UACE chemistry 2022

PAPER 2

DURATION: 2 HOUR 30 MINUTES

Instruction to candidates

*Answer **five** questions including **three** questions from section **A** and any **two** from section **B**.*

Use equations where necessary to illustrate your answer.

Mathematical tables and squared papers are provided

Silent non-programmable scientific calculators may be used

Where necessary use the following:

(H =1, C = 12, O = 16)

SECTION A (60MARKS)

Answer any three questions from this section

Any additional question answered will **not** be marked.

1. (a) State what is meant by the term order of reaction. (01mark)

   (b) The decomposition of hydrogen peroxide proceeds according to the following equation

   2H2O2 (aq) → $2H_2O(l) + O_2(g)$

   (i) Write the expression for the rate law of the reaction. (1 ½ marks)

   (ii) Describe how the order of the reaction can be determined. (05marks)

   (iii) Explain the effect of temperature on the rate of decomposition of hydrogen peroxide. (3 ½ Marks)

   (c) The following kinetic data in table 1 were obtained for the decomposition of hydrogen peroxide.

   Table 1

Concentration of H_2O_2 ($moldm^{-3}$)	1.6×10^{-3}	1.3×10^{-3}	7.6×10^{-4}	3.6×10^{-4}	1.4×10^{-4}	1.0×10^{-4}
Time (minutes)	0	5	12	20	33	40

   Pot a graph of concentration of hydrogen peroxide against time (04marks)

   (d) Using your graph determine the time required for;

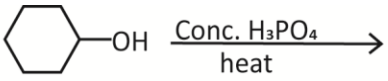
   (i) 1.0×10^{-3} moles of hydrogen peroxide to reduce to 5.0×10^{-4} moles (01mark)

   (ii) 6.0×10^{-4} moles of hydrogen peroxide to reduce to 3.0×10^{-4}moles (01mark)

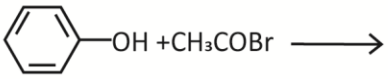
   (e) (i) What conclusion can be drawn from your answers in (d)(i) and (ii)? (1 ½ marks)

   (ii) Determine the rate constant for the reaction. (1 ½ marks)

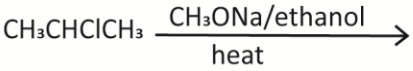
2. Complete the following equations and in each case, write mechanisms for the reactions:

   (a) 

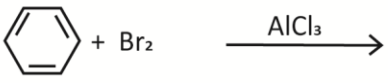
   (04marks)

   (b) 

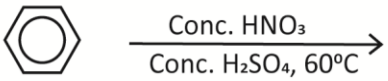
   (4½marks)

   (e) 

   (03marks)

   (d) 

   (3½marks)

   (e) 

   (05marks)

3. (a) Although the elements: fluorine, chlorine, bromine and iodine belong to group (VII) of the Periodic Table, fluorine behaves differently from the rest of the group members. State;
   (i) two reasons why fluorine differs from the other elements of group (VII). (01mark)
   (ii) any two reactions in which fluorine differs from the other elements of group (VII) and write equations to illustrate your answers. (06marks)

   (b) The atomic numbers of group (VII) elements and the boiling points of their hydrides are shown in table 2

   Table 2

Element	F	Cl	Br	I
Atomic number	9	17	35	53
Formula of the hydride	HF	HCl	HBr	HI
Boiling point of hydride (^{0}C)	+19.9	-85.0	-66.7	-35.4

   (i) Plot a graph of boiling points of the hydrides against atomic numbers of the elements. (04marks)
   (ii) Explain the shape of your graph. (4 1/2marks)

   (c) State what would be observed and write an equation for the reaction that would take place if;

   (i) sodium thiosulphate solution was added to iodine solution. (2 ½ marks)

   (ii) chlorine gas was bubbled through a solution of potassium bromide. (2marks)

4. (a)(i) State the difference between molar conductivity and electrolytic conductivity of solution. (01mark)
   (ii) A conductivity cell filled with 0.1M aqueous potassium chloride gave a resistance of 484Ω at 25^{0}C. Calculate its cell constant.
   (The molar conductivity of the solution at 25^{0}C = 129$\Omega^{-1}cm^2mol^{-1}$)(3 ½ marks)
   (b) The electrolytic conductivity of a saturated solution of silver chloride at 25^{0}C is $3.41 \times 10^{-6}\Omega^{-1}cm^{-1}$.
   Calculate the;
   (i) Molar conductivity of silver chloride at infinite dilution (1½ marks)
   (The molar conductivities at infinite dilution of silver nitrate, potassium nitrate and potassium chloride are 133.4, 145.0 and 149.9 $\Omega^{-1}cm^2mol^{-1}$ respectively)
   (ii) Solubility of silver chloride and hence its solubility product. (7 ½ mark)
   (The electric conductivity of water at 25^{0}C = $1.60 \times 10^{-6}\Omega^{-1}cm^{-1}$)

   (c) Explain the effect of each of the following factors on the molar conductivity of an electrolyte:

   (i) ionic radius (2 ½ marks)

   (ii) concentration (04 marks)

SECTION B (40MARKS)

Answer any two questions from this section

Any additional question(s) answered will not be marked

5. (a) The melting points and atomic numbers of some elements of group (IV) of the Periodic Table are shown in table 3.

Table 3

Element	Carbon	Silicon	Germanium	Tin	Lead
Atomic number	6	14	32	50	82
Melting point (^{0}C)	3750	1420	950	232	327

(a)(i) Explain the trend in the melting points of the elements (05marks)

(ii) Describe the reaction of the elements with sulphuric acid. (07marks)

(b) Group (IV) elements form tetrachlorides.

(i) Write equations for the reactions leading to formation of the tetrachlorides of carbon, silicon and lead. (4½ marks)

(ii) State what is observed when the tetrachlorides of carbon, silicon and lead are reacted with water. Explain your observations. (3½ marks)

6. (a) State what meant by the following terms:

(i) Electron affinity (01 marks)

(ii) First ionization energy (01 marks)

(iii) Enthalpy of solution (01 marks)

(b) The first ionization energy of an element is always less than the second ionization energy. Explain. (02 marks)

(c) Describe an experiment to determine the enthalpy of neutralization of hydrochloric acid by sodium hydroxide (05marks)

(d) Some thermo-chemical data about calcium and oxygen are shown below

Process	Energy ($kJmol^{-1}$)
Enthalpy of formation of calcium oxide	= -636.0
Enthalpy of sublimation of calcium	= +177.0
First ionization energy of calcium	= +590.0
Second ionization energy of calcium	= +1100.0
Bond dissociation energy of oxygen	= +498.0
First electron affinity of oxygen	= -141.4
Second electron affinity of oxygen	= +790.8

(i) Draw an energy level diagram for the formation of calcium oxide (04marks)
(ii) Calculate the lattice energy of calcium oxide (02marks)
(iii) Comment on the stability of calcium oxide. (01 mark)

(e) The hydration and lattice energies for the chlorides of lithium and sodium are shown in the table 4

Table 4

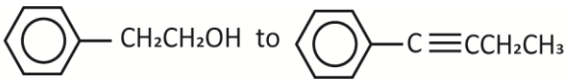
Compound	Lattice energy ($kJmol^{-1}$)	Hydration energy ($kJmol^{-1}$)
LiCl	843	883
NaCl	778	775

(i) Calculate the enthalpies of solution for lithium chloride and sodium chloride. (1 ½ marks)
(ii) Which one of the chlorides in (e)(i) is likely to dissolve more on heating? Explain your answer (1 ½ marks)

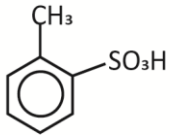
7. Write equations to show how the following conversions can be effected; indicate reagents and conditions for the reaction in each case.

(a) $CH_3\overset{\overset{O}{\|}}{C}CH_3$ to $CH_3CH_2CH_2OH$ (5½ marks)

(b) CH_3CH_2I to CH_3CH_2COOH (2½ marks)

(c)  (5½ marks)

(d) $CH_3\overset{\overset{Br}{|}}{C}HCH_2CH_3$ to $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$ (2½ marks)

(e) $HC \equiv CH$ to  (04 marks)

8. Explain each of the following observations and illustrate your answer with equations where necessary

(a) The reactivity of alcohols with hydrogen halides is in order;
tertiary > secondary > primary alcohols. (2 ½ marks)
(b) Alcohols are neutral organic compounds whereas phenol is weakly acidic, and yet both have hydroxyl groups. (04marks)

(c) Magnesium ions form precipitate with dilute ammonia solution, but no precipitates is formed if ammonium chloride is added to magnesium ions prior to ammonia solution (06 marks)

(d) Water boils at 100^0C whereas hydrogen fluoride boils at 19.5^0C although both compounds exhibit hydrogen bonding. (04marks)

(e) The nitronium ion, NO_2^+ has a linear shape whereas the nitrite ion, NO_2^- is V-shaped. (3½ marks)

END

Proposed answers

1. (a) State what is meant by the term order of reaction. (01mark)

Order of reaction is the sum of exponents to the concentration terms in a rate law.

(b) The decomposition of hydrogen peroxide proceeds according to the following equation

$2H_2O_2$ (aq) → $2H_2O$(l)+ O_2(g)

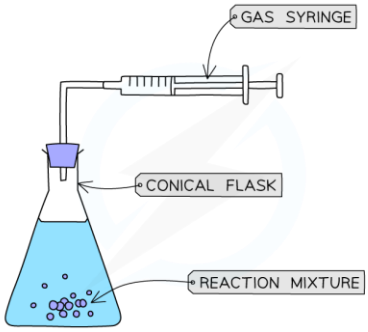
(i) Write the expression for the rate law of the reaction. (1 ½ marks)

Rate = $k[H_2O_2]^x$

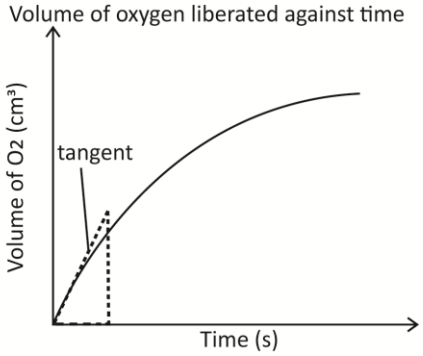
(ii) Describe how the order of the reaction can be determined. (05marks)

Measure the volume of oxygen gas released over time as the hydrogen peroxide solution decomposes at room temperature.

Set up



- Carry out two experiment using equal volumes but varying concentration of hydrogen peroxide to which add equal mass of manganese dioxide and start the clock.
- Measure the volume of oxygen liberated at specified intervals of time.
- Plot graphs of volume oxygen liberated against time.



- Find initial rates from the gradients of the tangent of graphs at zero concentration.
- Using the initial rates obtained calculate the order of the reaction x from the equation Rate = $k[H_2O_2]^x$.

(iii) Explain the effect of temperature on the rate of decomposition of hydrogen peroxide. (3 ½ Marks)

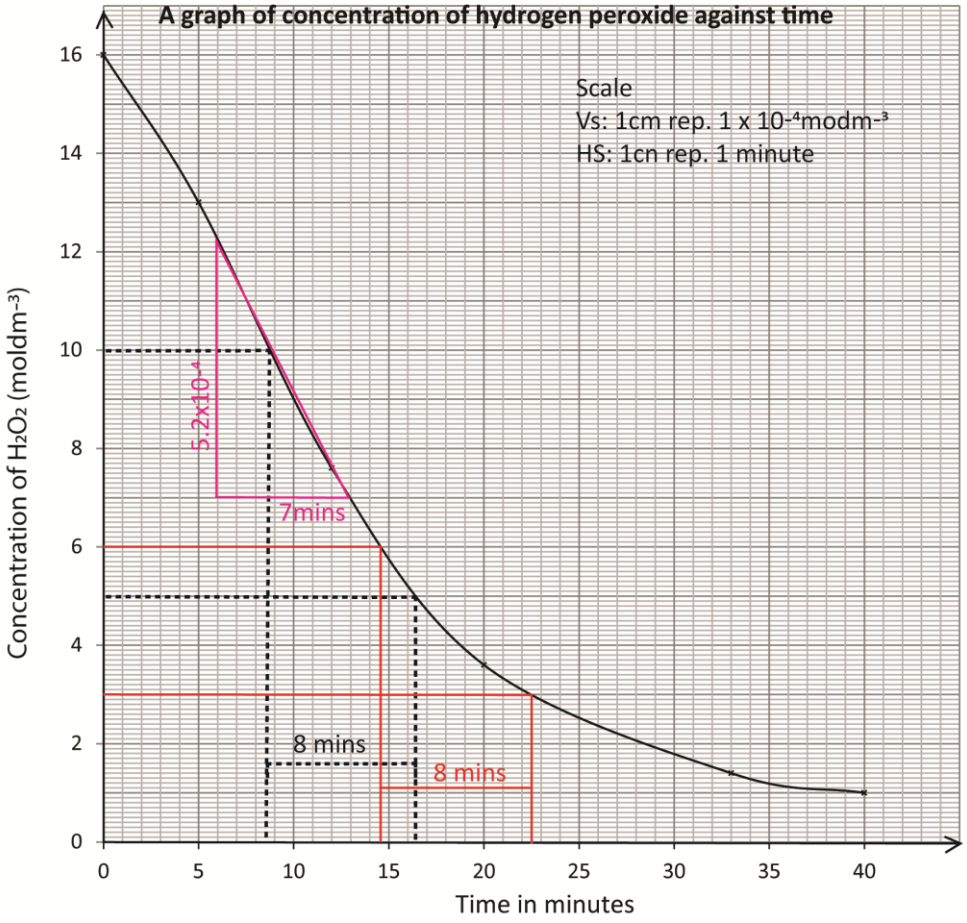
Increasing temperature increases the rate of decomposition by providing energy to break the bonds in hydrogenperoxide

(c) The following kinetic data in table 1 were obtained for the decomposition of hydrogen peroxide.

Table 1

Concentration of H_2O_2 ($moldm^{-3}$)	1.6×10^{-3}	1.3×10^{-3}	7.6×10^{-4}	3.6×10^{-4}	1.4×10^{-4}	1.0×10^{-4}
Time (minutes)	0	5	12	20	33	40

Pot a graph of concentration of hydrogen peroxide against time (04marks)



(d) Using your graph determine the time required for;

(i) 1.0×10^{-3} moles of hydrogen peroxide to reduce to 5.0×10^{-4} moles (01mark)

8 minutes

(ii) 6.0 x 10^{-4} moles of hydrogen peroxide to reduce to 3.0 x 10^{-4}moles (01mark)

8 minutes

(e) (i) What conclusion can be drawn from your answers in (d)(i) and (ii)? (1 ½ marks)

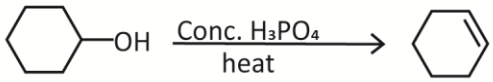
The reaction is a first order

(ii) Determine the rate constant for the reaction. (1 ½ marks)

Rate at the concentration of 1 x 10^{-3} = $\frac{5.2\ x\ 10^{-4}}{7}$ =7.43 x 10^{-5}moldm^{-3}min^{-1}

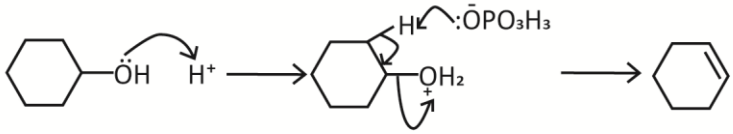
From Rate = k[H_2O_2]
7.43 x 10^{-5} =k(1 x 10^{-3})
k = 0.0743min^{-1}
therefore rate constant = 0.0743min^{-1}

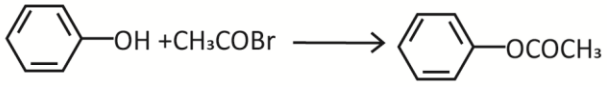
2. Complete the following equations and in each case, write mechanisms for the reactions:

(a) 

(04marks)

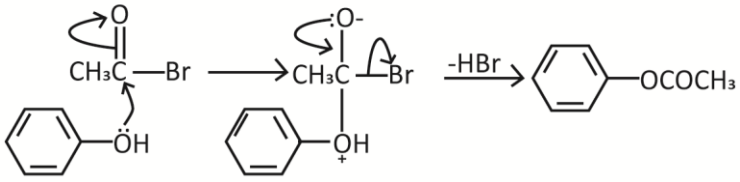
Mechanism

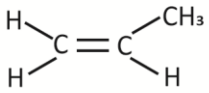


(b) 

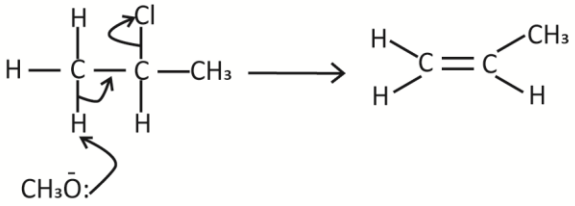
(4½marks)

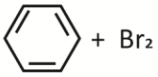
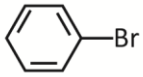
Mechanism



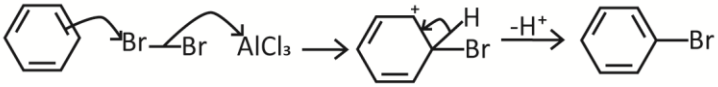
(c) $CH_3CHClCH_3 \xrightarrow[\text{heat}]{CH_3ONa/ethanol}$  (03marks)

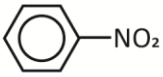
Mechanism



(d)  $+ Br_2 \xrightarrow{AlCl_3}$  (3½marks)

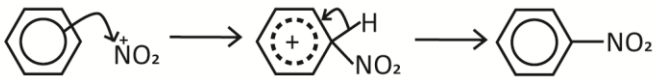
Mechanism



(e)  $\xrightarrow[\text{Conc. } H_2SO_4,\ 60^oC]{\text{Conc. } HNO_3}$  (05marks)

Mechanism

$HNO_3 + H_2SO_4 \longrightarrow \overset{+}{N}O_2 + H_2O + \bar{O}SO_3H$



3. (a) Although the elements: fluorine, chlorine, bromine and iodine belong to group (VII) of the Periodic Table, fluorine behaves differently from the rest of the group members. State;

   (i) two reasons why fluorine differs from the other elements of group (VII). (01mark)

   - Fluorine has low bond strength
   - Fluorine has high electronegativity
   - Fluorine has small atomic radius

   (ii) any two reactions in which fluorine differs from the other elements of group (VII) and write equations to illustrate your answers. (06marks)

   - Fluorine displaces chlorine from its salts

     $2Cl^- + F_2\ (g) \longrightarrow 2F^- + Cl_2$

   - Fluorine substitutes oxygen from silicon dioxide and water.

     $SiO_2\ (s) + 2F_2\ (g) \rightarrow SiF_4\ (g) + O_2\ (g)$

   - Fluorine reacts with cold dilute solutions of alkalis to give oxygen difluoride; F_2O, and with warm concentrated alkalis to give oxygen.

(Cold dilute) $2OH^-(aq) + 2F_2(g) \rightarrow F_2O(g) + 2F^-(aq) + H_2O(l)$

- Fluorine reacts with warm concentrated alkalis to give oxygen.

(Warm conc.) $4OH^-(aq) + 2F_2(g) \rightarrow O_2(g) + 4F^-(aq) + 2H_2O(l)$

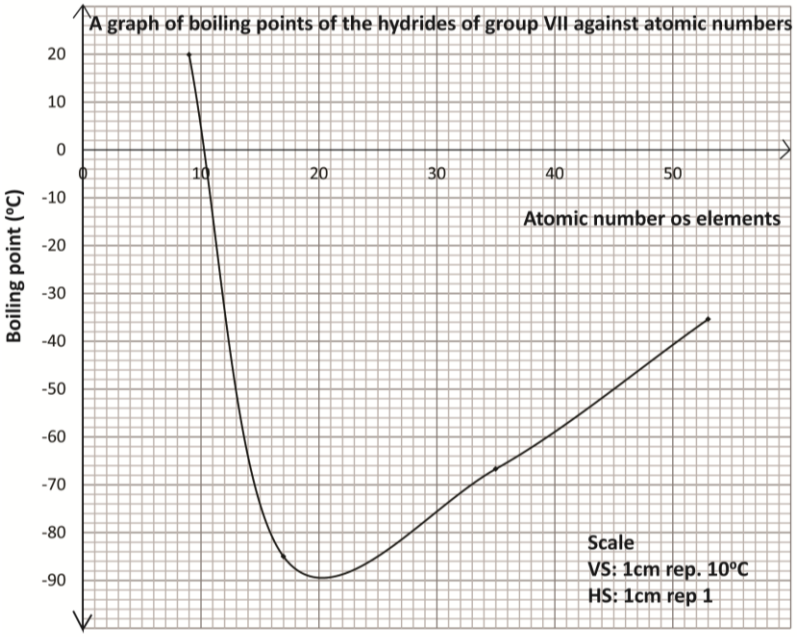
(any two reactions)

(b) The atomic numbers of group (VII) elements and the boiling points of their hydrides are shown in table 2

Table 2

Element	F	Cl	Br	I
Atomic number	9	17	35	53
Formula of the hydride	HF	HCl	HBr	HI
Boiling point of hydride (^{0}C)	+19.9	-85.0	-66.7	-35.4

(i) Plot a graph of boiling points of the hydrides against atomic numbers of the elements. (04marks)



(ii) Explain the shape of your graph. (4 ½ marks)

The boiling point of HF is considerably higher than that of hydrogen chloride because the individual HF units associate into larger aggregates $(HF)_n$ by means of strong hydrogen bonding.

From HCl to HI boiling points increase due to increase in molecular mass and thus the strength of molecular forces

(c) State what would be observed and write an equation for the reaction that would take place if;

(i) sodium thiosulphate solution was added to iodine solution. (2 ½ marks)

The brown Iodine color is discharged

$I_2(a) + 2S_2O_32^-(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

(ii) chlorine gas was bubbled through a solution of potassium bromide. (2marks)

A yellow solution forms due to liberation of bromine

$2Br^-(aq) + Cl_2(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$

4. (a)(i) State the difference between molar conductivity and electrolytic conductivity of solution. (01mark)

Electrolytic conductivity is the reciprocal of resistance of a solution between electrodes each $1cm^2$ in area and 1cm a part while molar conductivity is the contactivity of a solution that contain 1 mole of an electrolyte.

(ii) A conductivity cell filled with 0.1M aqueous potassium chloride gave a resistance of 484Ω at 25^0C. Calculate its cell constant.
(The molar conductivity of the solution at $25^0C = 129\Omega^{-1}cm^2mol^{-1}$)(3 ½ marks)

$K = \Lambda_c \times C = 129 \times 0.1 \times 10^{-3} = 0.0128\ \Omega^{-1}cm^{-1}$.

From $K = \frac{1}{R}$ x cell constant

Cell constant $= 0.0129 \times 484 = 6.24cm^{-1}$

(b) The electrolytic conductivity of a saturated solution of silver chloride at 25^0C is $3.41 \times 10^{-6}\Omega^{-1}cm^{-1}$.

Calculate the;

(i) Molar conductivity of silver chloride at infinite dilution (1½ marks)
(The molar conductivities at infinite dilution of silver nitrate, potassium nitrate and potassium chloride are 133.4, 145.0 and 149.9 $\Omega^{-1}cm^2mol^{-1}$ respectively.)

$\Lambda(AgCl) = \Lambda(AgNO_3) + \Lambda(KCl) - \Lambda(KNO_3)$

$= 133.4 + 149.9 - 145.0$

$= 138.3\ cm^2mol^{-1}$

(ii) Solubility of silver chloride and hence its solubility product. (7 ½ mark)
(The electric conductivity of water at $25^0C = 1.60 \times 10^{-6}\Omega^{-1}cm^{-1}$)

Electric conductivity of AgCl solution $= 3.41 \times 10^{-6} - 1.60 \times 10^{-6} = 1.81 \times 10^{-6}\ \Omega^{-1}cm^{-1}$

Let the solubility of silver chloride be C

From $\Lambda_c = \frac{K}{C}$

C = $\frac{1.81\ x\ 10^{-6}}{138.3}$ = 1.3 x 10^{-8}molcm^{-3} = 1.3 x 10^{-5} moldm^{-3}

Ksp = [Ag^+][Cl^-]= [1.3 x 10^{-5}] [1.3 x 10^{-5}]= 1.69 x 10^{-10}mol^{2}dm^{-6}

(c) Explain the effect of each of the following factors on the molar conductivity of an electrolyte:

(i) ionic radius (2 ½ marks)

The size of an ion: small ions have high speed of movement leading to high conductivity. However, small ions with high charge have high density that may attract a big cloud of water of hydration that its effective mass may bigger than that of a big ion. That is why the small cations may have lower conductivity that big cation.

(ii) concentration (04 marks)

For strong electrolyte at high concentration lowers conductivity high density of ions lead ion interaction which reduce mobility of ions

For weak electrolytes, high concentration lowers conductivity because it suppresses ionization.

SECTION B (40MARKS)

Answer any two questions from this section

Any additional question(s) answered will not be marked

5. (a) The melting points and atomic numbers of some elements of group (IV) of the Periodic Table are shown in table 3.

Table 3

Element	Carbon	Silicon	Germanium	Tin	Lead
Atomic number	6	14	32	50	82
Melting point (^{0}C)	3750	1420	950	232	327

(a)(i) Explain the trend in the melting points of the elements (05marks)

- Generally melting points decrease down the group due to reduction of electronegativity.
- **Carbon**, has a very high melting point because each carbon atom is bonded to four others with strong covalent bonds in a 3D network.
- **Silicon (Si) and Germanium (Ge)** also form giant covalent structures similar to diamond, but the bonds are slightly weaker due to the larger atomic size, leading to lower melting points compared to carbon.
- **Tin (Sn) and lead (Pb) are metal with low melting points** because metallic bonds are generally weaker than covalent bonds.

(ii) Describe the reaction of the elements with sulphuric acid. (07marks)

With dilute sulphuric acid

- C, Si and Ge do not react.
- Sn and Pb reacts hot concentrated sulphuric acid liberating sulphur dioxide.

$Pb(s) + 2H_2SO_4(aq) \rightarrow PbSO_4(s) + SO_2(aq) + 2H_2O(l)$

With hot concentrated sulphuric acid

- C, Si and Ge react to form dioxides

$C(s) + 2H_2SO_4(aq) \rightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$

$Sn(s) + 4H_2SO_4(aq) \rightarrow Sn(SO_4)_2(aq) + 2SO_2(g) + 2H_2O(l)$

$Ge(s) + 4H_2SO_4(aq) \rightarrow Ge(SO_4)_2(aq) + 2SO_2(g) + 2H_2O(l)$

- Pb is oxidized to lead II sulphate but the reaction is short lived due to insoluble lead II sulphate

$Pb(s) + 2H_2SO_4(aq) \rightarrow PbSO_4(s) + SO_2(g) + 2H_2O(l)$

(b) Group (IV) elements form tetrachlorides.

(i) Write equations for the reactions leading to formation of the tetrachlorides of carbon, silicon and lead. (4½ marks)

$CS_2(l) + 3Cl_2(g) \rightarrow CCl_4(l) + S_2Cl_2(l)$

$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$

$PbO_2(s) + 4HCl\ (Conc.and\ cold) \rightarrow PbCl_4\ (aq) + 2H2O(l)$

(ii) State what is observed when the tetrachlorides of carbon, silicon and lead are reacted with water. Explain your observations. (3½ marks)

- CCl_4 – no observation
- $SiCl_4$ and $PbCl_4$ white fumes of HCl due to hydrolysis
  $SiCl_4\ (aq) + 2H_2O(l) \rightarrow SiO_2\ (s) + 2H_2O(l)$
  $PbCl_4\ (aq) + 2H_2O(l) \rightarrow PbO_2\ (s) + 2H_2O(l)$

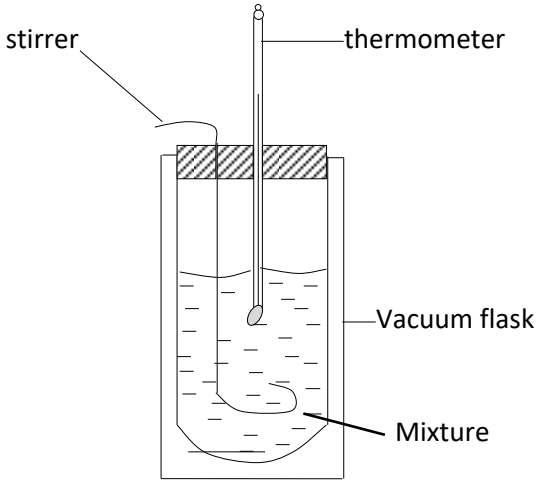
6. (a) State what meant by the following terms:
   (i) Electron affinity (01 marks)
   It enthalpy change when 1 mole of electrons is added to gaseous 1 mole of gaseous atoms or anions.
   (ii) First ionization energy (01 marks)
   It enthalpy change when 1 mole of electrons is removed to gaseous 1 mole of gaseous atoms to form 1 mole of gaseous cations with single positive charge
   (iii) Enthalpy of solution (01 marks)
   It is enthalpy change when 1 mole of ionic solid ionic compound is dissolved in excess water.

(b) The first ionization energy of an element is always less than the second ionization energy. Explain. (02 marks)

When the first electron is removed from an atom, the remaining electrons are strongly attracted to the nucleus, thus removal of the second electron requires extra energy.

(c) Describe an experiment to determine the enthalpy of neutralization of hydrochloric acid by sodium hydroxide (05marks)

Set up



A neutralization reaction is carried out in the calorimeter of known heat capacity, C .

$50cm^3$ of 1M HCl (v cm^3) and $50cm^3$ of 1M NaOH (v cm^3) of are added to calorimeter, and temperature change θ^0C is noted.

Calculations

The number of moles of water formed = $\frac{50\ x\ 1}{1000}$ = 0.05moles

Assumptions:

(i) The density of water = density of solution = $1gcm^{-3}$.

(ii) Specific heat of solution = specific heat capacity of water = 4.2 $Jg^{-1}K^{-1}$

(iii) Heat given out on neutralization = Heat received by water + calorimeter of capacity, C.

Thus, heat given out = Cθ + 100 x 4.2θ

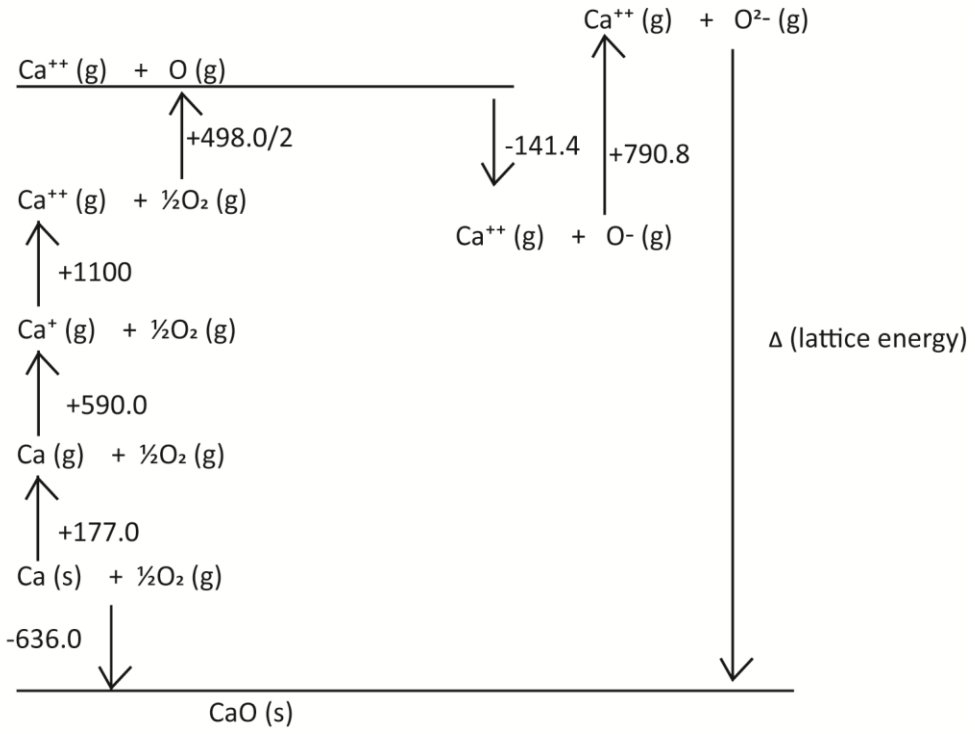
Thus 0.05 mole of water formed produce = (Cθ + 420θ)J

1mole of water will produce = $\frac{(C\theta+420\theta)}{0.05}$ $Jmol^{-1}$

(d) Some thermo-chemical data about calcium and oxygen are shown below

Process	Energy ($kJmol^{-1}$)
Enthalpy of formation of calcium oxide	= -636.0
Enthalpy of sublimation of calcium	= +177.0
First ionization energy of calcium	= +590.0
Second ionization energy of calcium	= +1100.0
Bond dissociation energy of oxygen	= +498.0
First electron affinity of oxygen	= -141.4
Second electron affinity of oxygen	= +790.8

(i) Draw an energy level diagram for the formation of calcium oxide (04marks)



(ii) Calculate the lattice energy of calcium oxide (02marks)

Δ(lattice) + 177.0 + 590.0 + 1100.0 + 498/2 – 141.4 + 790.8 = - 636.0

Δ(lattice) = -3,401.8

(iii) Comment on the stability of calcium oxide. (01 mark)

Very stable because high negative lattice energy

(e) The hydration and lattice energies for the chlorides of lithium and sodium are shown in the table 4

Table 4

Compound	Lattice energy ($kJmol^{-1}$)	Hydration energy ($kJmol^{-1}$)
LiCl	843	883
NaCl	778	775

(i) Calculate the enthalpies of solution for lithium chloride and sodium chloride. (1 ½ marks)

Enthalpy of solution of LiCl = 843 – 883 = $-40kJmol^{-1}$

Enthalpy of solution of NaCl = 778 – 775 = $+3kJmol^{-1}$

(ii) Which one of the chlorides in (e)(i) is likely to dissolve more on heating? Explain your answer (1 ½ marks)

NaCl because it has positive enthalpy of solution

7. Write equations to show how the following conversions can be effected; indicate reagents and conditions for the reaction in each case.

(a) $CH_3\overset{\overset{O}{\|}}{C}CH_3$ to $CH_3CH_2CH_2OH$ (5½ marks)

Solution

$$CH_3\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3\overset{\overset{OH}{|}}{C}HCH_3 \xrightarrow[\text{heat}]{\text{Conc. } H_2SO_4} CH_3CH{=}CH_2$$

then

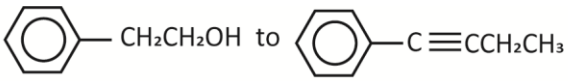
$$CH_3CH{=}CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3CH_2CHBr \xrightarrow[\text{heat}]{OH^-(aq)} CH_3CH_2CH_2OH$$

(b) CH_3CH_2I to CH_3CH_2COOH (2½ marks)

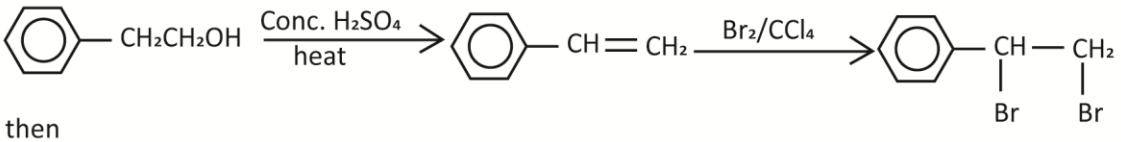
Solution

$$CH_3CH_2I \xrightarrow[\text{dry ether}]{Mg} CH_3CH_2MgI \xrightarrow[\text{dry ether}]{CO_2} CH_3CH_2CO_2MgI \xrightarrow{H^+} CH_3CH_2CO_2H$$

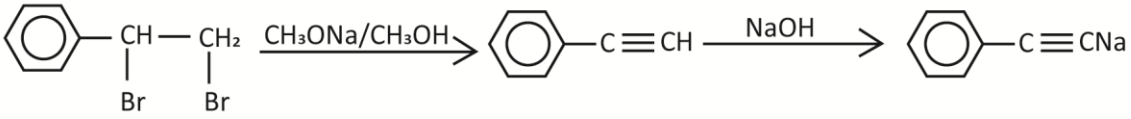
$$CH_3CH_2I \xrightarrow{KCN} CH_3CH_2CN \xrightarrow{H^+} CH_3CH_2CO_2H$$

(c)  (5½ marks)

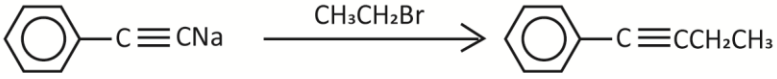
Solution



then



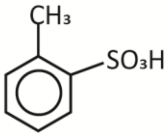
then



(d) $CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$ to $CH_3\overset{\displaystyle O}{\overset{||}{C}}CH_2CH_3$ (2½ marks)

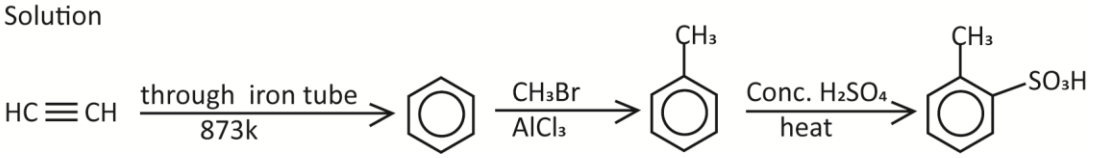
Solution

$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3 \xrightarrow{OH^-\ (aq)} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3 \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} CH_3\overset{\displaystyle O}{\overset{||}{C}}CH_2CH_3$$

(e) $HC \equiv CH$ to 

(04 marks)

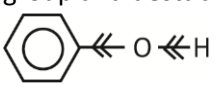
Solution



8. Explain each of the following observations and illustrate your answer with equations where necessary

(a) The reactivity of alcohols with hydrogen halides is in order;
tertiary > secondary > primary alcohols. (2 ½ marks)

Hydrogen halides react alcohols via formation of carbonium ions
Tertiary alcohols react fast because tertiary carbonium ions are stable readily formed from tertiary alcohols; and secondary alcohols are less reactive the tertiary alcohol because secondary carbonium ions are less readily formed; similarly primary alcohols are less reactive than secondary alcohols because primary carbonium ions are unstable and less likely to form.

(b) Alcohols are neutral organic compounds whereas phenol is weakly acidic, and yet both have hydroxyl groups. (04marks)
The alkyl group in alcohol has a positive inductive effect; it pushes electrons towards OH group and stabilizes O – H bond
R ⇉ O ⇉ H
The aromatic group in phenol has a negativr inductive effect; it withdraws electrons from OH group and destabilizes O – H bond


(c) Magnesium ions form precipitate with dilute ammonia solution, but no precipitates is formed if ammonium chloride is added to magnesium ions prior to ammonia solution (06 marks)

Ammonia hydrolyses in water to hydroxyl ions

NH_3 (aq) + H_2O (l) → NH_4^+(aq) + OH^-(aq)

Hydroxyl ions react with magnesium ions to form white ppt. of magnesium hydroxide

Mg^{2+}(aq) + $2OH^-$(aq) → $Mg(OH)_2$(s)

In presence of ammonium chloride magnesium ions do not form ppt. the hydroxyl ions are neutralized by ammonium ions

NH_4^+ (aq) + OH^- (aq) → NH_3 (aq) + H_2O(l)

(d) Water boils at 100^0C whereas hydrogen fluoride boils at 19.5^0C although both compounds exhibit hydrogen bonding. (04marks)

Water has higher boiling point than hydrogen fluoride because water molecule has two hydrogen atoms and two lone pairs on the oxygen atom; this makes able to form four hydrogen bonds with surrounding water molecules. While HF forms fewer hydrogen bonds per mole with surrounding HF molecules since it has fewer Hydrogen atoms per molecule. The hydrogen bonds in water thus, require higher temperature to beak leading to higher boiling point.

(e) The nitronium ion, NO_2^+ has a linear shape whereas the nitrite ion, NO_2^- is V-shaped. (3½ marks)

Nitronium ion lack a lone pair of electron while nitrite ion has alone pair of electron.

END