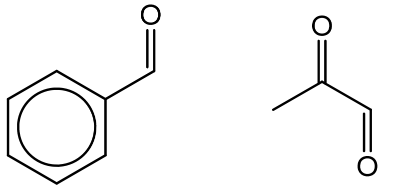
$SO_3(g) + H_2O\ (l) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2HCl(aq)$

OR $SO_4^{2-} + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

$SO_3(g) + MgO(aq) \rightarrow MgSO_4(aq)$ [7]

[Total: 15]

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



benzaldehyde 2-oxopropanal

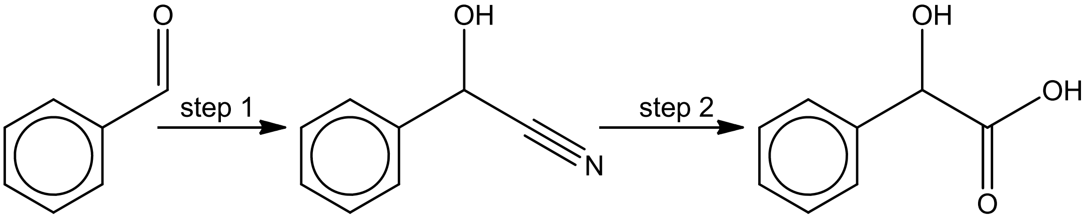
(i) Suggest a simple chemical test that could distinguish between the two compounds above. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: I_2 (aq), NaOH (aq), heat **or** Fehling's reagent/solution, heat

	Observations:	Products:
benzaldehyde	**No Yellow ppt** seen. OR **No Red ppt** seen.	No products
2-oxopropanal	**Yellow ppt** seen. OR **Red ppt** seen.	CHI_3(s) *for iodoform* Cu_2O(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.



benzaldehyde mandelic acid

State the reagents and conditions for steps 1 and 2.

Step 1: HCN (aq), trace amount of NaOH (aq), cold 10-20 °C

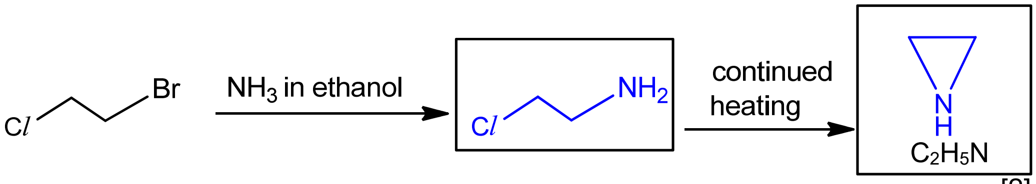
Step 2: Dilute H_2SO_4 (aq), heat under reflux [2]

(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.

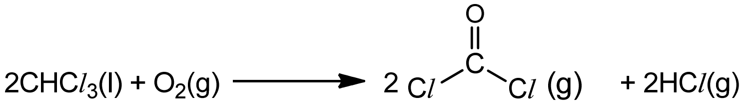
CH_3Br would be **more reactive** towards hydrolysis than CH_3Cl. This is because the **C–Br bond is weaker** than C–C*l* bond and would be more easily broken during hydrolysis. [1]

(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.



[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.



$$2CHCl_3(l) + O_2(g) \longrightarrow 2\,Cl{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl\,(g) \quad + 2HCl(g)$$

(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 $CHCl_3(l)$ is +31 kJ mol^{-1}.

$$\begin{tikzcd}
2CHCl_3(l) + O_2(g) \arrow[rr, "\Delta H_r"] \arrow[d, "2(+31)\ kJ\ mol^{-1}"] & & 2COCl_2(g) + 2HCl(g) \arrow[dl, "2(740 + 2(340)) + 2(431)\ kJ\ mol^{-1}"] \\
2CHCl_3(g) + O_2(g) \arrow[dr, "2(410 + 3(340)) + 496\ kJ\ mol^{-1}"'] & & \\
& 2C(g) + 2H(g) + 6Cl(g) + 2O(g) &
\end{tikzcd}$$

[3]

$\Delta H_r = 2(31) + 2[\underline{410} + 3(\underline{340})] + \underline{496} - [2(\underline{740}+2(\underline{340})) + 2(\underline{431})]$
$= -\underline{284\ kJ\ mol^{-1}}$ (3.s.f.)

(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]

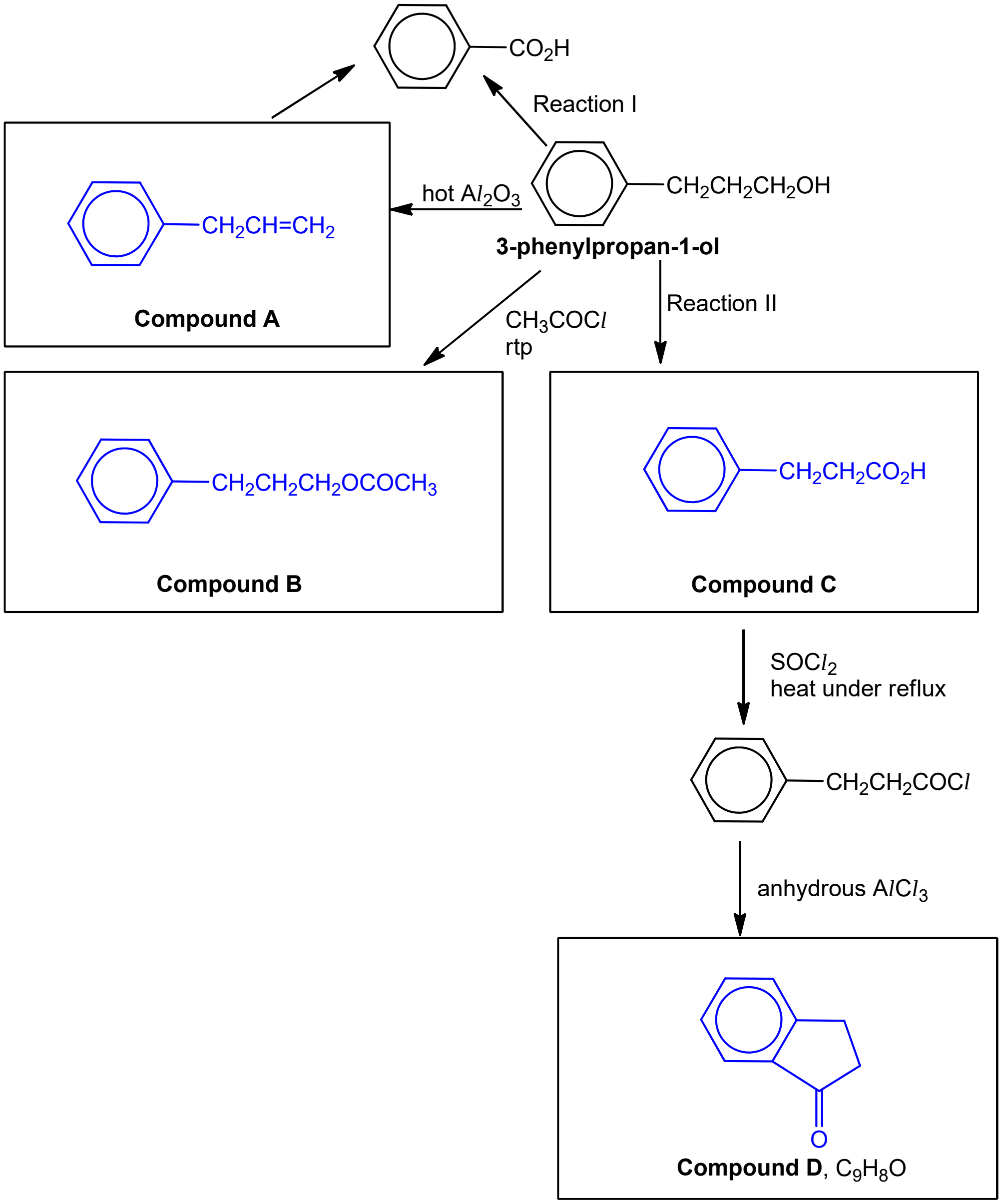
(iii) Hence, state the sign of the standard Gibbs free energy change and comment on the spontaneity of the reaction.

$\Delta G = \Delta H - T\Delta S$, 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 ..$KMnO_4$, dilute H_2SO_4, heat under reflux..........

Reaction II ..$K_2Cr_2O_7$, dilute H_2SO_4, 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.

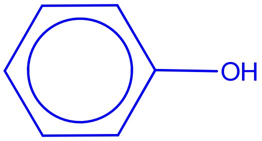
Benzoic acid and phenol are examples of such benzene derivatives which exhibit acidic character when dissolved in water.

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

acid	**structural formula**	**K_a / 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]

CO_2 dissolves in water to give carbonic acid, H_2CO_3 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.

....

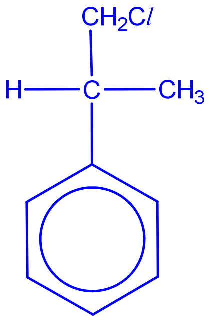
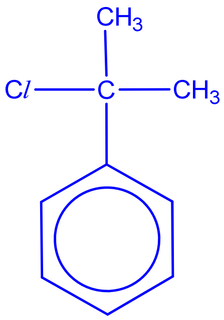
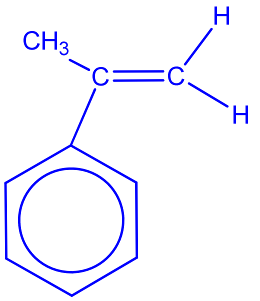
(c) Cumene, C_9H_{12}, is another benzene derivative that can be used to produce phenol and propanone.

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]

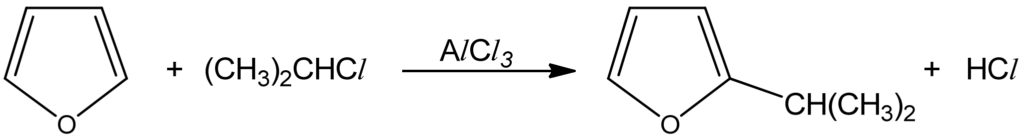
NaOH dissolved in ethanol / alcoholic NaOH/ NaOH (alc)

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

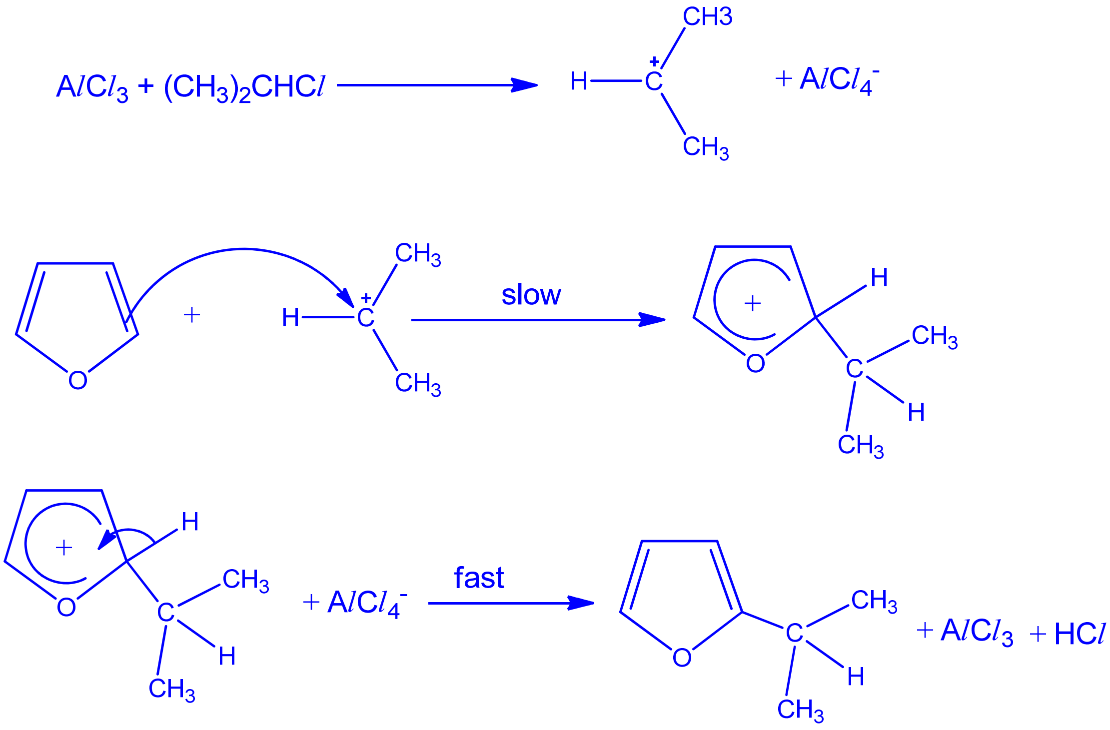
Compound X	**Compound Y**	**Compound Z**
		

(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.



furan



[3]

[Total: 15]

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

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.

$$CH_2{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_3$$

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

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

$$CH_2{=}CHCH_3 + BrCl \rightarrow CH_2BrCHClCH_3$$

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 $CH_2(OH)CH(OH)CH_3$.

(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 mol dm^{-3} acidified $KMnO_4$(aq). The resulting solution was titrated against Fe^{2+}(aq) of concentration 0.0750 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 Fe^{2+}(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 1.66×10^5 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.

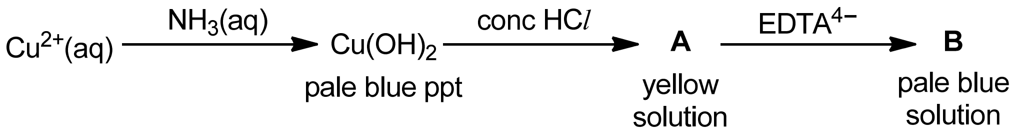


Fig. 2.1

(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 $Cu(OH)_2$ is 2.20×10^{-20} at 25 °C. Write the expression for K_{sp} and state its units. Calculate the solubility of $Cu(OH)_2$ 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.

$$NH_3(aq) \rightleftharpoons NH_3(organic) \qquad \textit{equilibrium 1}$$

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 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 mol dm^{-3} of ammonia, some of which reacted with $Cu^{2+}(aq)$ according to the following equation

$$Cu^{2+}(aq) + nNH_3 \rightarrow [Cu(NH_3)_n]^{2+}$$

The organic layer contained 0.0104 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 $[NH_3(aq)]$ present, show that the value of n in $[Cu(NH_3)_n]^{2+}$ 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

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

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

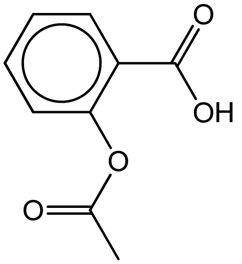
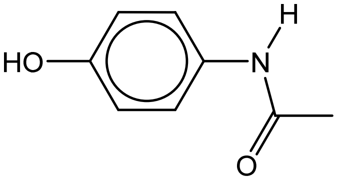
(i) By considering relevant half equations from the *Data Booklet*, construct chemical equations to show how cobalt(II) ions behave as a catalyst in this reaction. No calculation is required. [2]

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

[Total: 20]

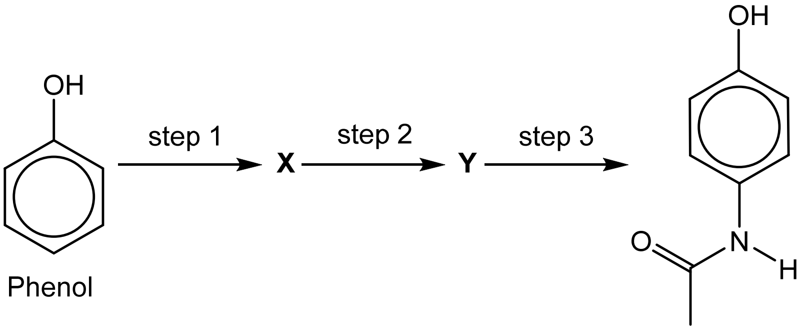
3 **(a)** Analgesics are medicines used to relieve pain. The two most common analgesics in the market are aspirin and paracetamol. Their structures and corresponding pK_a values are shown in Table 3.1.

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.



Paracetamol

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, $Mg(OH)_2$, and calcium carbonate, $CaCO_3$.

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

Table 3.2

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

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

(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 HC*l*. 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.

$$2\,MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

A study of the kinetics of this reaction was carried with a suitable catalyst and with $[C_2O_4^{2-}]$ at 2.00 mol dm^{-3} and data collected are shown in Table 4.1

Table 4.1

time / min	$[MnO_4^-]$ / 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 $[MnO_4^-]$, showing your working clearly including construction lines on your graph. [2]

(iii) Given that the reaction is first order with respect to $[C_2O_4^{2-}]$ and zero order with respect to $[H^+]$, 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 [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.

$$N_2H_4 \rightarrow 2H_2 + N_2$$

(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]

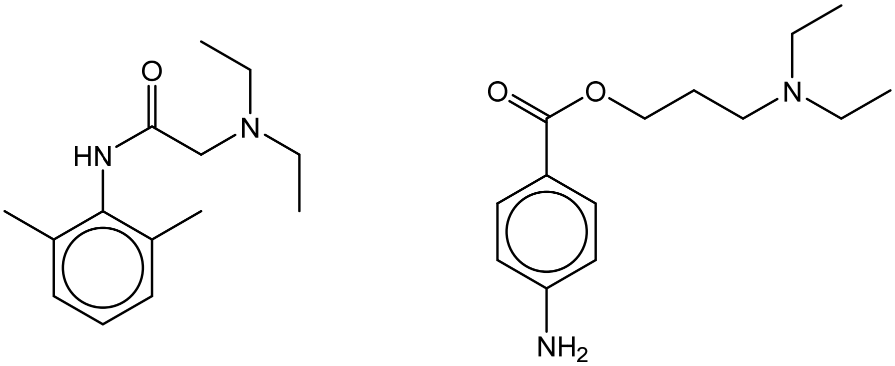
(ii) Hence, write the overall equation. [1]

(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]

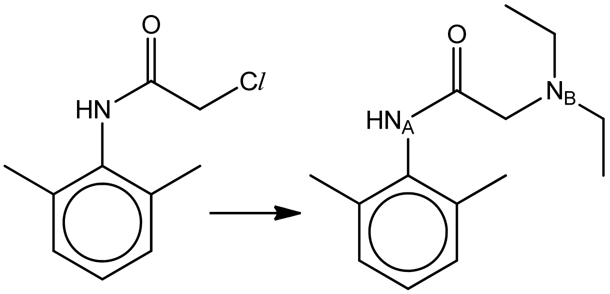
(c) Local anesthesia is used in surgeries where it is applied to numb the feelings of a specific part of a body. Lidocaine and procaine are examples of local anesthesia shown in Fig 5.1



lidocaine procaine

Fig. 5.1

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



lidocaine

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.

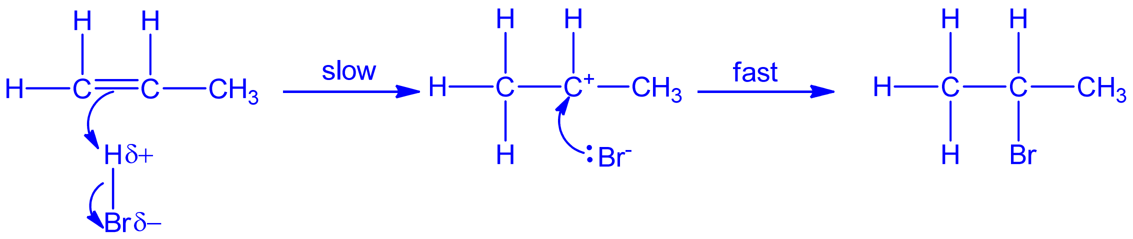
1 Propene is a colourless gas that is produced in large quantities by the petrochemical industry. It is used in the production of synthetic rubber and as a propellant in aerosols.

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

$$CH_2{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_3$$

(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 BrC*l*, 1-bromo-2-chloropropane is produced as the major product.

$$CH_2{=}CHCH_3 + BrCl \rightarrow CH_2BrCHClCH_3$$

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 C*l*, hence Br acquires a partial positive charge in BrC*l*. 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-bromopropane reacts with hot aqueous sodium hydroxide, whereas 2-bromopropene 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 $CH_2(OH)CH(OH)CH_3$.

(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]

$CH_2{=}CHCH_3 + 2H_2O \rightarrow CH_2(OH)CH(OH)CH_3 + 2H^+ + 2e^-$

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

$5CH_2{=}CHCH_3 + 2MnO_4^- + 2H_2O + 6H^+ \rightarrow 5CH_2(OH)CH(OH)CH_3 + 2Mn^{2+}$

(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 $KMnO_4(aq)$. The resulting solution was titrated against $Fe^{2+}(aq)$ 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 $Fe^{2+}(aq)$ needed to reach endpoint. [3]

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

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

No. of moles of MnO_4^- reacted with propene $= \frac{1.167\times10^{-3}}{5} \times 2$

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

No. of moles of MnO_4^- originally $= \frac{40.0}{1000} \times 0.0200$

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

No. of moles of MnO_4^- left = $8.000 \times 10^{-4} - 4.667 \times 10^{-4}$

= 3.333×10^{-4} mol

No. of moles of Fe^{2+} = $3.333 \times 10^{-4} \times 5$

= 1.667×10^{-3} mol

Volume of Fe^{2+} = $\frac{1.667\times10^{-3}}{0.0750} \times 1000$

= 22.2 cm^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 1.66×10^5 Pa. The mole fraction of propene in the mixture is 0.28.

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

[Total: 20]

Average M_r = $0.28 \times 42.0 + (1 - 0.28) \times 122.9$

= 100.2

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

$m = \frac{pVM_r}{RT}$

$= \frac{1.66\times10^{5}\times3.60\times10^{-3}\times100.2}{8.31\times(75+273)}$

= 20.7 g

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.

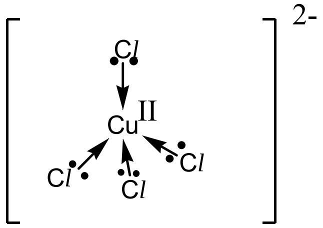
$$Cu^{2+}(aq) \xrightarrow{NH_3(aq)} \underset{\text{pale blue ppt}}{Cu(OH)_2} \xrightarrow{\text{conc } HCl} \underset{\text{yellow solution}}{\mathbf{A}} \xrightarrow{EDTA^{4-}} \underset{\text{pale blue solution}}{\mathbf{B}}$$

Fig. 2.1

(i) State the complex ion **A**. [1]

$[CuCl_4]^{2-}$

(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]

$[Cu(EDTA)]^{2-}$

(iv) Suggest why complex **B** is readily formed from complex **A**. [1]

$[Cu(EDTA)]^{2-}$ is <u>more stable</u> as compared to $[CuCl_4]^{2+}$, 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 <u>ligands approach/are attached/bonded to the copper ion</u>, they will cause the <u>incompletely/ partially-filled/3d^9</u> degenerate d-orbitals to <u>split into two slightly different energy levels</u>, d and d* <u>[OR] two groups of non-degenerate d-orbitals</u> with small energy gap.

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

The <u>complementary colours,</u> 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 $Cu(OH)_2$ is 2.20 x 10^{-20} at 25 °C. Write the expression for K_{sp} and state its units. Calculate the solubility of $Cu(OH)_2$ at 25 °C. [3]

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^{-}(aq)$

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

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

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

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

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

$x = 1.77 \times 10^{-7}$ 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.

$NH_3(aq) \rightleftharpoons NH_3(organic)$ *equilibrium 1*

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 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 mol dm^{-3} of ammonia, some of which reacted with $Cu^{2+}(aq)$ according to the following equation

$$Cu^{2+}(aq) + nNH_3 \rightarrow [Cu(NH_3)_n]^{2+}$$

The organic layer contained 0.0104 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 <u>left</u> and K_c for this reaction is relatively low.

(iv) By calculating [NH_3(aq)] present, show that the value of n in $[Cu(NH_3)_n]^{2+}$ is 4. [2]

$$0.04 = \frac{[NH_3(\text{organic})]}{[NH_3(\text{aqueous})]}$$

$$0.04 = \frac{0.0104}{[NH_3(\text{aqueous})]}$$

$$[NH_3(\text{aqueous})] = \frac{0.0104}{0.04} = 0.26 \text{ mol dm}^{-3}$$

Concentration of NH_3 which reacted with Cu^{2+}(aq) = 0.660 – 0.26
= 0.40 mol dm^{-3}

Mol ratio of Cu^{2+} : NH_3 = 0.100 : 0.400 = 1 : 4
n is 4.

(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

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

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]

$$S_2O_8^{2-} + \underset{\text{catalyst}}{2Co^{2+}} \longrightarrow 2SO_4^{2-} + 2Co^{3+}$$

$$2Co^{3+} + 2I^- \longrightarrow I_2 + \underset{\text{catalyst regenerated}}{2Co^{2+}}$$

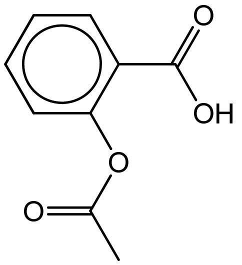
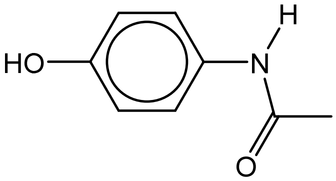
(ii) Suggest another transition metal ion, which will be able to catalyse this reaction. [1]

Fe^{2+}, Fe^{3+}, Mn^{3+}, Mn^{2+}, VO_2^+, VO^{2+}.
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01V$
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54V$
(Transition metal ion redox system requires a $E^\ominus$ of between +0.54V and +2.01V.)

[Total: 20]

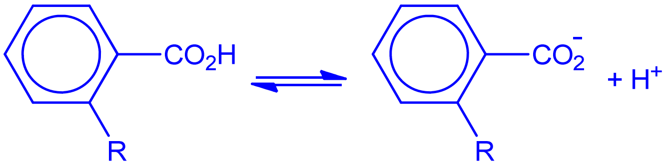
3 **(a)** Analgesics are medicines used to relieve pain. The two most common analgesics in the market are aspirin and paracetamol. Their structures and corresponding pK_a values are shown in Table 3.1.

Table 3.1

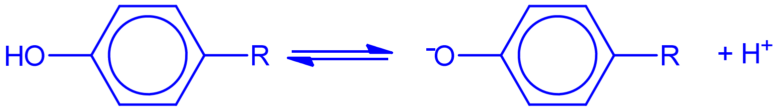
Name of analgesic	Structure	pK_a value
Aspirin		3.49
Paracetamol		10.30

(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.

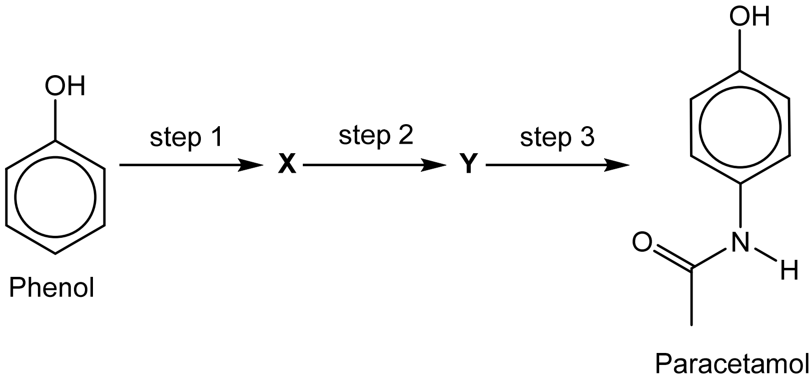
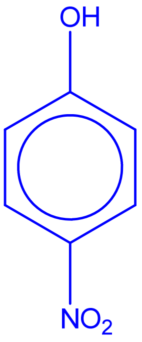
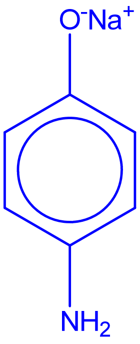


Fig. 3.1

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



X



Y

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

Step 1: dilute HNO_3

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

Step 3: CH_3COCl

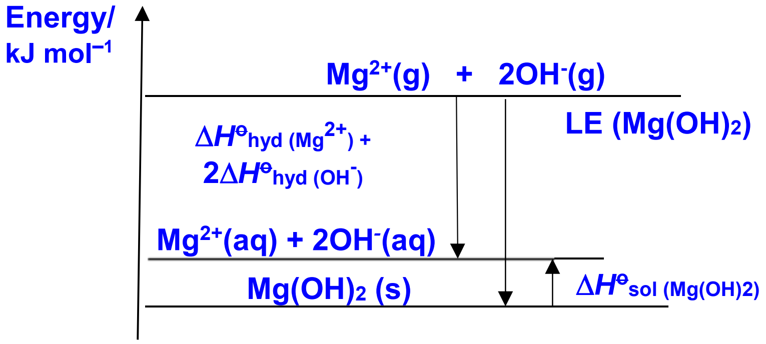
(b) The use of aspirin has been shown to increase the risk of gastrointestinal bleeding. Hence buffering agents are added to aspirin to mitigate the problem of gastrointestinal bleeding. These buffering agents work by preventing the aspirin from concentrating in the walls of the stomach. Common buffering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

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

Table 3.2

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

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

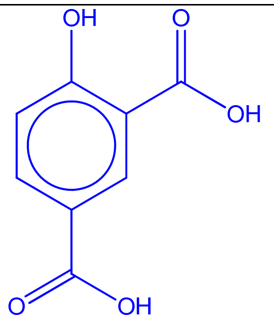


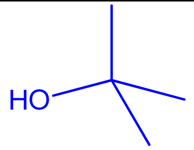
$$\Delta H_{sol} = -\text{ lattice energy } + \Sigma\Delta H_{hyd}$$
$$= -(-2998) + (-1926 - 2 \times 460)$$
$$= +152\ kJ\ mol^{-1}$$

(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.

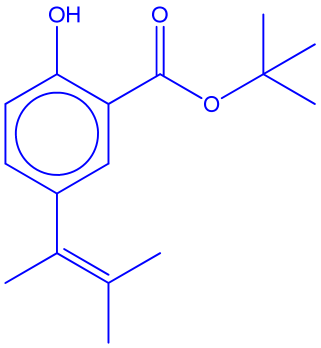
On heating with acidified $KMnO_4$, **A** gives three organic products, **C**, $C_8H_6O_5$, **D**, $C_4H_{10}O$ and propanone (CH_3COCH_3). 1 mole of **C** reacts with excess PCl_5 to produce 2 moles of HCl. Effervescence is observed when a small piece of sodium metal is added to **D**.

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

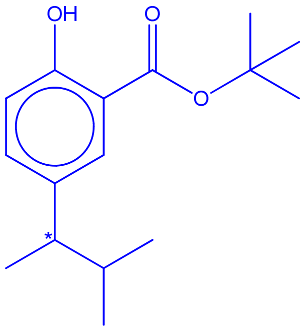
Observation/data	**Type of reaction**	**Deduction**	**Structure**
A reacts with neutral $FeCl_3$ to give violet colouration.	-	**A** is a phenol/ contains a phenolic group.	-
A reacts with H_2 in the presence of Ni to produce compound **B** ($C_{16}H_{24}O_3$).	catalytic addition/ reduction of C=C bond	**A** is likely to contain only one C=C bond since there is an addition of 2 H atoms in **B**.	-
B exhibits enantiomerism whereas **A** does not.	-	**B** contains a chiral carbon 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 carboxylic acid and an alcohol. There is side chain oxidation on the benzene ring since there is loss of 1 C atom (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 2 carboxylic acid groups and 1 phenol group.	 **C**

Effervescence is observed when a small piece of sodium metal is added to **D**.	Redox reaction	**D** is likely to be a tertiary alcohol since it is not oxidised by acidic $KMnO_4$.	 **D**

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]

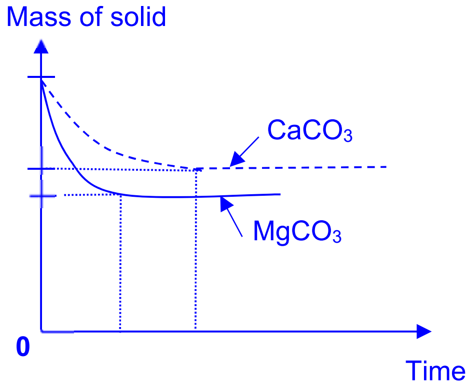
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

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

$CaCO_3$ decomposes at a higher temperature as compared to $MgCO_3$. This is because Ca^{2+} has a larger ionic radius than Mg^{2+}, and a lower charge density. Thus Ca^{2+} 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 $CaCO_3$ acts as a flame retardant. [1]

CO_2 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.

$$2\,MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

A study of the kinetics of this reaction was carried with a suitable catalyst and with $[C_2O_4^{2-}]$ at 2.00 mol dm^{-3} and data collected are shown in Table 4.1

Table 4.1

time / min	$[MnO_4^-]$ / 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 $[MnO_4^-]$, showing your working clearly including construction lines on your graph. [2]

(iii) Given that the reaction is first order with respect to $[C_2O_4^{2-}]$, 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 $[MnO_4^-]$ 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

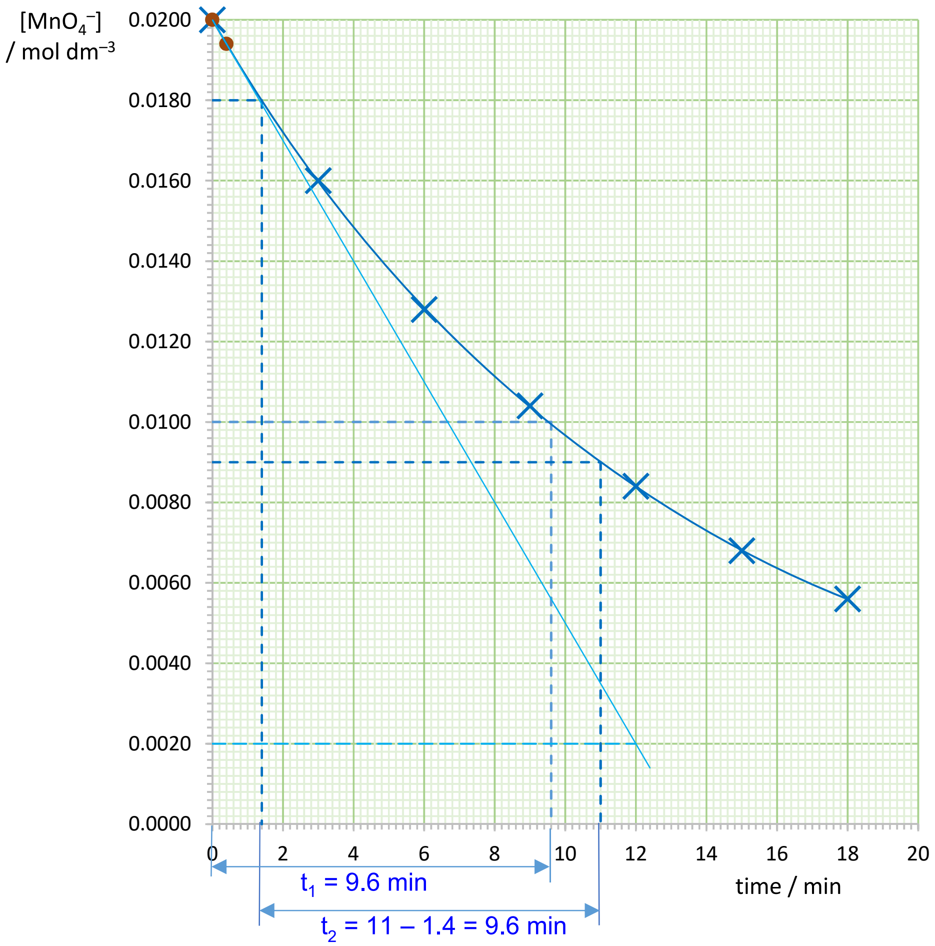
Since both half-lives are constant, the order of reaction with respect to $[MnO_4^-]$ is 1.

(iii) rate = k $[C_2O_4^{2-}]\,[MnO_4^-]$

(iv) rate = $-\dfrac{0.0200-0.0020}{0-12}$

= 0.00150 mol dm^{-3} min^{-1}

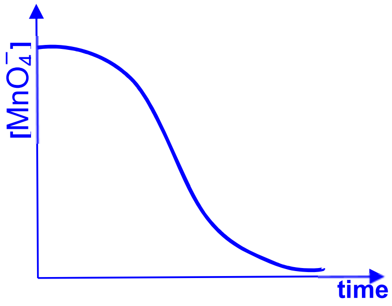
k = $\dfrac{\text{rate}}{[C_2O_4^{2-}][MnO_4^-]} = \dfrac{0.00150}{2.00\,(0.0200)}$ **= 0.0375 mol^{-1} dm^{3} min^{-1}**



t_1 = 9.6 min

t_2 = 11 – 1.4 = 9.6 min

(v)



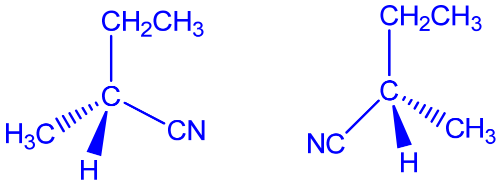
(c) Another way to study reaction mechanisms is to make deductions from the ease of obtaining the products as well as the identity of products formed.

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 (S_N1)



(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 S_N1 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]

BE (C–C*l*) = 340 kJ mol^{-1}; BE (C–Br) = 280 kJ mol^{-1}

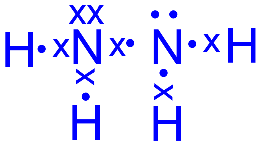
The C–C*l* bond is stronger than C–Br bond, and the breaking of this bond is involved in the slow or rate-determining step (*required if S_N1 given in (i)*), hence the reaction is slower with 2-chlorobutane

[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.

$$N_2H_4 \rightarrow 2H_2 + N_2$$

(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/ °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]

Anode: $N_2H_4 + 4OH^- \rightarrow 4H_2O + N_2 + 4e^-$

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

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

$N_2H_4 + O_2 \rightarrow 2H_2O + N_2$

(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]

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

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

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

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

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

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

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

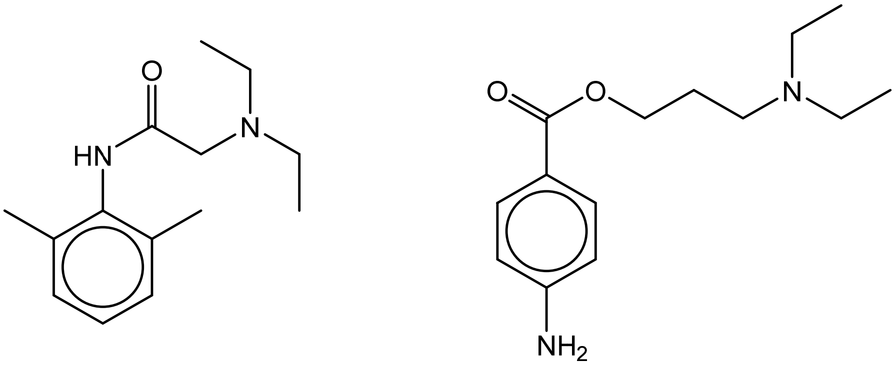
(v) State one possible advantage of using fuel cell compared to burning hydrocarbons in car engines. [1]

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.

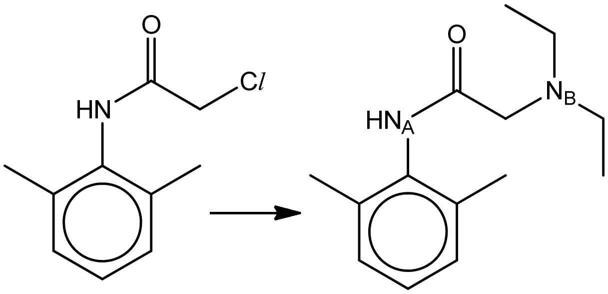
(c) Local anesthesia is used in surgeries where it is applied to numb the feelings of a specific part of a body. Lidocaine and procaine are examples of local anesthesia shown in Fig 5.1



lidocaine procaine

Fig. 5.1

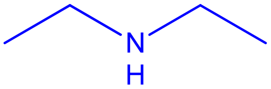
The final step of the synthesis of lidocaine is shown in Fig 5.2.



lidocaine

Fig. 5.2

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

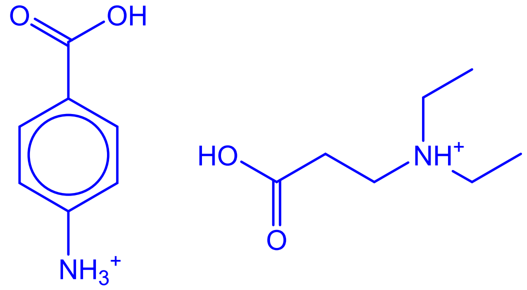


(ii) Suggest how the basicity of N_A might compare to that of N_B. Give reasons for your answers. [2]

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]

Catholic Junior College

JC 2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/04

Paper 4 Practical

Thursday 16 August 2018

2 hours 30 minutes

Candidates answer on the Question Paper

READ THESE INSTRUCTIONS FIRST

Write your class and name on all the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
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.
You may lose marks if you do not show you working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 14 and 15.

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

Shift
Laboratory

For Examiner's Use	
1	17
2	18
3	20
Total	55

This document consists of **15** printed pages and **1** blank page.

[Turn over

1 **Z** is an oxidising agent. You are required to use a solution of iodine in potassium iodide to determine the mass of **Z** needed to liberate 1 mole of iodine from potassium iodide.

FA3 is an aqueous solution of iodine, I_2, in potassium iodide, KI.
FA4 is a 0.100 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3.5H_2O$.
FA5 is an aqueous solution containing 2.00 g dm^{-3} **Z**, an oxidising agent.

You are to follow the following procedure and record your results as instructed.

Titration 1

1 By using a pipette, transfer 25.0 cm^3 of **FA3,** an aqueous solution of iodine in potassium iodide, into a conical flask.
2 Titrate the iodine present with **FA4**, 0.100 mol dm^{-3} aqueous sodium thiosulfate, from a burette until the solution becomes colourless.
3 Repeat the titration as many times as you think necessary to obtain accurate results.
4 Record your results of titration in a suitable tabulated form below.

Titration of iodine in **FA3** with **FA4**

Summary

………….. cm^3 of **FA3** required …………….. cm^3 of **FA4** for titration.

Show which results you used to obtain this value of the volume of **FA4** by placing a tick (√) under the readings used.

[5]

(a) Calculate how many moles of sodium thiosulfate were contained in the volume of **FA4** found necessary to react with 25.0 cm^3 of **FA3**.

Moles of $Na_2S_2O_3$ = …………………………..

[1]

(b) Calculate how many moles of I_2 present in 25.0 cm^3 of **FA3** using the following equation for the reaction between iodine and thiosulfate ions.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Moles of I_2 = ……………………………

[1]

Titration 2

1 By using a pipette, transfer 25.0 cm^3 of **FA3,** an aqueous solution of iodine in potassium iodide, into a conical flask and then using a second pipette, add 25.0 cm^3 of **FA5**, an aqueous solution containing 2.00 g dm^{-3} of the oxidising agent, **Z**.

2 Titrate the total iodine present with **FA4**, 0.100 mol dm^{-3} aqueous sodium thiosulfate, from a burette as before until the solution becomes colourless.

3 Repeat the titration as many times as you think necessary to obtain accurate results.

4 Record your results of titration in a suitable tabulated form below.

Titration of total iodine now in **FA3** with **FA4**

Summary

……… cm^3 of **FA3** to which 25.0 cm^3 of **FA5** had been added required …………… cm^3 of **FA4** for titration.

Show which results you used to obtain this value of the volume of **FA4** by placing a tick (√) under the readings used.

[3]

[Turn over

(c) Calculate how many moles of sodium thiosulfate were contained in the volume of **FA4** found necessary to react with the total iodine in the flask after 25.0 cm^3 of **FA3** and 25.0 cm^3 of **FA5** had been mixed.

Moles of $Na_2S_2O_3$ = …………………………..

[1]

(d) Calculate how many moles of I_2 present in the flask after 25.0 cm^3 of **FA3** and 25.0 cm^3 of **FA5** had been mixed.

Moles of I_2 = ……………………………

[1]

(e) Calculate how many moles of I_2 were liberated from potassium iodide in the flask by 25.0 cm^3 of **FA5**.

Moles of I_2 = ……………………………

[2]

(f) Calculate the mass of **Z** present in 25.0 cm^3 of **FA5**.

Mass of **Z** = ……………………………
[1]

(g) Hence, from **(e)** and **(f)**, calculate the mass of **Z** needed to liberate 1 mole of I_2.

Mass of **Z** = ……………………………
[2]

[Total: 17]

[Turn over

2 You are required to determine the basicity of an acid by carrying out some experiments with aqueous sodium hydroxide.

FA1 is a 1.00 mol dm^{-3} aqueous sodium hydroxide, NaOH.
FA2 is a 1.00 mol dm^{-3} aqueous acid which is either monobasic with the formula **HA**, or dibasic with the formula **H_2A**.

By using the results of the following experiments, you are to going to determine the basicity of **FA2**.

You are to follow the following procedure and record your results as instructed.

Experiment 1

1 By using a measuring cylinder, pour 25 cm^3 of **FA1** into the Styrofoam cup provided and record the steady temperature. Rinse the thermometer with deionised water.
2 Use another 50 cm^3 measuring cylinder to measure 25 cm^3 of **FA2** and record its temperature.
3 Carefully add **FA2** to **FA1**, stir with the thermometer and record the highest temperature reached.
4 Record your results in the table provided below.

	Experiment 1	**Experiment 2**	**Experiment 3**
Initial temperature of **FA1** /˚C			
Initial temperature of **FA2** /˚C			
Highest temperature /˚C			
Mean initial temperature /˚C			
Temperature rise, ΔT /˚C			

Experiment 2
Thoroughly rinse out the Styrofoam cup with deionised water and repeat the experiment using 25 cm^3 of **FA1** and 50 cm^3 of **FA2**. Record your results in the table above.

Experiment 3
Thoroughly rinse out the Styrofoam cup with deionised water and repeat the experiment using 50 cm^3 of **FA1** and 25 cm^3 of **FA2**. Record your results in the table above.

(a) Complete the table of results by calculating the mean initial temperature of **FA1** and **FA2** for each of the three experiments. When calculating mean initial temperatures for **Experiments 2** and **3**, ignore the fact that the volumes mixed are unequal.

Fill in the corresponding rises in temperatures, ΔT in the table provided above.

[5]

(b) Use your results to deduce the basicity of the acid.

[2]

(c) Write a full equation for the reaction between **FA1** and **FA2**. Do not omit spectator ions.

…………………………………………………………………………………………………

[1]

(d) Calculate the amount of heat evolved in **Experiment 1**.
Assume 4.3 J are required to raise the temperature of 1 cm^3 of solution by 1.0 °C.

Heat evolved = ……………………………

[1]

(e) Using your answers to **(c)** and **(d)**, calculate the enthalpy of neutralisation, ΔH_n, per mole of water formed.

ΔH_n = …………………………………..

[1]

[Turn over

Assessment of Planning Skills

You are provided with 150 cm^3 of each of three solutions, **FA6**, **FA7** and **FA8**. You are to identify which of these solutions correspond to the following solutions:

1 mol dm^{-3} sodium hydroxide, NaOH
2 mol dm^{-3} hydrochloric acid, HCl
1 mol dm^{-3} hydrochloric acid, HCl

You are also provided with the following apparatus:

A thermometer
A plastic cup
2 measuring cylinders

You are to plan a simple experiment which will allow an identification of the three solutions to be made, using only the apparatus and materials listed above and deionised water. (Note that you are **not** provided with any pH indicator).

You are **not** required to carry out the plan but you have to present your results in an appropriate manner based on your plan so that the identification can be made.

PLAN

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[5]

RESULTS

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[3]

[Total: 18]

[Turn over

3 You are to determine the identity of **FA9**.

Carry out the following experiments on the solid **FA9** which contains the **sodium cation** and **one anion** from the following list: CO_3^{2-}, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, SO_4^{2-} and SO_3^{2-}.

In all tests, reagents should be added gradually until no further change is observed, with shaking after each addition.

Record your observations you make from them in the spaces provided.

Your answer should include
(i) details of colour change and precipitate formed, if any;
(ii) the identity of gases evolved, if any, and details of the test used to identify the gas.

You should indicate clearly at what stage in a test a change occurs.

No additional or confirmatory tests for ions present should be attempted.

Test	Observation
(a) Place one third of the solid **FA9** in a test-tube and heat strongly until the solid melts and a gas is given off. Identify the gas evolved. Continue the strong heating for 2–3 minutes then leave the tube to cool and retain the residue for test (d). (Melt a second sample of **FA9** and heat for 2–3 minutes. Leave this to cool and retain for test (h).	
(b) Using a dropper, place 1 cm depth of aqueous of sodium hydroxide into a test-tube and tip into it the remaining solid **FA9**. Warm gently and retain for test (c).	
(c) Cool the test-tube and solution from (b). Add a half spatula full of aluminium powder and warm gently.	

Test	Observation
(d) Dissolve the residue from (a) in deionised water about 3 cm depth and divide the solution into three parts. Use these tests for (e) to (g).	
(e) To one part of the solution from (d), add aqueous potassium iodide followed dilute sulfuric acid.	
(f) To the second part of the solution from (d), add aqueous potassium manganate(VII) followed by dilute sulfuric acid.	
(g) To the third part of the solution from (d), add aqueous sodium hydroxide and a half spatula full of aluminium powder. Warm gently.	
(h) Take the second sample of solid, heated **FA9** that you prepared in (a). Add to dilute sulfuric acid and warm gently.	

[9]

What anion is present in **FA9** before it is heated? …………………………………………

What anion is present in **FA9** after it is heated? …………………………………………...

In test (e), the anion is behaving as …………………………………………………………

In test (f), the anion is behaving as …………………………………………………………

[4]

Hence, write a balanced chemical equation for the thermal decomposition of **FA9**.

……………………………………………………………………………………………………

[1]

[Turn over

Assessment of Planning Skills

Each of the solutions **FA10**, **FA11** and **FA12** contains one of the cations Al^{3+}, Mg^{2+} and Zn^{2+} ions but not in that order.

You are provided with a set of test-tubes and the following reagents:

Aqueous ammonia, NH_3
Dilute hydrochloric acid, HCl
Aqueous sodium carbonate, Na_2CO_3
Aqueous sodium hydroxide, NaOH

You are required to devise and perform an experiment which will enable you to identify the cation present in each of the solutions **FA10**, **FA11** and **FA12**. You may only use any of the reagents provided above and **no** other reagent. **You should aim to use the minimum number of reactions**, where possible.

This space below is for you to plan your steps which should then be recorded, together with the observations you make in the table in the next page.

PLAN

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[2]

In the table below, record all of your observations, and the identity of a cation as soon as this is established.

Reagent added	Observations and identities of cations		
	FA10	**FA11**	**FA12**

[3]

Deduction

Solution **FA10** contains the cation …………………………………………………………………

Solution **FA11** contains the cation …………………………………………………………………..

Solution **FA12** contains the cation …………………………………………………………………..

[1]

[Total: 20]

[Turn over

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

[Turn over

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Catholic Junior College

JC 2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/04

Paper 4 Practical

Thursday 16 August 2018

2 hours 30 minutes

Candidates answer on the Question Paper

WORKED SOLUTIONS

This document consists of **14** printed pages.

[Turn over

1 **Z** is an oxidising agent. You are required to use a solution of iodine in potassium iodide to determine the mass of **Z** needed to liberate 1 mole of iodine from potassium iodide.

FA3 is an aqueous solution of iodine, I_2, in potassium iodide, KI.
FA4 is a 0.100 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3.5H_2O$.
FA5 is an aqueous solution containing 2.00 g dm^{-3} **Z**, an oxidising agent.

You are to follow the following procedure and record your results as instructed.

Titration 1

1 By using a pipette, transfer 25.0 cm^3 of **FA3,** an aqueous solution of iodine in potassium iodide, into a conical flask.
2 Titrate the iodine present with **FA4**, 0.100 mol dm^{-3} aqueous sodium thiosulfate, from a burette until the solution becomes colourless.
3 Repeat the titration as many times as you think necessary to obtain accurate results.
4 Record your results of titration in a suitable tabulated form below.

Titration of iodine in **FA3** with **FA4**

	Rough	Accurate		
Final burette reading /cm^3	**19.90**	**39.60**	**19.70**	
Initial burette reading /cm^3	**0.00**	**19.90**	**0.00**	
Volume of **FA4** used /cm^3	**19.90**	**19.70**	**19.70**	
		√	√	

Summary

25.0 cm^3 of **FA3** required **19.70** cm^3 of **FA4** for titration.

Show which results you used to obtain this value of the volume of **FA4** by placing a tick (√) under the readings used.

[5]

At least 2 sets of burette readings taken.
Burette readings recorded to 2 d.p.
Precision of V_{FA4} ± 0.10 cm^3 and correct average of V_{FA4} taken.

(a) Calculate how many moles of sodium thiosulfate were contained in the volume of **FA4** found necessary to react with 25.0 cm^3 of **FA3**.

Amount of $Na_2S_2O_3$ = $(\frac{19.70}{1000} \times 0.100)$ mol
= 1.97×10^{-3} mol
Moles of $Na_2S_2O_3$ = 1.97×10^{-3}

[1]

(b) Calculate how many moles of I_2 present in 25.0 cm^3 of **FA3** using the following equation for the reaction between iodine and thiosulfate ions.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Amount of I_2 = $(\frac{1}{2} \times 1.97 \times 10^{-3})$ mol
= 9.85×10^{-4} mol

Moles of I_2 = 1.97×10^{-3}

[1]

Titration 2

1 By using a pipette, transfer 25.0 cm^3 of **FA3,** an aqueous solution of iodine in potassium iodide, into a conical flask and then using a second pipette, add 25.0 cm^3 of **FA5**, an aqueous solution containing 2.00 g dm^{-3} of the oxidising agent, **Z**.

2 Titrate the total iodine present with **FA4**, 0.100 mol dm^{-3} aqueous sodium thiosulfate, from a burette as before until the solution becomes colourless.

3 Repeat the titration as many times as you think necessary to obtain accurate results.

4 Record your results of titration in a suitable tabulated form below.

Titration of total iodine now in **FA3** with **FA4**

	Rough	Accurate		
Final burette reading /cm^3	**29.70**	**29.50**	**29.50**	
Initial burette reading /cm^3	**0.00**	**0.00**	**0.00**	
Volume of **FA4** used /cm^3	**29.70**	**29.50**	**29.50**	
		√	√	

Summary

25.0 cm^3 of **FA3** to which 25.0 cm^3 of **FA5** had been added required **29.50** cm^3 of **FA4** for titration.

Show which results you used to obtain this value of the volume of **FA4** by placing a tick (√) under the readings used.

[3]

Precision of V_{FA4} ± 0.10 cm^3 and correct average of V_{FA4} taken.
Accuracy of titration results.

(c) Calculate how many moles of sodium thiosulfate were contained in the volume of **FA4** found necessary to react with the total iodine in the flask after 25.0 cm^3 of **FA3** and 25.0 cm^3 of **FA5** had been mixed.

Amount of $Na_2S_2O_3$ = $(\frac{29.50}{1000} \times 0.100)$ mol
= 2.95×10^{-3} mol

Moles of $Na_2S_2O_3$ = 2.95×10^{-3}

[1]

(d) Calculate how many moles of I_2 present in the flask after 25.0 cm^3 of **FA3** and 25.0 cm^3 of **FA5** had been mixed.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq$$

Amount of I_2 = $(\frac{1}{2} \times 2.95 \times 10^{-3})$ mol
= 1.475×10^{-3} mol

Moles of I_2 = 1.475×10^{-3}

[1]

(e) Calculate how many moles of I_2 were liberated from potassium iodide in the flask by 25.0 cm^3 of **FA5**.

[Turn over

Amount of I_2 liberated = $(1.475 \times 10^{-3} - 9.85 \times 10^{-4})$ mol
= 4.90×10^{-4} mol

Moles of I_2 = 4.90×10^{-3}
[2]

(f) Calculate the mass of **Z** present in 25.0 cm^3 of **FA5**.

Mass of Z = $(\frac{25.0}{1000} \times 2.00)$ g
= 0.0500 g

Mass of Z = 0.0500 g
[1]

(g) Hence, from **(e)** and **(f)**, calculate the mass of **Z** needed to liberate 1 mole of I_2.

Mass of Z needed to liberate 1 mol of I_2 = $(\frac{0.0500}{4.90 \times 10^{-4}})$ g
= 102 g

Mass of Z = 102 g
[2]

[Total: 17]

2 You are required to determine the basicity of an acid by carrying out some experiments with aqueous sodium hydroxide.

FA1 is a 1.00 mol dm^{-3} aqueous sodium hydroxide, NaOH.
FA2 is a 1.00 mol dm^{-3} aqueous acid which is either monobasic with the formula **HA**, or dibasic with the formula **H_2A**.

By using the results of the following experiments, you are to going to determine the basicity of **FA2**.

You are to follow the following procedure and record your results as instructed.

Experiment 1

1. By using a measuring cylinder, pour 25 cm^3 of **FA1** into the Styrofoam cup provided and record the steady temperature. Rinse the thermometer with deionised water.
2. Use another 50 cm^3 measuring cylinder to measure 25 cm^3 of **FA2** and record its temperature.
3. Carefully add **FA2** to **FA1**, stir with the thermometer and record the highest temperature reached.
4. Record your results in the table provided below.

	Experiment 1	**Experiment 2**	**Experiment 3**
Initial temperature of **FA1** /°C	**31.0**	**31.0**	**31.0**
Initial temperature of **FA2** /°C	**31.0**	**31.0**	**31.0**
Highest temperature /°C	**37.9**	**35.6**	**40.1**
Mean initial temperature /°C	**31.0**	**31.0**	**31.0**
Temperature rise, ΔT /°C	**6.9**	**4.6**	**9.1**

Experiment 2
Thoroughly rinse out the Styrofoam cup with deionised water and repeat the experiment using 25 cm^3 of **FA1** and 50 cm^3 of **FA2**. Record your results in the table above.

Experiment 3
Thoroughly rinse out the Styrofoam cup with deionised water and repeat the experiment using 50 cm^3 of **FA1** and 25 cm^3 of **FA2**. Record your results in the table above.

(a) Complete the table of results by calculating the mean initial temperature of **FA1** and **FA2** for each of the three experiments. When calculating mean initial temperatures for **Experiments 2** and **3**, ignore the fact that the volumes mixed are unequal.

Fill in the corresponding rises in temperatures, ΔT in the table provided above.

[5]

Initial temperatures of FA1, FA2 & highest temperatures taken and recorded to 1 decimal place.
Correct mean initial temperatures recorded.
Correct ΔT recorded.

[Turn over

(b) Use your results to deduce the basicity of the acid.

From Expts 2 and 3 (Total volume of the reaction mixture is the same, 75 cm^3).

Expt 2: $NaOH(aq) + HA(aq) \longrightarrow NaA(aq) + H_2O(l)$
0.0250 0.0250 **0.0250 mol**

$2NaOH(aq) + H_2A(aq) \longrightarrow Na_2A(aq) + 2H_2O(l)$
0.0250 0.0125 **0.0250 mol**

Expt 3: $NaOH(aq) + HA(aq) \longrightarrow NaA(aq) + H_2O(l)$
0.0250 0.0250 **0.0250 mol**

$2NaOH(aq) + H_2A(aq) \longrightarrow Na_2A(aq) + 2H_2O(l)$
0.0500 0.0250 **0.0500 mol**

Since the rise in temperature, ΔT, is greater in Expt 3 as compared to that of Expt 2 (almost twice), FA2 is a dibasic acid, H_2A.

If the acid is monobasic, then the rise in temperature, ΔT, in Expts 2 and 3 should be the same.

[2]

(c) Write a full equation for the reaction between **FA1** and **FA2**. Do not omit spectator ions.

$2NaOH(aq) + H_2A(aq) \longrightarrow Na_2A(aq) + 2H_2O(l)$ **state symbols not required**

[1]

(d) Calculate the amount of heat evolved in **Experiment 1**.
Assume 4.3 J are required to raise the temperature of 1 cm^3 of solution by 1.0 °C.

Heat evolved = (50 x 4.3 x 6.9) J
= 1483.5 J

Heat evolved = 1483.5 J

[1]

(e) Using your answers to **(c)** and **(d)**, calculate the enthalpy of neutralisation, ΔH_n, per mole of water formed.

$2NaOH(aq) + H_2A(aq) \longrightarrow Na_2A(aq) + 2H_2O(l)$
0.0250 0.0125 0.0250 mol

$$\Delta H_n = -\left(\frac{1483.5}{0.0250}\right) \text{ J mol}^{-1}$$

$$= -59.3 \text{ kJ mol}^{-1}$$

$\Delta H_n = -59.3 \text{ kJ mol}^{-1}$

[1]

Assessment of Planning Skills

You are provided with 150 cm^3 of each of three solutions, **FA6**, **FA7** and **FA8**. You are to identify which of these solutions correspond to the following solutions:

1 mol dm^{-3} sodium hydroxide, NaOH
2 mol dm^{-3} hydrochloric acid, HC*l*
1 mol dm^{-3} hydrochloric acid, HC*l*

You are also provided with the following apparatus:

A thermometer
A Styrofoam cup
2 measuring cylinders

You are to plan a simple experiment which will allow an identification of the three solutions to be made, using only the apparatus and materials listed above and deionised water. (Note that you are **not** provided with any pH indicator).

You are **not** required to carry out the plan but you have to present your results in an appropriate manner based on your plan so that the identification can be made.

PLAN

1 **Using a measuring cylinder, pour 30 cm^3 of FA6 into the Styrofoam cup provided and record its temperature using the thermometer. Rinse the thermometer with deionised water.**

2 **Using another measuring cylinder to measure 30 cm^3 of FA7 and add it to FA6 in the Styrofoam cup. Stir, using the thermometer and record the highest temperature rise.**
3 **Thoroughly rinse out the Styrofoam cup with deionised water and repeat the Expt using 30 cm^3 of FA6 and 30 cm^3 of FA8.**
4 **Thoroughly rinse out the Styrofoam cup with deionised water and repeat the Expt using 30 cm^3 of FA7 and 30 cm^3 of FA8.**
(Refer to table 1 in results. The base, NaOH can be identified.)

5 **Thoroughly rinse out the Styrofoam cup with deionised water and repeat the Expt using 30 cm^3 of FA6 and 15 cm^3 of FA7.**

6 **Thoroughly rinse out the Styrofoam cup with deionised water and repeat the Expt using 30 cm^3 of FA6 and 15 cm^3 of FA8.**
(Refer to table 2 in results. The acid, HC*l* of higher concentration can be identified.)

(Note: Specific volumes must be mentioned and the permutations of the respective solutions must be evident enough to allow identification possible. However, the total volume used for each of the three solutions used cannot exceed 150 cm^3 given.)

[5]

[Turn over

RESULTS

Table 1

V_{FA6} /cm^3	30	30	-
V_{FA7} /cm^3	30	-	30
V_{FA8} /cm^3	-	30	30
ΔT /°C	T1	T1	No change

FA7 + FA8, no change in temperature, so they do not react with each other. So, FA7 and FA8 are both acids.

Therefore, FA6 is NaOH.

Table 2

V_{FA6} /cm^3 (base)	30	30
V_{FA7} /cm^3	15	-
V_{FA8} /cm^3	-	15
ΔT /°C	T1	T2

Assume that T1 > T2.

Since the rise in temperature is higher for reaction between FA7 and the base, therefore FA7 is HC*l* of higher concentration (2 mol dm^{-3}).

$$\underset{0.0300}{\overset{\text{FA6}}{NaOH(aq)}} + \underset{0.0300}{\overset{\text{FA7}}{HCl(aq)}} \longrightarrow NaCl(aq) + \underset{0.0300\text{ mol}}{H_2O(l)}$$

$$\underset{0.0150}{\overset{\text{FA6}}{NaOH(aq)}} + \underset{0.0150}{\overset{\text{FA8}}{HCl(aq)}} \longrightarrow NaCl(aq) + \underset{0.0150\text{ mol}}{H_2O(l)}$$

[3]

[Total: 18]

3 You are to determine the identity of **FA9**.

Carry out the following experiments on the solid **FA9** which contains the **sodium cation** and **one anion** from the following list: CO_3^{2-}, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, SO_4^{2-} and SO_3^{2-}.

In all tests, reagents should be added gradually until no further change is observed, with shaking after each addition.

Record your observations you make from them in the spaces provided.

Your answer should include
(i) details of colour change and precipitated formed, if any;
(ii) the identity of gases evolved, if any, and details of the test used to identify the gas.

You should indicate clearly at what stage in a test a change occurs.

No additional or confirmatory tests for ions present should be attempted.

Test	**Observation** [9]
(a) Place one third of the solid **FA9** in a test-tube and heat strongly until the solid melts and a gas is given off.	**FA9 melts to give a yellow liquid which then resolidifies to a give a white solid. Effervescence observed.**
Identify the gas evolved.	**Gas evolved rekindles/relights a glowing splint. O_2 liberated.**
Continue the strong heating for 2-3 minutes then leave the tube to cool and retain the residue for test (d).	**White residue.**
Melt a second sample of **FA9** and heat for 2-3 minutes. Leave this to cool and retain for test (h).	
(b) Using a dropper, place 1 cm depth of aqueous of sodium hydroxide into a test-tube and tip into it the remaining solid **FA9**.	**FA9 dissolves / no ppt.**
Warm gently and retain for test (c).	**Damp red litmus, no change. No NH_3 gas liberated.**
(c) Cool the test-tube and solution from (b).	
Add a half spatula full of aluminium powder and warm gently.	**Gas liberated turns damp red litmus blue. NH_3 gas evolved.**

[Turn over

Test	Observation
(d) Dissolve the residue from (a) in deionised water about 3 cm depth and divide the solution into three parts. Use these tests for (e) to (g).	[redacted]
(e) To one part of the solution from (d), add aqueous potassium iodide followed dilute sulfuric acid.	**Brown solution / iodine liberated.**
(f) To the second part of the solution from (d), add aqueous potassium manganate(VII) followed by dilute sulfuric acid.	**Purple acidified $KMnO_4$ is decolourised.**
(g) To the third part of the solution from (d), add aqueous sodium hydroxide and a half spatula full of aluminium powder. Warm gently.	**Gas liberated turns damp red litmus blue.** **NH_3 gas evolved.**
(h) Take the second sample of solid, heated **FA9** that you prepared in (a). Add to dilute sulfuric acid and warm gently.	**Brown fumes liberated.**

[9]

What anion is present in **FA9** before it is heated? **NO_3^-**

What anion is present in **FA9** after it is heated? **NO_2^-**

In test (e), the anion is behaving as **an oxidising agent**.

In test (f), the anion is behaving as **a reducing agent**.

[4]

Hence, write a balanced chemical equation for the thermal decomposition of **FA9**.

$$NaNO_3(s) \longrightarrow NaNO_2(s) + \tfrac{1}{2} O_2(g)$$

[1]

Assessment of Planning Skills

Each of the solutions **FA10**, **FA11** and **FA12** contains one of the cations Al^{3+}, Mg^{2+} and Zn^{2+} ions but not in that order.

You are provided with a set of test-tubes and the following reagents:

Aqueous ammonia, NH_3
Dilute hydrochloric acid, HCl
Aqueous sodium carbonate, Na_2CO_3
Aqueous sodium hydroxide, NaOH

You are required to devise and perform an experiment which will enable you to identify the cation present in each of the solutions **FA10**, **FA11** and **FA12**. You may only use any of the reagents provided above and **no** other reagent. **You should aim to use the minimum number of reactions**, where possible.

This space below is for you to plan your steps which should then be recorded, together with the observations you make in the table in the next page.

PLAN

1 **Add aqueous ammonia, NH_3 till excess to separate samples of the 3 solutions. If a white ppt is obtained and dissolves in excess NH_3, suggests the presence of Zn^{2+}.**

2 **Add aqueous sodium hydroxide, NaOH till excess to separate samples of the remaining 2 solutions.**

If a white ppt is obtained and dissolves in excess NaOH, suggests the presence of Al^{3+}, if insoluble in excess NaOH, Mg^{2+}.

[2]

In the table below, record all of your observations, and the identity of a cation as soon as this is established.

Reagent added	Observations and identities of cations		
	FA10	**FA11**	**FA12**
NH_3(aq)	**White ppt soluble in excess.** **Zn^{2+}**	**-**	**-**
NaOH(aq)	**-**	**White ppt soluble in excess.** **Al^{3+}**	**White ppt insoluble in excess.** **Mg^{2+}**

[3]

[Turn over

Deduction

Solution **FA10** contains the cation $\mathbf{Zn^{2+}}$

Solution **FA11** contains the cation $\mathbf{Al^{3+}}$

Solution **FA12** contains the cation $\mathbf{Mg^{2+}}$

[1]

[Total: 20]

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

[Turn over

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple