NGAIZA EDUCATION HUB ORGANISATION (NEH)

COMPETENCY ASSESSMENT SERIES (CA SERIES)

CA IN ADVANCED CHEMISTRY

With samples of competency based NECTA examinations

Prepared by NGAIZA LUSIMA

Competency based Examination questions and their complete marking schemes

CA series

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EXAMINATION QUESTIONS

MARKING SCHEMES AND MODEL SOLUTIONS FOR NECTA 2020 - 2023

PREFACE

A student who strongly determined to have great ability in academic needs to solve a lot of examination questions. A student who strongly desire to have pretty result in the final NECTA examination, needs to test his/her ability by doing examination questions resembling to those of NECTA. A student who strongly dream to achieve best grade in the NECTA results, need to understand tactics, technics and arts of answering NECTA examination questions.

This book is certainly going to serve those purposes for advanced chemistry. It is the one book in **'CA series'** under Ngaiza Education Hub organisation (NEH). Other wonderful books in the 'CA series' are: **CA in advanced mathematics, CA in advanced physics** and **CA in advanced biology**.

ORGANISATION

CA in advanced chemistry book is divided in two parts: examination questions and examination marking schemes.

Examination questions: These constitute first part of the book. It consists of 224 different examination questions in twenty-eight (28) examinations. Out of the twenty-eight examinations; fourteen examinations are in paper one format and the rest are in paper two format in accordance to the new NECTA examination format for advanced chemistry. The examinations are prepared in pairs in such a way that for each paper one there is its corresponding paper two examination. The pairs are distinguished by letters; for example: paper one labelled 'examination 1**A**' has its corresponding paper two labelled 'examination 2**A**' while paper one labelled 'examination 1**B**' has its corresponding paper two labelled 'examination 2**B**' and so on up to 1**K** and its corresponding 2**K**. It is recommended to do the examinations in sequence that is 1A followed by 2A, then 1B followed by 2B and so on. Also you are supposed to do self-analysis of your score by calculating the average score for each pair.

Examination marking schemes: These constitute the second and the last part of the book. The marking schemes are creatively designed and intelligently written to enhance correct and efficient marking, to sharpen understanding of contents and to expand the knowledge and arts of answering examination questions cleverly.

I hope both teachers and students will find this book helpful and interesting.

ACKNOWLEDGEMENTS

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Ngaiza, Lusima

GENERAL INSTRUCTIONS

ADVANCED CHEMISTRY 1

Time: 3Hours

INSTRUCTIONS

1. This paper consists of **two (2)** sections A, and B with a total of **ten (10)** questions.
2. Section A consists of **seven (7)** questions while section B consists of **three (3)** questions.
3. Each question of section A carries **ten** (**10**) marks while each question of section B carries **fifteen (15)** marks.
4. Answer **all seven (7)** questions from section A and **any two (2)** questions from section B.
5. Marks for each question or part thereof are indicated.
6. Non – programmable calculators may be used.
7. Cellular phones and any unauthorized materials are strictly **NOT** allowed in the examination room.
8. **CONSTANTS:**

$c = 3.0 \times 10^8\ m/s$ $R_H = 1.09678 \times 10^7 m^{-1}$

$h = 6.63 \times 10^{-34} Js$ $N_A = 6.02 \times 10^{23}$

$R = 8.31 Jmol^{-1}K^{-1}$ or $0.0821 atmmol^{-1}K^{-1}dm^3$

ATOMIC MASSES:

$S = 32$, $He = 4$, $Cl = 35.5$, $Ne = 20$

$O = 16$, $N = 14$, $C = 12$, $H = 1$, Ca = 40

ADVANCED CHEMISTRY 2

Time: 3 Hours

INSTRUCTIONS

1. This paper consists of total **six (6)** questions.
2. Each question carries **twenty** (**20**) marks.
3. Answer **any five (5)** questions.
4. Marks for each question or part thereof are indicated.
5. Non – programmable calculators may be used.
6. Cellular phones and any unauthorized materials are strictly **NOT** allowed in the examination room.
7. **CONSTANTS:**

$c = 3.0 \times 10^8\ m/s$ $R_H = 1.09678 \times 10^7 m^{-1}$

$h = 6.63 \times 10^{-34} Js$ $N_A = 6.02 \times 10^{23}$

$R = 8.31 Jmol^{-1}K^{-1}$ or $0.0821 atmmol^{-1}K^{-1}dm^3$

ATOMIC MASSES:

$H = 1, Cl = 35.5, Ag = 108, N = 14, Br = 80, K = 39, Mn = 55, O = 16,\ Na = 23, F = 19, C = 12, Ca = 40, Cr = 52, Pb = 207.$

Examination One
CHEMISTRY 1A

SECTION A

Answer **all** questions in this section.

Question 1

(a) Explain in your own words what is meant by:
- (i) The Pauli Exclusion principle
- (ii) Hund's rule
- (iii) A line in an atomic spectrum
- (iv) The principle quantum number

(4marks)

(b) What designation is given to the orbitals having:
- (i) $n = 2,\ l = 0$
- (ii) $n = 1,\ l = 0$
- (iii) $n = 3,\ l = 2$
- (iv) $n = 4,\ l = 1,\ m_l = -1$

(2marks)

(c) An element **X** has 2 electrons in K shell, 8 electrons in L shell, 13 electrons in M shell and 2 electrons in N shell. Deduce the following:
- (i) Its full electronic configuration
- (ii) Atomic number of **X**
- (iii) Total number of principle quantum numbers with electrons in an atom of **X** at ground state
- (iv) Total number of sublevels with electrons in an atom of **X** at ground state
- (v) Total number of unpaired electrons in an atom of **X** at ground state
- (vi) In which block of periodic table does element **X** belong?

(4marks)

Question 2

(a)
- (i) What is the meaning of hybrid bonds?
- (ii) What types of hybridized orbitals can be formed by elements of the third period that cannot be formed by elements in the second period? Give a reason.

(2marks)

(b) Give reason(s) for each of the following:
- (i) The bond angle in ice is 109° and not 104° like in liquid water.
- (ii) Argon and fluorine have similar boiling point.

(2marks)

(c) Differentiate between:
- (i) Atomic orbital and molecular orbital
- (ii) Sigma and pi bonds

(2marks)

(d) Briefly explain why ammonia (NH_3) is soluble in water while phosphine (PH_3) is not despite the fact that both have similar structure.

(2marks)

(e) Give name of geometrical structure and one example of the molecule formed from the following hybridised atomic orbitals:

(i) sp^2 hybridised orbitals

(ii) d^2sp^3 hybridised orbitals

(2marks)

Question 3

(a)

(i) State the law which governs the total pressure in the container of mixture of two or more gases.

(ii) From kinetic equation of gases, derive the law stated in (i) above.

(3marks)

(b) "A gas consists of very small molecules in a random motion of which there is a collision between gas molecules and walls of the container"

(i) What is the characteristics feature of that collision? (Assume the gas is ideal)

(ii) The collision will result into important property of the gas: mention it.

(iii) Explain clearly how, the presence of intermolecular forces in real gas, will affect facts mentioned in (i) and (ii) above

(3marks)

(c)

(i) Under what conditions does the behaviour of real gas begin to differ significantly from the ideal gas law?

(ii) What is the physical meaning of the 'a' and 'b' constants in the Van der Waals equation?

(2marks)

(d) It takes 22 hours for neon-filled balloon to shrink to half its original volume at s.t.p. If the same balloon is filled with helium, then how long it have taken for the balloon to shrink to one third of its original volume at s.t.p?

(2marks)

Question 4

(a)

(i) What is boiling point of liquid?

(ii) How boiling point is affected by external pressure?

(1mark)

(b)

(i) What are colligative properties?

(ii) Mention limitations for colligative properties to be observed

(iii) You take a bottle of a soft drink out of your refrigerator. The contents are liquid and stay liquid even when you shake them. Thirstily, you remove the cap, and the liquid freezes solid! Offer a possible explanation of this observation. **(4marks)**

(c) The vapour pressure of CS_2 at certain temperature is 5333Pa. At the same temperature, a solution of 5.5g of sulphur in $63cm^3$ of CS_2 has a pressure of 5223Pa. The density of CS_2 is $1.27g/cm^3$. Find:
   (i) The R.M.M of sulphur
   (ii) The molecular formula of sulphur in CS_2.

   (Show your work clearly including manipulation of units).

(5marks)

Question 5

(a) Metal hydroxides can be prepared in the laboratory by either **direct method** or **indirect method** depending on the nature of the hydroxide. Below are hydroxides which may be prepared by one of the two methods. For each given hydroxide, **state** whether the hydroxide can be prepared by direct or indirect method and **give** the corresponding **balanced chemical equation** for each.
   (i) Magnesium hydroxide
   (ii) Barium hydroxide
   (iii) Sodium hydroxide
   (iv) Iron (II) hydroxide

(4marks)

(b) With the help of chemical equation, state the suitable method to prepare the following sulphates:
   (i) Calcium sulphate
   (ii) Zinc sulphate
   (iii) Potassium sulphate

(3marks)

(c) Outline three uses of metal hydroxides.

(3marks)

Question 6

(a) Give the meaning of the following terms:
   (i) Standard state of an element or compound
   (ii) Born-Haber cycle
   (iii) Standard enthalpy of neutralization
   (iv) Standard dissociation energy

(4marks)

(b) Why the enthalpy of neutralization involving strong acid and strong base is higher compared to those involving strong acid and weak base or weak acid and strong base?

(1.5marks)

(c) **Kekule**, a student at Benzene secondary school was asked to determine the enthalpy of neutralization by taking $100cm^3$ of $0.3MNaOH$ and mixing it with $115cm^3$ of $0.3MHNO_3$ in a polystyrene beaker. If both solutions were initially at 35℃ and the temperature of the resulting solution was recorded as 39℃ and he was told to assume that there was no heat lost to the calorimeter or surroundings; but by mistake he took $100cm^3$ of $0.3MNaOH$ and mixed $20cm^3$ of distilled water in a beaker unknowingly. This led

Kekule to have an error to his experimental results. Assists **Kekule** to calculate the percentage error enthalpy between the real expected and the one he calculated. (Show your work clearly including manipulation of units).

(4.5marks)

Question 7

(a) Define the following terms:
   (i) Le Chatelier's principle.
   (ii) Reversible reaction
   (iii) Law of mass action
   (iv) Catalyst

(2marks)

(b) Most metal ions combine with other ions in solution for example in aqueous ammonia; silver (I) ions are in equilibrium with different complex ions.

$$[Ag(H_2O)_2]^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + 2H_2O(l)$$

A room temperature,K_c for this reaction is 1×10^7.Which of the two silver complex ions is the more stable? Give a reason for your choice.

(2marks)

(c) Consider the production of HI by direct combination between I_2 and H_2 as per question;

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Can you alter the yield of HI at equation by adding hydrogen gas or decreasing the volume of the container? Explain.

(3marks)

(d) Dinitrogen tetraoxide in its liquid state was used as one of fuels on the Lunar lander expeditions for the NASA space vessels. In the gas phase it decomposes to gaseous nitrogen dioxide as shown in the following equation:

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

N_2O_4 was allowed to reach at equilibrium at $400°C$ where $K_p = 0.133atm$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm.
   (i) Write the equilibrium expression in terms of concentration.
   (ii) Write the equilibrium expression in terms of partial pressures.
   (iii) Calculate the equilibrium pressure of NO_2.

   (Show your work clearly including manipulation of units).

(3marks)

SECTION B

Answer **any two** questions from this section

Question 8

(a) What do you understand by the following terms:
   (i) Free radical substitution
   (ii) Electrophiles
   (iii) Functional group
   (iv) Chain isomerism

(2marks)

(b) Explain the following:
  (i) Hydrocarbons are most dependable world's source of gaseous fuels
  (ii) The first three members of homologous series, alkane do not exhibit isomerism
  (iii) Bromination of but-1-ene by hydrogen bromide result into the formation of 2-bromobutane as the major product and not 1-bromobutane
  (iv) Methane does not react with chlorine in dark at room temperature

(4marks)

(c) Suggest suitable tests to distinguish the following compounds:
  (i) But-2-yne and butane
  (ii) 2-butyne and 1-butyne

(2marks)

(d) Compound **Q** has the molecular formula, C_8H_{14}. Chlorination of **Q** yielded $C_8H_{14}Cl_4$. When **Q** was treated with Ammonical silver nitrate solution it gave no precipitate. Ozonolysis of one mole of **Q** yielded two moles of C_2H_5CHO and one mole of $H_2C_2O_2$.
  (i) Give the structural formula of compound **Q**
  (ii) Write all reactions taking place when Q reacts with chlorine and when reacting with ozone followed by hydration in the presence of zinc dust.

(7marks)

Question 9

(a)
  (i) Name all structural isomers of molecular formula C_4H_9Cl
  (ii) Explain by using chemical equations the chemical test which can be used to distinguish isomers in 9(a) (i) above.

(4marks)

(b) Write equations for the following reactions:
  (i) Benzene and chloromethylbenzene (benzyl chloride) in presence of anhydrous $AlCl_3$
  (ii) 1-chloromethyl-4-nitrobenzene and benzene in presence of anhydrous $AlCl_3$

(2marks)

(c) Two isomeric hydrocarbons **P** and **Q** have molecular formula C_9H_{12}. On oxidation, **P** gives monocarboxylic acid, when treated with soda lime yields benzene. **Q** is oxidised to give tricarboxylic acid and can undergo nitration to give two mono-nitro derivatives.
  (i) Write down the structural formula of **P** and **Q**
  (ii) Write an equation to show how **Q** is oxidised to give tricarboxylic acid
  (iii) Name the compound which is formed when **P** undergoes oxidation

(5marks)

(d) **DDT** is the commercial name for 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane**.** The compound is very useful industrial halohydrocarbon.
  (i) Write the structure of **DDT**
  (ii) What is the main use of **DDT**?
  (iii) List down two hazards associated with the use of **DDT**.

(4marks)

Question 10

(a) In the upper atmosphere, ozone is very important to healthy environment where it acts as the primary ultraviolet radiation shield. However, when it is at lower atmosphere, ozone has harmful effects on many living things because it is toxic.

(i) With help of chemical equation, show how ozone is formed in lower atmosphere through electrical discharge.

(ii) Explain how ozone prevents harmful ultraviolet light to reach earth's surface and explain why these harmful radiations cannot be prevented by oxygen gas which is more abundant than ozone in the atmosphere.

(iii) Mention at least four harmful effects of ground – level ozone

(8marks)

(b) With at least one example in each case, give the meaning of the following:

(i) Straight fertilizer

(ii) Mixed fertilizer

(2marks)

(c)

(i) Outline at least three advantages of using manure.

(ii) A farmer was advised to supply 160kg of N to his maize farm. Calculate the mass of fertilizer (of 80% by mass $Ca(NO_3)_2$ which has to buy to meet the requirements.

(5marks)

Examination Two
CHEMISTRY 2A

Answer **five (5)** questions

Question 1

(a) Provide the meaning the following terms:
   (i) Saturated vapour pressure
   (ii) Raoult's law
   (iii) Azeotropic point
   (iv) Ideal solution

(2marks)

(b) Components of binary mixture of two liquids A and B were being separated by distillation. After sometime, separation of components stopped and composition of vapour phase became same as that of liquid phase. Both components start coming in the distillate. Explain why this happened.

(2marks)

(c) Ethanol and water form an azeotropic mixture which boils at 78.1℃ with 95.6% ethanol. The boiling point of pure ethanol and water are 78.4℃ and 100℃ respectively.
   (i) Draw a temperature-mole fraction phase diagram of ethanol-water solution.
   (ii) What happens when a solution of less than 50% ethanol is boiled?
   (iii) How pure ethanol may be obtained from the azeotropic mixture**?**

(6marks)

(d)
   (i) State Nernst's distribution law.
   (ii) List any three limitations of the distribution law.
   (iii) Briefly explain how the law stated in (i) above is useful in daily life.

(4marks)

(e) Liquid X and Y are completely miscible. A mixture of two liquids boils at 410K when the pressure is $1.013 \times 10^5 \mathrm{Nm}^2$. If the vapour pressure of X at this temperature is $1.15 \times 10^5 \mathrm{Nm}^{-2}$ and that of Y is $6.04 \times 10^5 \mathrm{Nm}^{-2}$; Calculate the mole fraction of X in the vapour phase.

(6marks)

Question 2

(a) Briefly explain the following terms as used in chemical kinetics:
   (i) Reaction order
   (ii) Reaction mechanism
   (iii) Activation energy

(4.5marks)

(b) The ionisation constant of $\mathrm{NH_4^+}$ in water is $5.6 \times 10^{-10} \mathrm{moldm}^{-3}$ at 25℃. The rate constant for the reaction of $\mathrm{NH_4^+}$ ions and $\mathrm{OH^-}$ ions to form $\mathrm{NH_3}$ and water at 25℃ is $3.4 \times 10^{10} \mathrm{dm^3mol^{-1}sec^{-1}}$. Calculate the rate constant for the proton transfer from water to $\mathrm{NH_3}$. **(5.5marks)**

(c) What do the following terms say?

(i) Standard electrode potential
(ii) Redox reaction
(iii) Corrosion
(iv) Disproportionation reaction

(2marks)

(d) Write a balanced ionic equation and identify the oxidants and reductants in each of the following chemical reactions:
(i) Iron (II) sulphate reacts with an acidified potassium dichromate solution.
(ii) Potassium iodide reacts with an acidified potassium iodate solution.
(iii) Copper (II) sulphate solution and potassium iodide solution react together.
(iv) Chlorine gas and hot concentrated potassium hydroxide react together.

(6marks)

(e) Explain the function of moisture in the rusting process.

(2marks)

Question 3

(a) Explain clearly what is wrong with each of the following definitions:
(i) **Buffer solution**: *Is the solution which can maintain its pH value on addition of any amount of acid or base.*
(ii) **Common ion effect***: Is the depression in solubility of sparingly soluble substance after introducing strong electrolyte with the same ion as that present in sparingly soluble substance.*

(4marks)

(b) Calculate concentration of calcium carbonate precipitate in $\mathrm{gdm^{-3}}$ if 0.1M of calcium chloride as added to equal volume of 0.1M of sodium carbonate solution. Given that: $\mathrm{K_{sp}}$ of $\mathrm{CaCO_3} = 1.69 \times 10^{-8}\ \mathrm{mol^2dm^{-6}}$

(5marks)

(c) The following data are values for $\mathrm{K_w}$ at different temperature, in units of $\mathrm{mol^2dm^{-6}}$

Temperature (°C)	10	20	30
$\mathrm{K_w} \times 10^{-14}$	0.293	0.681	1.471

(i) What is the pH of pure water at 30°C
(ii) What is the pH at equivalent point of titration of aqueous hydrochloric acid with potassium hydroxide at 10°C?

(4marks)

(d) For weak acid HA, $\mathrm{K_a} = 1.0 \times 10^{-6}\mathrm{moldm^{-3}}$. Given two solutions, one containing $0.1\mathrm{moldm^{-3}}$ of HA and other $0.1\mathrm{moldm^{-3}}$ of sodium hydroxide. Explain how would you make:
(i) A solution with pH = 6
(ii) A solution with pH = 5
Explain which of these solution would constitute the best buffer solution.

(7marks)

Question 4

(a) Account for the following:

- (i) Hydration energy is the function of ionic radius.
- (ii) It is easier to atomize sodium than magnesium.
- (iii) Compounds of magnesium give negative flame test while those of calcium give positive test although both elements are found in the same group.
- (iv) Molten NaCl is more mobile than molten KCl.
- (v) Compounds which consist of small sized ions do not dissolve in water.

(10marks)

(b) Using relevant balanced chemical equations. Explain the process of extracting copper from copper pyrites under the following headings:

- (i) Concentration of the ore
- (ii) Roasting of the ore
- (iii) Removal of iron impurities
- (iv) Self-reduction

(10marks)

Question 5

(a)

- (i) Write the electronic configurations of the following species: Mn^{2+}, V^{3+} and Fe^{3+}.
- (ii) Give reason(s) why in manganese the oxidation state of $+2$ is more stable than the oxidation state of $+3$.

(4marks)

(b) Briefly explain each of the following phenomena:

- (i) The radii of Fe, Co and Ni show a much smaller variation in size than those of Na, Mg and Al.
- (ii) Zinc has two electrons in the outermost shell as does magnesium but they are not classified in the same group.
- (iii) Iron element exhibits magnetic properties while zinc element does not.

(6marks)

(c)

- (i) Account for the different coordination numbers between $[\mathrm{FeCl_4}]^{2-}$ and $[\mathrm{FeF_6}]^{4-}$
- (ii) What is the origin of paramagnetism in transition elements?
- (iii) Use the 3d electronic configuration cobalt (III) ions to explain why $[\mathrm{CoF_6}]^{3-}$ is paramagnetic while $[\mathrm{Co(CN)_6}]^{3-}$ is diamagnetic.
- (iv) Briefly explain why $[\mathrm{Fe(CN)_6}]^{4-}$ is said to be inner orbital complex while $[\mathrm{CoF_6}]^{3-}$ is said to be outer orbital complex. Determine the type of hybridisation exhibited by each of the two complexes.

(10marks)

Question 6

(a) Show how ethylamine reacts with the following molecules:

- (i) Benzaldehyde

(ii) Cyclohexane
(iii) Nitrous acid at freezing temperature
(iv) Propanoyl chloride

(4mark)

(b) From the knowledge you have on the functional groups, write chemical equations showing what happen when compound $OC(CH_3)CH_2CH_2CH(OH)CH_2CO_2H$ reacts with the following reagents:
(i) Ethanol in the presence of acid
(ii) Potassium pentachloride
(iii) Lithium aluminium tetrahydride catalyst
(iv) Iodine in presence of sodium hydroxide and, then warm

(4marks)

(c) An aromatic derivative of benzene P is composed of 80% carbon, 6.66% hydrogen and 3.33% oxygen. P has vapour density equal to 60 and it does not respond to silver mirror test
(i) Find empirical and molecular formula of P
(ii) Write the molecular structure of P

(5marks)

(d) Write structures of the products obtained when P:
(i) React with iodine in the presence of alkali
(ii) React with hydrogen cyanide followed by lithium aluminium hydride in dry ether
(iii) React with chlorine in presence of ferric chloride

(3marks)

(e) List down two uses and two hazards of carbonyl compounds.

(4marks)

Examination Three
CHEMISTRY 1B

SECTION A

Answer **all** questions in this section.

Question 1

(a) *"The electron in the atom is located at a definite distance from the nucleus in an orbit which has discrete energy"*

(i) Which atomic model is this statement based?
(ii) Challenge this statement according to wave mechanical model of the atom?

(2marks)

(b) Give an account for an experiment which led Rutherford to conclude that every atom has heavy positively charged nucleus which occupies small volume.

(2marks)

(c) Give two examples to show that electronic configuration of half-filled and completely-filled orbitals are more stable.

(2marks)

(d) Calculate the energy emitted when electrons of 1g atoms of hydrogen undergo transition giving line of lowest energy in the visible region of its atomic spectrum. Show your work clearly including manipulation of units.

(Show your work clearly including manipulation of units).

(4marks)

Question 2

(a) Give the meaning of the following, giving one example in each case:
(i) Hydrogen bond
(ii) Coordinate bond
(iii) Polar covalent bond

(2marks)

(b) Compare and contrast the following:

(i) Metallic bond and electrovalent bond
(ii) Hydrogen bond and Van der Waals forces

(4marks)

(c) Among the following pairs identify the compound with higher melting point. Give reason(s).
(i) CH_3CH_2OH and CH_3CHO
(ii) NaCl and $AlCl_3$

(3marks)

Question 3

(a) State at least one application of each of the following:

(i) Grahm's law of diffusion
(ii) Dalton's law of partial pressures
(iii) Avogadro's hypothesis

(1.5marks)

(b) Then Van der Waals equation for real gases is: $\left(P+\frac{n^2a}{v^2}\right)(V-nb)=nRT$

Where all symbols carry their usual meaning:

(i) Explain briefly the significance of the term $\frac{n^2a}{v^2}$ and nb in the equation.
(ii) The compressibility factor for one mole of a real gas at 273K and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecules is negligible, calculate Van der Waals constant. Show your work clearly including manipulation of units.

(3.5marks)

(c) Traditionally, high-flying aircraft and Formula 1 racing cars have had their tyres inflated with nitrogen gas instead of air. Recently, this practice has been extended to some other cars.

A car tyre is filled with nitrogen gas to a volume of 8.98dm^3 and a pressure of 207kPa at 20°C.

(i) Using the ideal gas equation, calculate the mass of nitrogen gas, in grams, present in the car tyre under these conditions. Show your work clearly including manipulation of units.
(ii) During a car journey, the tyres become warm. Use the ideal gas equation to deduce the effect of that this has on the pressure in the tyres.
(iii) One reason for the use of nitrogen gas in car tyres is that less gas is lost from the tyres during use because nitrogen molecules are larger than oxygen molecules.NA suggested explanation for this is that nitrogen atoms are larger than oxygen atoms. Explain why a nitrogen atom is larger than an oxygen atom.

(5marks)

Question 4

(a) What is the meaning of the following terms?

(i) Colligative properties
(ii) Ebullioscopic constant
(iii) Osmotic pressure

(1.5marks)

(b) A 100mL aqueous sodium chloride solution is 13.5% NaCl by mass and has a density of 1.12g/mL. What would you add (solute or solvent) and what mass of it to make the boiling point of the solution 104.4°C?

(Use Van't Hoff's factor for NaCl as 1.8 and $K_b = 0.512°\text{Ckgmol}^{-1}$).

(Show your work clearly including manipulation of units).

(5.5marks)

(c) A solution is prepared from 90g of water and 10.6g of a non-volatile, non-dissociating solute. The vapour pressure of the solution at 60°C is found to be $1.891\times10^4\text{Nm}^{-2}$. Calculate the approximate molecular mass of the solute given that, the vapour pressure of water at 60°C is $1.992 \times 10^4 \text{Nm}^{-2}$. Show your work clearly including manipulation of units. **(3marks)**

Question 5

(a) Giving at least one example of each of the following:

- (i) Normal oxide
- (ii) Peroxide
- (iii) Mixed oxide
- (iv) Superoxide

(2marks)

(b) Briefly explain the following observations. Support your explanation with equation(s) where applicable.

- (i) Sodium peroxide is used in emergency breathing devices in submarine.
- (ii) Bicarbonates cannot be prepared by precipitation method.
- (iii) Sodium bicarbonate is used as baking powder to raise cakes.
- (iv) Although sodium reacts readily with dilute sulphuric acid, the reaction is not commonly employed in the preparation of sodium sulphate.

(5marks)

(c) Complete each of the following reactions:

- (i) $B(OH)_3 + HCl \longrightarrow$
- (ii) $NO_2 + H_2O \longrightarrow$
- (iii) $Na_2O_2 + H_2SO_4 \longrightarrow$
- (iv) $MgCl_2(s) + H_2O(g) \longrightarrow$
- (v) $AgNO_3 + KOH \longrightarrow$
- (vi) $Na_2CO_3 + H_2CO_3 \longrightarrow$

(3marks)

Question 6

(a) What is your understanding on the following terms?

- (i) Heat of dilution
- (ii) Heat of solution

What is the relation between the two terms?

(3marks)

(b) Calculate the enthalpy change of solution of magnesium hydroxide, using the following data:

Energy or enthalpy change	Value / kJmol^{-1}
Lattice energy of $Mg(OH)_2(s)$	-2842
$\Delta_{hyd}(Mg^{2+}(aq))$	-1920
$\Delta_{hyd}(OH^-(aq))$	-460

(3marks)

(c) Ethanol, which is used as a fuel, burns in air according to the equation shown below;

$$C_2H_5OH(1) + 3O_2(g) \longrightarrow 3H_2O(g) + 2CO_2(g) + \text{heat}$$

In an experiment to determine the heat value of ethanol, the heat produced by an ethanol burner was used to heat $200cm^3$ of water. The following result were obtained:
Initial mass of lamp + ethanol =56.69g
Final mass of lamp +ethanol =56.46g
Initial temperature of water =25.00℃
Final temperature of water =31.24℃

(i) Assuming there were no heat loss, calculate the heat value of ethanol.
(ii) If the experiment was carried out at standard temperature and pressure (STP), what volume of carbon dioxide gas was produced?
(C = 12, H = 1, 0 =16; specific heat capacity of water, c = 4.18kJ/kg K; molar volume of gas at STP = $22.41dm^3/mol$)

Show your work clearly including manipulation of units.

(4marks)

Question 7

(a) State the meaning of the following:
(i) Reaction quotient
(ii) Equilibrium constant

(1mark)

(b) When 20.85g of PCl_5 was heated in a sealed tube of $4dm^3$ volume, the pressure in the vessel was found to be 1.5 atm. At this pressure it was found that PCl_5 dissociated to 80%. Calculate the partial pressure of each gas.

(4marks)

(c) Nitrogen and oxygen combine endothermically at elevated temperature according to the equation:

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2\ (g)$$

If the equilibrium constant for the reaction is 4.3×10^{-3} at 3000℃ and 1atm, calculate the composition of each in the equilibrium if 2 moles of each nitrogen and oxygen were heated.

(5marks)

SECTION B

Answer **any two** questions from this section

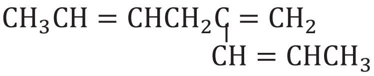
Question 8

(a) Briefly explain the following terms and give an example of family of organic compounds in each case:
(i) Hydrocarbon
(ii) Saturated hydrocarbon
(iii) Unsaturated hydrocarbon

(3marks)

(b) Give systematic names of the following organic compounds
(i) $CH_3CH(C_2H_5)CH_3$
(ii) $CH \equiv C - CH = CH_2$

(iii) Propylene

(iv) 
$CH_3CH=CHCH_2\underset{\displaystyle CH=CHCH_3}{C}=CH_2$

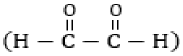
(2marks)

(c) Alkanes are obtained by processing crude oil.
  (i) Explain why different alkanes in crude oil can be separated by fractional distillation.
  (ii) By using molecular formulae; complete the equation for the cracking of octane to produce ethene and only one other organic compound. Give at least two possible equations.

(3marks)

(d) Explain the following phenomena briefly with chemical reaction where possible:
  (i) Addition of hydrogen iodide to pent-1-ene give 2-iodopentane and not 1-odopentane.
  (ii) But-1-yne gives red precipitate with copper (I) chloride but-2-yne does not.
  (iii) Cis-but-2-ene and trans-but-2-ene have different boiling points although they have the same molecular formula.

(3marks)

(e)
  (i) What is ozonolysis?
  (ii) A hydrocarbon having molar mass of 96g/mol and molecular formula C_7H_{12} was ozonolysed and then hydrolysed in presence of zinc. The product of ozonolysis were ethanal, propanone and glyoxal 
$(H-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-H)$. Determine the structure of hydrocarbon and show ozonolysis of the compound.

(4marks)

Question 9

(a) In aqueous sodium hydroxide, 1-bromoethane reacts to produce ethanol.
  (i) Write the mechanism for this reaction, including all relevant curly arrows, lone pairs and dipoles. Include the transition state.
  (ii) Give the reagents that are used to test that bromide ions are formed in this reaction mixture. Include the result of the test.

(4marks)

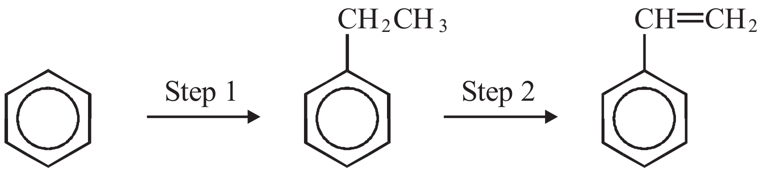
(b) Is the conversion of propane to 1-bromopropane single step or multi-step? Give brief explanation to defend your answer and show how the conversion is carried out.

(2.5marks)

(c) Benzene reacts with nitric acid in the presence of a catalyst to form nitrobenzene.
  (i) Write an equation for the overall reaction.
  (ii) State the name of the catalyst used.
  (iii) Write the formula, including its charge, of the electrophile involved in the reaction.
  (iv) State the type of reaction involved.

(2marks)

(d) In industry, phenylethene is made from benzene and ethene in a two-step process:



(i) Give one major use of phenylethene.
(ii) Identify the reactive species which attacks benzene in Step 1 and write an equation to show how this species is generated.
(iii) Name the type of reaction which occurs in Step 2.

(2marks)

(e) Account for the following facts:
(i) Most of chemical reactions of benzene are electrophilic substitution reactions.
(ii) Acylation reaction occurs in lower temperature in aniline than in chlorobenzene.
(iii) Nitration of haloalkane by potassium nitrite gives alkyl nitrites while nitration of the same compound by silver nitrite gives nitroalkane.

(4.5marks)

Question 10

(a)
(i) In what form is phosphorous absorbed by plant roots?
(ii) How the absorption of phosphorous by plant roots affected by soil pH?
(iii) Name the four functions of phosphorous in plants
(iv) Give the names of two phosphorous –based synthetic fertilizer

(3marks)

(b)
(i) What are soil colloids?
(ii) What role do colloids play in the soil?
(iii) List down any five properties of soil colloids.

(4marks)

(c) Ten grams of oven dry soil were shaken in $20cm^3$ of 0.1M hydrochloric acid solution. The mixture was then filtered and the soil thoroughly washed in distilled water; the filtrate and washings were neutralized by $12cm^3$ of 0.1M sodium hydroxide. If the total cation exchange capacity of the soil is 25mill-equivalentts per 100g of oven dry soil, calculate the percentage base saturation of the soil.

(7marks)

Examination Four
CHEMISTRY 2B

Answer **five (5)** questions

Question 1

(a)

(i) What is the solvent extraction?

(ii) Explain two conditions for solvent for solvent extraction to be more successful.

(3marks)

(b)

(i) What are immiscible liquids

(ii) Outline two important characteristics of immiscible liquid system

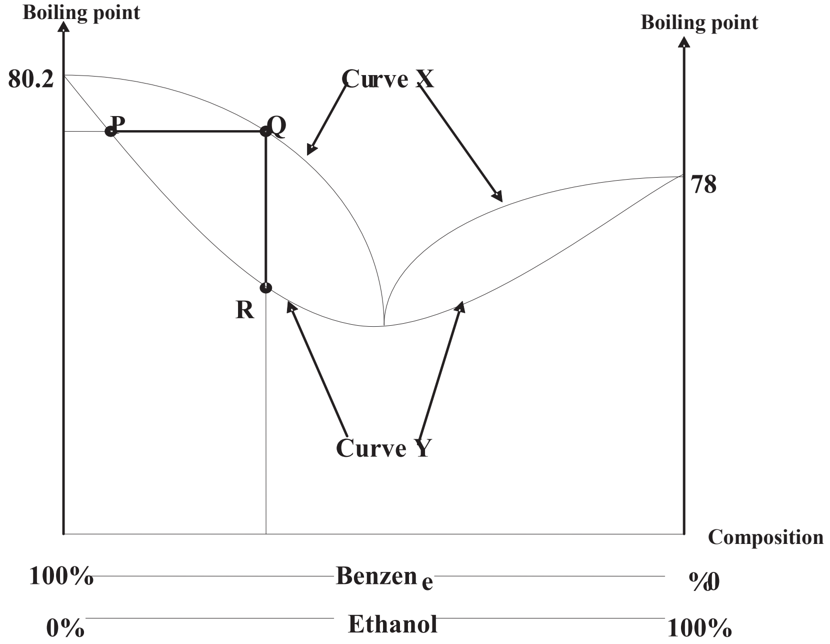
(iii) Liquid immiscible with water can be efficiently separated from their mixture with water through steam distillation. State any two conditions necessary for steam distillation to be efficient.

(2marks)

(c) An organic acid liquid distills in steam. The partial pressure of the two liquids, i.e. an organic acid and water at the boiling point are 5.3kPa and 95kPa respectively. If the distillate contains the organic to water mass ratio of 0.48, calculate the molar mass of the organic acid.

(4marks)

(d) The diagram below illustrates the boiling point- composition relationship for benzene – ethanol system.



(i) What do the curves **X** and **Y** represent?

(ii) What is the relation between **P**, **Q** and **R**

(iii) From the above boiling point-composition diagram, sketch labelled diagram to illustrate the vapour pressure - composition relationships for the benzene –ethanol system.

(5marks)

(e) The vapour pressure of ethanol at 20°C is 43.6mmHg while that of benzene at the same temperature is 75.2mmHg. The mole fraction of benzene is 0.09 for a mixture of benzene and ethanol at 20°C. Calculate the:

(i) Total vapour pressure of the mixture
(ii) Mole fraction of benzene in vapour phase

(4marks)

Question 2

(a) For each of the following statement, say whether you **agree** or **disagree** with the given argument and give brief explanation to defend your response:
(i) Rate of every reaction is fovoured by change in concentration.
(ii) Rate constant can be affected by temperature only.
(iii) Every chemical reaction involving gaseous reactants is favoured by high pressure.
(iv) Exothermic reactions are always fast reactions.

(6marks)

(b) Manganate (VII) ions, MnO_4^-, reacts with ethanedioate ions in acid solution.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

The reaction starts slowly, the rate of reaction then increases, before it decreases again. Explain this sequence.

(3marks)

(c) A salt bridge is used to connect the two half-cells.
(i) State what chemical is contained in the salt bridge.
(ii) Give a possible reason why the salt bridge cannot be replaced by an unreactive metal wire.

(3marks)

(d) $50cm^3$ of solution of hydrogen peroxide were diluted to $1dm^3$ with water. $25cm^3$ of this solution, when acidified with dilute sulphuric acid, needed 20.25cm^3 of $0.02MKMnO_4$ on the titration.
(i) What is the concentration of the original hydrogen peroxide in $moldm^{-3}$?
(ii) Why $NaMnO_4$ should not be used as an oxidant in this experiment? What would be the effect on the value of the obtained titre volume if $NaMnO_4$ would be used instead of $KMnO_4$?
(iii) Why concentrated sulphuric acid should not be used as an acidic medium in this experiment? What would be effect on the obtained titre volume if concentrated sulphuric acid would be used instead of dilute sulphuric acid?

(8marks)

Question 3

(a) State Bronsted – Lowry theory of acids and bases and hence list down at least four advantages of the Bronsted – Lowry concept over the Arrhenius concept.

(3marks)

(b) When excess magnesium hydroxide is added to water and shaken, a saturated solution is formed and the mixture reaches equilibrium;

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

The solubility product, $\mathrm{K_{sp}}$ for this process is;

$$\mathrm{K_{sp} = [Mg^{2+}(aq)][OH^-(aq)]^2}$$

(i) Give a reason why the magnesium hydroxide is not included in the expression for $\mathrm{K_{sp}}$.

(ii) Derive units of $\mathrm{K_{sp}}$

(3marks)

(c) The pH of 10^{-2} MHCl is 2 and that of 10^{-3} MHCl is 3. However the pH of 10^{-9} MHCl is not equal to 9. Suggest an explanation for this observation and hence calculate the pH 10^{-9} MHCl.

(6marks)

(d) An unknown student taken an unknown weight of an unknown weak monobasic acid, dissolves it in an unknown amount of water, and titrates it with a strong monoacid base of unknown concentration. When he has added 10.00mL of base, he noticed that the concentration of $\mathrm{H_3O^+}$is 1.0×10^{-5}M. He continues the titration until he reaches the equivalent point. At this time burette reads 22.22mL. What is the dissociation constant of acid?

(8marks)

Question 4

(a) **Electronegativity** difference is very important in determining degree of ionic characters in the covalent bonded molecule. **Oxidation number** may help to measure electronegativity difference between two covalent bonded atoms.

(i) Define the terms: electronegativity and oxidation number.

(ii) What is the relationship between the electronegativity difference and the percentage of ionic characters in the covalent bonded molecule?

(iii) How the electronegativity difference between two covalent bonded atoms can be deduced from their oxidation numbers?

(iv) Why noble gases do not have electronegativity value?

(v) List down at least two differences between oxidation number and valence number.

(5marks)

(b) An inorganic salt **A** contains one cation and one anion. The results of two tests on salt **A** are shown in the table.

Test	Observation
Add aqueous sodium hydroxide to solid **A**. Warm the mixture. Test any gas evolved with damp red litmus paper.	A gas was evolved. The gas turned red litmus paper blue.
Add dilute nitric acid followed by aqueous silver nitrate to an aqueous solution of **A**.	A cream precipitate formed.

(i) Deduce the **cation** and **anion** and hence the **name** of salt **A.**

(ii) Describe additional tests, with the results, that will confirm the identity of the **anion** in the cream precipitate.

(iii) Give the balanced chemical equation to show the reaction between salt A and aqueous sodium hydroxide.

(6marks)

(c) Lithium is the first element in group of alkali metals. Like other first elements in other groups of modern periodic table, properties of lithium are peculiar compared to other alkali metals.

(i) Why properties of first element in the group, are always different compared to other members?

(ii) List down at least five differences between lithium and other alkali metals.

(iii) Explain why:

A. Lithium cannot form peroxide like other alkali metals

B. Unlike other alkali metals, lithium can form nitride

(iv) List down at least four diagonal relationships between lithium and magnesium.

(9marks)

Question 5

(a) Give reason(s) for the following facts concerning transition elements.

(i) Transition metals are very hard compared to s – block metals.

(ii) Transition elements have almost the same atomic radii.

(iii) Transition metals have tendency to form interstitial compound.

(iv) Transitional metals and their compounds are commonly used as catalysts.

(6marks)

(b) Iodide ions, , reacts with peroxodisulphate (VI) ions, $S_2O_8^{2-}$**;**

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

The reaction is catalysed by iron (II) ions, $Fe^{2+}(aq)$.

With help of ionic equations, explain how iron (II) ions act as catalyst in this reaction.

(4marks)

(c) Give at least one example of each of the following:

(i) Natural polymer

(ii) Thermosetting polymer

(iii) Elastomer

(iv) Fiber **(2marks)**

(d) Give structure(s) of monomer which gives the following polymer in the polymerisation:
  (i) PVC
  (ii) Polystyrene
  (iii) Nylon-6,6
  (iv) Dacron

(4marks)

(e)
  (i) Give the structure of repeating unit in terylene and state the type of polymerisation involved during its formation.
  (ii) Give the structure of repeating unit in poly (phenylethene) and state the type of polymerisation involved during its formation.
  (iii) Explain why dilute sodium hydroxide will cause holes to appear in clothing made from polymers such as terylene but a poly (phenylethene) container can be used to store sodium hydroxide.

(4marks)

Question 6

(a) Give a chemical test to distinguish between:
  (i) Methyl methanoate and methyl ethanoate
  (ii) N-methylethanamine and N,N –dimethylethanamine

(2marks)

(b) Give reason(s) for the following:
  (i) Phenylamine undergoes nitration more readily than benzene carbaldehyde.
  (ii) Propanone gives positive iodoform test but not propan-1-ol.
  (iii) Propanone is less readily attacked by nucleophile than propanal.

(**3.5marks**

(c) An organic compound P was boiled with dilute H_2SO_4 to produce an acid Q which was monobasic. Q was esterified with ethanol to give an ester R of molecular mass 150. Compound Q can undergo reduction to form S. Give the structural of formula of P, Q, R, and S.

(6 marks)

(d) Compound **A** which has unbranched carbon chain, react with methyl magnesium bromide to give after hydrolysis compound **B**. Chromic acid oxidation of **B** gives $\mathbf{C(C_2H_5O)}$ which give crystalline product with 2,4-dinitrophenylhydrazine and positive iodoform test.
  (i) Give formula of A,B and C and equation for all reactions mentioned
  (ii) Give the formula of possible isomer of A that would give the same result as A in the above transformation.

(8.5marks)

Examination Five

CHEMISTRY 1C

SECTION A

Answer **all** questions in this section.

Question 1

(a) Give the meaning of following terms:
   (i) Nuclides
   (ii) Isotones
   (iii) Isotopes

(1.5marks)

(b) The nucleus of certain element is presented as $^{15}_{7}\mathbf{X}$**.** Clearly deduce the number of each of the fundamental particles in atom **X**.

(1.5marks)

(c) With reference to calcium at ground state, how many electrons have the following quantum numbers?
   (i) $n = 3$
   (ii) $m_l = 0$
   (iii) $l = 1$

(3marks)

(d) Paul Exclusion principle may be stated as; *"No two electrons in an atom may have all four quantum numbers the same."* Explain two pieces of information which may be extracted from the principle.

(2marks)

(e) The first ionisation energy of sodium atom is 145.684kJ/mol. Calculate the wavelength of electromagnetic radiation in angstrom which is sufficient to ionize the atom.

(2marks)

Question 2

(a) Explain what is meant by:
   (i) Intermolecular hydrogen bonding by using hydrogen fluoride as an example.
   (ii) Intramolecular hydrogen bonding by using 2-nitrophenol as an example.

(3marks)

(b) Arrange the following entities in order of increasing bond angle between a non-central atom, the central atom and a non-central atom: carbonate ion, carbon tetrachloride molecule, water molecule and hydrogen cyanide molecule.

(2marks)

(c) Explain the difference in size of bond angle in H_2O, NH_3 and CH_4.

(2marks)

(d) Indicate the type of hybridisation of orbitals by the central atom in each of the following:
   (i) SO_3^{2-}
   (ii) SCl_2
   (iii) CO_3^{2-}

(3marks)

Question 3

(a) Provide the meaning of the following terms with reference to gases:

(i) Critical temperature
(ii) Critical volume
(iii) Critical pressure **(1.5marks)**

(b) When an open flask containing air is heated from $27°\mathrm{C}$ to $87°\mathrm{C}$, what percentage of the air in the flask is expelled? Assume that the volume of the flask and atmospheric pressure are constant.

(4marks)

(c) The Van der Waals equation of state for one mole of real gas is as follows:-

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

For any given gas, the values of the constants, **'a'** and **'b'** can be determined experimentally.

(i) Indicate which physical properties of molecule determine the magnitudes of the constants **'a'** and **'b'**
(ii) Which of the two molecules, H_2 or H_2S , has the higher value for **'a'** and which has the higher value for **'b'**? Explain
(iii) One of the Van der Waals constants can be correlated with the boiling point of a substance. Specify which constant and how it is related to the boiling point

(4.5marks)

Question 4

(a)

(i) Is molarity or molality dependent on temperature? Explain your answer.
(ii) Why is molality and not molarity used in mathematical equations describing the amount of freezing point depression and boiling point elevation?
(iii) Why is the observed freezing point for electrolyte sometimes less than the calculated value?
(iv) Is the discrepancy in (iii) above, greater for concentrated or diluted solution? Explain.

(5marks)

(b)

(i) Define the following two terms: osmotic pressure and reverse osmosis.
(ii) Calculate the osmotic pressure at $25°\mathrm{C}$ of a suspension containing $60\mathrm{g/L}$ of solid particles each particle having a mass of 10^{-9}g.

(5marks)

Question 5

(a) Write chemical equation to show action of heat in the following compounds:

(i) $Zn(OH)_2$
(ii) K_2CO_3
(iii) $CuSO_4$
(iv) $Mg(NO_3)_2$

(2marks)

(b) Explain the following:

(i) It is inappropriate to name $B(OH)_3$ as boron hydroxide.
(ii) Although calcium can displace hydrogen from dilute acids, calcium sulphate cannot be prepared by displacement method.
(iii) Molecules of $BeCl_2$ can associate to polymer while molecules of $AlCl_3$ can only associate to dimer.
(iv) All metal nitrates are soluble in water.

(4marks)

(c) Explain clearly two major uses of metal nitrates. In each case state the feature that makes nitrate suitable for such use.

(4marks)

Question 6

(a) What is the meaning of the following terms:
(i) Enthalpy of reaction
(ii) Standard enthalpy of neutralization
(iii) Enthalpy of atomization
(iv) Standard enthalpy of combustion

(4marks)

(b)
(i) Given the following standard enthalpies of combustion, ΔH_f^θ:
$C(s) = -393kJ/mol; H_2(g) = -285.6kJ/mol$
$C_2H_6(g) = -1560kJ/mol$
Calculate the standard enthalpy of formation of ethane.
(ii) Given the following bond enthalpies (Bond energies in kJ/mol;
$C-H\ 412; C-C\ 347; O-H\ 464; O=O\ 498;$
$C=O\ 805\ (\text{for } CO_2 \text{only}); C-O\ 358$
Calculate the enthalpy of combustion of ethane (assuming all species are gaseous) and explain why do you not get value of – 1560kJ/mol as given in data of a (i) above?

(6marks)

Question 7

(a) With an example in each case, define the following:
(i) Physical equilibrium
(ii) Chemical equilibrium

(2marks)

(b) Consider the production of HI by direct combination between I_2 and H_2 as per question;

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Can you alter the yield of HI at equation by adding hydrogen gas or decreasing the volume of the container? Explain.

(3marks)

(c) For the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
Equilibrium mixture contains NO_2 with partial pressure of 1.1atm and N_2O_4 with partial pressure of 0.28atm at 350K.The volume of the container is doubled. Calculate the equilibrium pressure of the two gases when the system reaches new equilibrium.

(5marks)

SECTION B

Answer **any two** questions from this section

Question 8

(a) Give the meaning of the following:
  (i) Steric hindrance
  (ii) Peroxide effect
  (iii) Tautomerism
  (iv) Skeletal isomers

(2marks)

(b) Write equations for the following reactions:
  (i) Propane and chlorine gas in presence of ultra-violet light
  (ii) Ethene and dilute sulphuric acid
  (iii) Ethyne and chlorine water

(3marks)

(c) **Musa** intended to prepare pentane by Wurtz reaction as per equation:

$$CH_3CH_2Br + CH_3CH_2CH_2Br + 2Na \xrightarrow{\text{Dry ether}} CH_3CH_2CH_2CH_2CH_3 + 2NaBr$$

  (i) What is the Wurtz reaction?
  (ii) Why ether solution should not be used in the Wurtz reaction?
  (iii) Write equations to show the formation of the other two products and hence say if the method for preparation of pentane was correct or not?
  (iv) Is the method suitable for preparation of methane? Explain.

(5marks)

(d) In dichlorination of propane, four isomeric products with formula of $C_3H_6Cl_2$ were isolated and designated **A**…………..**D.** Each was separated and further chlorinated to give one or more trichloropropanes, $C_3H_6Cl_3$. **A** and **B** give three chloro compounds, C give one and D give two
  (i) Deduce structures of **C** and **D**
  (ii) One of the products of **A** was identical with product from further chlorination of C. suggest structures of **A** and **B**.

(5marks)

Question 9

(a) Briefly explain the following:
  (i) The $C - C$ bonds are all equal and intermediate in length between a single and double bond in benzene.
  (ii) Dry ether is necessary in the preparation and use of the Griginard reagent.
  (iii) The ease for nucleophilic substitution reaction of alkyl halide, $R - X$, with OH is in the following order:

$$R - I > R - Br > R - Cl > R - F$$

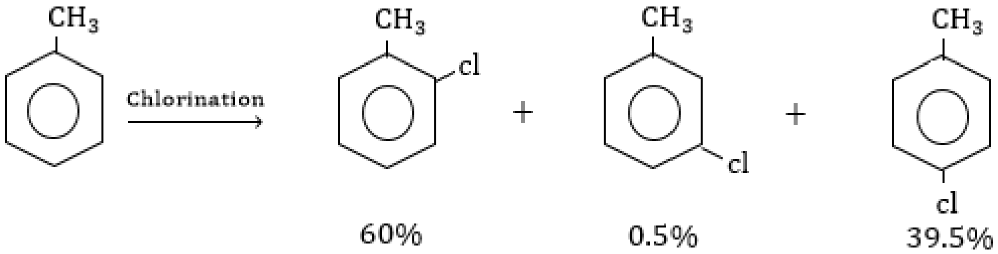
  (iv) $(CH_3)_3CBr$ reacts by S_N1 mechanism while CH_3CH_2Br reacts by S_N2 mechanism.

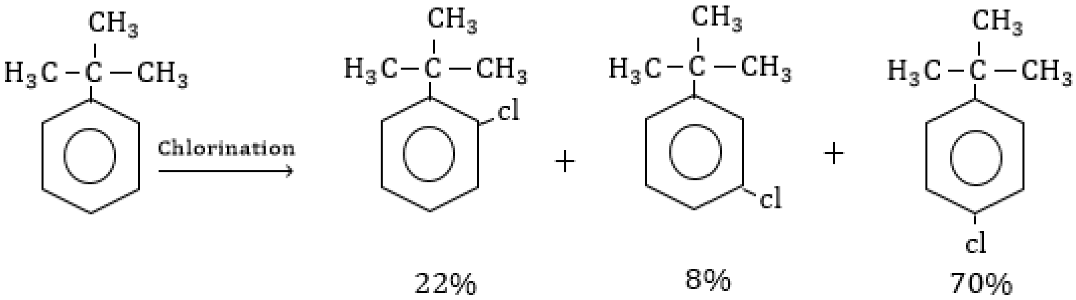
(7marks)

(b) Show mechanism of sulphonation of benzene and hence gives overall reaction equation.

(4marks)

(c) The chlorination of methylbenzene and 1,1,1-trimethyltoluene yield the following isomers:





Study the isomers and then explain the observed different product ratio.

(4marks)

Question 10

(a) Before damping, it is important for sewage to be firstly treated either physically or chemically. The selection of treatment process for hazardous waste stream depends on various factors including the nature of waste. Below are hazardous chemicals which you are required to suggest a chemical treatment (with help of chemical equation(s) in each case) for the hazardous chemical contained in the sewage.

(i) Cyanides
(ii) Cr^{3+}
(iii) Pb^{2+}
(iv) Nitric acid
(v) Calcium carbide

(10marks)

(b) What do you understand by the following terms?

(i) Saline soil
(ii) Cation exchange capacity

(1mark)

(c) Piece of land requires 120kg of nitrogen (N) and 60kg of phosphorous (P) to be applied per hectare. What amount of each fertilizer will be needed to be applied per hectare on piece of land if the following fertilizers are available?

(i) Sulphate of ammonia (21%N)
(ii) Single superphosphate (18%P)

(4marks)

Examination Six
CHEMISTRY 2C

Answer **five (5)** questions

Question 1

(a)

(i) State Raoult's law

(ii) Identify whether the mixture of nitric acid and water shows positive or negative deviation from Raoult's law.

(iii) What interaction between nitric acid and water leads to this type of deviation?

(iv) With reference to Raoult's law, distinguish positive deviation from negative deviation. **(5marks)**

(b) On your own words, what do you understand by the following terms?

(i) Vapour tension

(ii) Saturated vapour pressure

(iii) Azeotrope

(1.5marks)

(c) Explain how an increase in temperature, increases vapour pressure of a liquid. **(1.5marks)**

(d)

(i) Define boiling point of liquid?

(ii) How boiling point is affected by external pressure?

(iii) Calculate the boiling point (at 1atm) of a solution containing 116g of acetone (MWt = 58) and 72g of water (Mwt = 18) by using data in the following table:

Table: Vapour pressure of acetone and water

Temperature(°C)	Vapour pressure (atm) acetone	Vapour pressure (atm) water
60	1.14	0.198
70	1.58	0.312
80	2.12	0.456
90	2.81	0.694

(5marks)

(e)

(i) Briefly explain the principle of solvent extraction.

(ii) Compare and contrast fractional distillation from steam distillation.

(iii) Nitrobenzene ($C_6H_5NO_2$) and water form a mixture of immiscible liquids which boils at 99°C. Calculate the percentage by mass of nitrobenzene in the distillate when the mixture is distilled at 1.013×10^5Pa given that the vapour pressure of water at 99°C is 9.749×10^4Pa. Show your work clearly including manipulation of units. **(7marks)**

Question 2

(a) Give the meaning of the following terms:
- (i) Elementary reaction
- (ii) Intermediate product
- (iii) Molecularity
- (iv) Autocatalyst

(2marks)

(b) Give one reason to support or oppose each of the following:
- (i) Every reaction is fovoured by increasing temperature
- (ii) Catalysed reaction has higher activation energy than uncatalysed reaction
- (iii) Rate of reaction increase with concentration in a zeroth order reaction

(4.5marks)

(c) The equation; $K = A e^{-Ea/RT}$ is for specific reaction rate constant. Specify all the terms used and explain what each means.

(2.5marks)

(d) For each of the following reaction, suggest any two properties which can be followed in measuring the rate of its reaction.
- (i) $KMnO_4(aq) + 5H_2C_2O_4(aq) \rightarrow K_2SO_4(aq) + MnSO_4(aq) + 8H_2O(l) + 10CO_2(g)$
- (ii) $CuCl_2(aq) + 2AgNO_3(aq) \rightarrow CuNO_3(aq) + 2AgCl(l)$

(4marks)

(e) One of the dozens of reactions that may occur in a single ridden area is the linked oxidation of carbon monoxide and nitric oxide.

$$CO + NO + O_2 \rightarrow CO_2 + NO_2$$

One suggested mechanism for this reaction involves the unstable molecular fragment HO as catalysts.
- (i) Verify that these steps add to give the correct net reaction
- (ii) Identify the intermediates in the mechanism
- (iii) Tell why HO is considered to be a catalysts in this reaction path – way

(7marks)

Question 3

(a)
- (i) Ammonia is a base. What is meant by the term base?
- (ii) What feature of the ammonia molecule enables it to react as a base?
- (iii) Calculate the pH of a 0.100M solution of ammonia if its $K_b = 1.8 \times 10^{-5}M$

(3marks)

(b) Acids differ in the number of hydrogen ions that can be liberated from one molecule of the undissociated acid. Hydrochloric acid is a strong monobasic, or monoprotic acid, liberating one hydrogen ion per molecule. Sulphuric acid is a dibasic, or diprotic acid, its ionisation in aqueous solution being:

I: $H_2SO_4(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq)$ $K_a = \text{Very large}$

II: $HSO_4^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$ $K_a = 0.01moldm^{-3}$

K_a values are quoted for 25 ºC.

(i) State the hydrogen ion concentration in $0.01 moldm^{-3}$ hydrochloric acid, which is a strong acid, and hence find the pH of this solution.

(ii) State the hydrogen ion concentration of $0.1 moldm^{-3}$ sulphuric acid arising from the first stage of ionisation, **I**.

(iii) A solution of sodium hydrogensulphate, $NaHSO_4$, of concentration $0.1\ moldm^{-3}$, ionises according to equation **II** above. Find the hydrogen ion concentration in this solution, and **hence** state what you would expect the hydrogen ion concentration in $0.1 moldm^{-3}$sulphuric acid to be.

(iv) In fact the pH of 0.1 $moldm^{-3}$sulphuric acid is about 0.98. This indicates a hydrogen ion concentration of 0.105 $moldm^{-3}$. By considering the reactions **I** and **II** in the presence of one another explain why this is so. You are not expected to perform any further calculations.

(5marks)

(c) Calculate the depression in freezing point of water when 10g of $CH_3CH_2CHClCOOH$ is added to 250g of water. $K_a = 1.4 \times 10^{-3}, K_f = 1.86$

(4marks)

(d) Solution of unknown monobasic acid was titrated with the base and equivalent point reached when 36.12mL of 0.1MNaOH had been added. The 18.06mL of 0.1MHCl were added to the solution and the measured pH was found with pH meter to be 4.92. Calculate the dissociation constant of unknown acid.

(8marks)

Question 4

(a)

(i) What is the meaning of the representative elements?

(ii) Name the groups of the periodic table, which contain representative elements.

(2.5marks)

(b) Which one of the following pairs of elements would have higher electron gain enthalpy?

(i) Phosphorous or sulphur

(ii) Fluorine or chlorine

In each case give reason for your choice

(3marks)

(c) Properties of lithium are anomalous. Justify this statement.

(5.5marks)

(d) Account for the following:

(i) Trend of atomic radius in transition elements is quite difference to that of typical elements.

(ii) Potassium ion has smaller size than chloride ion even though they have the same number of electrons.

(2marks)

(e) Describe the electrolytic purification of copper under headings:

(i) The chemical nature of the electrodes
(ii) The chemical nature of the electrolytes
(iii) The redox reaction involved

(7marks)

Question 5

(a) Give the meaning the following terms:
(i) Depolymerisation
(ii) Biopolymers
(iii) Oligomer
(iv) Polyester

(2marks)

(b) Give at least one example of :
(i) Homopolymer
(ii) Copolymer
(iii) Polyester
(iv) Polyamide

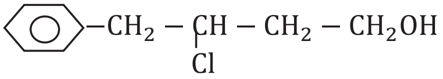
(2marks)

(c) Discuss briefly vulcanisation of rubber under the following headings:

(i) Meaning
(ii) Importance
(iii) How the process is carried out

(9marks)

(d) Refer to the structural formula of compound **A** below;



Write chemical equation to show the reaction which will take if compound **A** is mixed with:

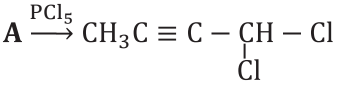
(i) Magnesium turnings in presence of dry ethyl ethoxide then warmed

(ii) Concentrated sulphuric acid at 0°C
(iii) Aqueous solution of sodium hydroxide at 25°C
(iv) Chlorine gas and iron(III) chloride at 25°C
(v) Sodium ethoxide at 55°C
(vi) Acetic and concentrated sulphuric acid then warmed
(vii) Concentrated nitric acid and concentrated sulphuric acid at room temperature

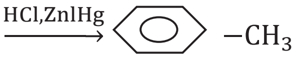
(7marks)

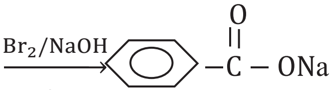
Question 6

(a) Identify by giving structural formula of organic compound **A** to **D**

(i) 

$$\mathbf{A} \xrightarrow{PCl_5} CH_3C \equiv C - \underset{\substack{| \\ Cl}}{CH} - Cl$$

(ii) **B** 

(iii) **C** 

(iv) **D** $\xrightarrow[\Delta]{Br_2/OH^-}$ $CH_3CH_2NH_2$

(4marks)

(b) Account for the following:

(i) Benzoic acid is stronger acid than ethanoic acid
(ii) Presence of α-hydrogen is necessary for aldehyde to undergo aldol condensation reaction
(iii) Boiling point of trimethylamine is 3°C while that of dimethylamine is 6°C.
(iv) Aniline has larger pK_b value than ethylamine.

(6marks)

(c) Give product(s) of the following organic reactions:

(i) $CH_3COCH_3 + CH_3CHO \xrightarrow{OH^-}$
(ii) $\text{Acetic acid} + \text{Brady's reagent} \longrightarrow$
(iii) $\text{Ethylbenzene} + \text{Acidified potassium permanganate} \longrightarrow$

(4marks)

(d) Give a chemical test to distinguish between:

(i) Phenol and aniline
(ii) Phenol and benzoic acid
(iii) Ethanedioic acid and succinic acid
(iv) Ethanamine and N-methylmethanamine

(6marks)

Examination Seven

CHEMISTRY 1D

SECTION A

Answer **all** questions in this section.

Question 1

(a) Provide the meaning of the following:
  (i) Atom
  (ii) Element

(1mark)

(b) What is the relationship between the two terms in (a) above?

(1.5 mark)

(c) X is the hypothetical element with two isotopes; ^{m}X and ^{n}X. If the element, X exists as triatomic molecule, X_3, explain how many peaks the element will show in its mass spectrum.

(3.5 marks)

(d)
  (i) How does the atomic spectrum differ from continuous spectrum?
  (ii) Calculate the wave number for the longest wavelength in the Balmer series of atomic hydrogen.

(4marks)

Question 2

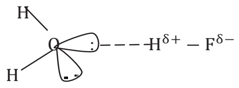
(a) In molecular orbital terms, describe bonding in methane.

(4marks)

(b) The water molecule is polar, explain how does this offer experimental proof that the molecule cannot be linear?

(2.5marks)

(c) The diagram below show how a water molecule interacts with hydrogen fluoride molecule.



  (i) What is the value of the bond angle in a single molecule of water?
  (ii) Explain your answer to part (i) by using the concept of electron pair repulsion
  (iii) Explain the origin of the δ^{+} charge shown on the hydrogen atom in the diagram.
  (iv) When water interacts with hydrogen fluoride, the value of bond angle in water change slightly. Predict how the angle is different from that in a single molecule of water and explain your answer.

(3.5marks)

Question 3

(a) Which of the following gases would be nearly impossible to collect over water? Why?
CO_2, HCl, CH_4, NH_3

(2marks)

(b) A mixture of excess carbon monoxide and oxygen gas was allowed to diffuse through a porous diaphragm (after their reaction) in one half the time taken for the same volume of bromine vapour to diffuse through the same diaphragm. What is the composition by volume of the mixture?

(4marks)

(c) A certain dry gas is composed of 21% by volume of oxygen, 1% of argon and 78% of nitrogen. Find its density in grams per dm^3 at $20^\circ\mathrm{C}$ and $98.65\mathrm{kNm}^{-2}$ pressure.

(4marks)

Question 4

(a) What do you understand by the following:
  (i) Cryoscopic constant
  (ii) Colligative properties
  (iii) Mole fraction of a solute in a solution

(1.5marks)

(b) Briefly explain with reason(s) whether the osmotic pressure method would be satisfactory for determining relative molecular mass of ethanoic acid in a concentrated solution of the acid in a suitable solvent.

(1.5marks)

(c) The freezing point of pure benzene was found to be $5.481^\circ\mathrm{C}$. A solution of $0.21\mathrm{g}$ of hydrocarbon naphthalene (C_8H_8) in 25g of this benzene began to freeze at $4.971^\circ\mathrm{C}$. A solution of 0.305g of benzoic acid in 25g of the same solvent began to freeze at $5.226^\circ\mathrm{C}$.
  (i) Calculate the molar freezing point depression constant for 1000g of benzene.
  (ii) Calculate the relative molecular mass of benzoic acid in benzene solution and hence clearly explain the state of benzoic acid in the benzene.

(7marks)

Question 5

(a) Define the term deliquescence and explain what makes a hydrated salt to deliquescence.

(1.5marks)

(b) List down at least three useful applications of sulphates. Give at least one example for each.

(4.5marks)

(c) Using chemical equation, explain the following:
  (i) The test to distinguish between sodium carbonate and bicarbonate.
  (ii) The Brown ring test.

(4marks)

Question 6

(a) State the following:
  (i) Heat of reaction
  (ii) Exothermic reaction
  (iii) Endothermic reaction

(1.5marks)

(b) 1.5 g of ammonium nitrate (NH_4NO_3) was added to 35 g of water in a plastic beaker and stirred until the salt is dissolved. The temperature of the solution dropped from $22.7°C$ to $19.4°C$. Basing on the given information respond to the following:

(i) Is the process endothermic or exothermic? Explain.

(ii) Calculate the heat of solution of NH_4NO_3 in kJ/mol; given that specific heat capacity of water is $4.184J/g°C$.

(5.5marks)

(c)

(i) State Laplace law

(ii) If the heat of combustion data for diamond and graphite is $-395.4kJ/mol$ and $-393.5kJ/mol$ respectively. Calculate the heat of transition of diamond to graphite.

(3marks)

Question 7

(a)

(i) Briefly explain the dynamic nature of equilibrium reaction.

(ii) Use hydrogen (H_2) and iodine (I_2) gases which produce hydrogen iodide (HI) gas to illustrate the point mentioned in (a)(i)

(6marks)

(b) At temperature near $8000°C$, steam is passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The mixture of gases that results is an important industrial fuel called water gas. At $880°C$, the equilibrium constant for this reaction is $K_P = 14.1$. What are the equilibrium partial pressures of H_2O, CO and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.1000 mol of H_2O in a 1L vessel?

(4marks)

SECTION B

Answer **any two** questions from this section

Question 8

(a) What is the meaning of the following terms?

(i) Nucleophile

(ii) Electronic effect

(iii) Enantiomers

(iv) isomers

(2marks)

(b) The following names are incorrect according to IUPAC system. Give the structural formula and correct names as per IUPAC.

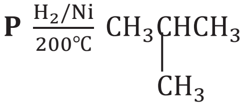
(i) $3-$methylbutane

(ii) $2-$isopropylpropane

(iii) 4 – methylpent – 1 – ene
(iv) 1 – ethyl – 2,2 – dimethylpropane
(v) 2 – propylbut – 2 – ene

(5marks)

(c) Identify by giving structural formula of organic compound **P** and **Q**.

(i) 

$$\mathbf{P} \xrightarrow[200^\circ C]{H_2/Ni} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$$

(ii) $\mathbf{Q} \xrightarrow{H_2O, H_2SO_4, HgSO_4} CH_3 - CO - CH_3$

(2marks)

(d) $10cm^3$ of a gaseous hydrocarbon Q required $45cm^3$ of oxygen for complete combustion. Q reacts with 1 mole of bromine to give a compound of relative molecular mass of 200.02 which contains 79.2% bromine.

(i) Determine the molecular formula of Q
(ii) Give the structural formula of Q

(6marks)

Question 9

(a)

(i) Briefly explain the reaction which involves the replacement of chlorine from 1-chlorobutane by hydroxyl group.
(ii) Give the mechanism for the reaction above and indicate in what ways it differ from the mechanism for corresponding reaction with its isomer 2-chloro-2-methylpropane.
(iii) For each of reaction mechanism in (ii) above, list down three conditions which favour the formation of products.

(6marks)

(b) With the support of chemical reactions, show how the following compounds can be prepared from ethanol as sources of carbon atoms:

(i) Benzene
(ii) Ethylbenzene

(6marks)

(c) As benzene substituents, halogens are exceptional to the general deactivating rules of substituents in benzene. Briefly explain this unusual influence of halogens in benzene.

(3marks)

Question 10

(a) Under the landfill directive of **Iringa municipal council,** the amount of **biodegradable** waste going to landfill is to be reduced by 50% after 10years.

(i) What is the meaning of biodegradable?
(ii) State at least two advantages of the decomposition of biodegradable waste.

(3marks)

(b) One advantage of waste incineration is the recovery of energy.

(i) How may the recovered energy be used?
(ii) Explain the need of temperature control during the incineration of some wastes.

(3marks)

(c) The **greenhouse effect** is often largely associated with carbon dioxide although many other gases are able to make a more substantial contribution. The compound CCl_2F_2 commercial known as CFC-12 has relative greenhouse effect 25000 times greater than that a carbon dioxide. CFC-12 can also be involved in process that damages the ozone layer.

(i) Explain the **greenhouse effect.**

(ii) Why is carbon dioxide considered to make significant contribution to greenhouse effect?

(iii) Approximately 79% of the atmosphere consists of nitrogen. Explain why this does not contribute to the greenhouse effect.

(iv) Suggest why CFC-12 has a large relative greenhouse effect.

(v) Write an equation to show how CFC-12 produces a free radical which will attack the ozone layer and hence show mechanism of ozone depletion resulting from the produced radical. Deduce the overall balanced reaction equation from the mechanism.

(9marks)

Examination Eight
CHEMISTRY 2D

Answer **five (5)** questions

Question 1

(a) What is the meaning of the following?
   (i) Saturated vapour pressure
   (ii) Raoult's law
   (iii) Azeotropic point
   (iv) Ideal solution

(2marks)

(b) When liquid A is mixed with liquid B to form a solution at room temperature, the solution becomes warm to the touch. Does this suggest a positive or negative deviation from Raoult's law? Explain

(2marks)

(c) Liquid M and N forms two components ideal solution when they are mixed together. The graph of the vapour pressure of the solution against mole fraction of M was found to obey the following equation;

$P = -150x + 600$ (At $10°C$)

Where P is the vapour pressure of the solution in mmHg; x is the mole fraction of M. Find the following
   (i) Mole fraction of N when the vapour of the solution is 495mmHg
   (ii) The vapour pressure of pure component which is less volatile
   (iii) Vapour pressure of pure component which is more volatile
   (iv) The amount of atmospheric pressure needed to boil the solution with mole fraction of M, 0.1 at $10°C$

(6marks)

(d) Explain why addition of 1mol of NaCl to 1L of water, increases the boiling point of water, while addition of 1mol of methyl alcohol to 1L of water decreases its boiling point.

(2marks)

(e)
   (i) Show how the equation of partition law of solute **'x'** dissolved in two immiscible solvents **A** and **B** will be represented when solute **'x'**:
      A: Associate in solvent **A** and remain normal in solvent **B**
      B: Dissociate in solvent **A** and associate in solvent **B**
      C: Dissociate in solvent **B** and remain normal in solvent **A**
   (ii) 50g of acid are dissolved in 1L of water. The distribution coefficient, K_d, of acid between ether and water is 3.

That is $K_d = \frac{\text{concentration of acid in ether}}{\text{concentration of acid in water}} = 3$

A volume of $1000cm^3$ of ether is available for the use in the extraction process. Two experiments were performed to extract acid from water. In the first experiment, $1000cm^3$ of ether was used once in single extraction. In the second experiment, two extractions were performed, each using $500cm^3$ of ether. Compare the amounts of acid left in the aqueous solution in each case and recommend the best method to extract the acid from water.

(iii) Strictly, the distribution coefficient given in (ii) above is not correct. What is the main reason of this?

(8marks)

Question 2

(a) How the following are related to the rate of chemical reaction?

(i) Collision frequency
(ii) Collision energy
(iii) Activation energy

In each case say how can each of these be changed in a chemical system?

(5marks)

(b)

(i) What is meant by the term order of reaction?

(ii) The rate constant of a reaction is $1.2 \times 10^{-2} \mathrm{Lmol^{-1}s^{-1}}$; what is the order of the reaction?

(2marks)

(c) Changing the temperature and no other conditions changes the rates of most chemical reactions. Two factors are commonly cited as accounting for the increased rate of chemical reaction as the temperature is increased. State and briefly discuss the two factors.

(3marks)

(d) Would you use an oxidising agent or reducing agent in order for the following reactions to occur?

(i) $NO_3^- \rightarrow NO_2$
(ii) $MnO_4^- \rightarrow Mn^{2+}$
(iii) $Cr_2O_7^{2-} \rightarrow Cr^{3+}$
(iv) $Mg \rightarrow MgSO_4$

(2marks)

(e)

(i) Use the data below to explain why copper (I) ions disproportionate in aqueous solution, but silver (I) ions do not.

	E^θ/V
$Ag^{2+}(aq) + e \rightarrow Ag^+(aq)$	+ 1.98
$Ag^+(aq) + e \rightarrow Ag(s)$	+ 0.80
$Cu^{2+}(aq) + e \rightarrow Cu^+(aq)$	+ 0.34
$Cu^+(aq) + e \rightarrow Cu(s)$	+ 0.52

(ii) In the light of the information in (i), suggest what you might observe when copper (I) oxide is added to excess dilute sulphuric acid and write an equation for the reaction.

(iii) Predictions from E^θ values concerning the feasibility of a reaction (as done in (i) above) are not always realised in practice. Suggest reasons for this.

(8marks)

Question 3

(a) Give the meaning of the following terms:
  (i) Solubility
  (ii) Saturated solution
  (iii) Saturated point
  (iv) Supersaturated solution
  (v) Fractional precipitation **(2.5marks)**

(b) Calculate the solubility of CaF_2:
  (i) In water
  (ii) In 0.01MNaF
  (iii) In IMHF

Given that: K_a of HF $= 5.6 \times 10^{-4}$ moldm^{-3}; K_{sp} of CaF_2 $= 4 \times 10^{-11}$ mol^{3}dm^{-9}

(7.5marks)

(c) A certain acid – base indicator has K_a of 10^{-4} with pH range of 3.4 – 4.7. The colour of ionised indicator is yellow and that of unionised indicator is red. When a half of the indicator has been ionised, the colour of the indicator becomes orange.
  (i) Define an acid – base indicator
  (ii) Calculate the pH at which the colour of the indicator is orange.
  (iii) Is the indicator suitable test for acid and base? Explain.
  (iv) Can the indicator be used to indicate the end point of the titration between strong acid and weak base or weak acid and strong a base? Give reasons for your choice.
  (v) What colour the indicator will show in 10^{-2} MHCl? Give reason(s) for your answer.

(10marks)

Question 4

(a) Justify the following:
  (i) Oxidising power of halogens decreases on descending the halogen group.
  (ii) Reducing power of hydrogen halides increases on descending the halogen group.

(4marks)

(b) Explain briefly similarities between beryllium and aluminium under the following headings:
  (i) Chlorides
  (ii) Oxides
  (iii) Carbonates
  (iv) Carbides **(8marks)**

(c) With help of chemical equation; explain the following:
  (i) Strontium does not react with dilute sulphuric acid but it reacts when the acid is concentrated.

(ii) Among earth metals only beryllium reacts with dilute sodium hydroxide.
(iii) Beryllium oxide is amphoteric while other oxides of earth metals are basic.
(iv) Silver chloride dissolves in the ammonia solution while silver bromide does not.

(8marks)

Question 5

(a) Between water and methanol, which one is stronger acid? Give reason for your choice.

(2marks)

(b) **Ambitious** wanted to prepare ethanol from ethyl chloride. She is thinking about the following possible routes:

Route 1: $CH_3CH_2Cl + KOH \longrightarrow CH_3CH_2OH + KCl$

Route 2: $CH_3CH_2Cl + H_2O \longrightarrow CH_3CH_2OH + HCl$

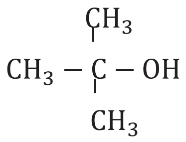
Which **route** is more successful if **Ambitious** wishes to prepare alcohol:

(i) As fast as possible
(ii) With greater percentage yield
In each case, give reason(s) for your choice.

(6marks)

(c) Complete the following organic reactions:

(i) $CH_3CH_2OH + CH_3COOH \xrightarrow{H^+}$

(ii) 

$$CH_3 - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - OH \quad + \quad I_2 + NaOH \rightarrow$$

(iii) Benzene − 1,4 − dioic acid + ethane − 1,2 − diol ⟶
(iv) Hexanedioic acid + hexane − 1,6 − diamine ⟶

(4marks)

(d) Write formula of the following complexes:

(i) Pentaamminebromocabalt(III) sulphate
(ii) Pentaamminesulphatocabalt(III) bromide
(iii) Tetraammineaquachlorocobalt(III) bromide
(iv) Tetraammineaquabromocabalt(III) chloride monohydrate

(4marks)

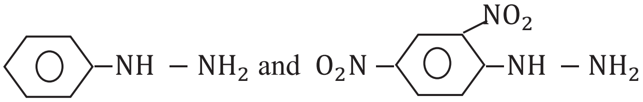
(e) In (d) above:

(i) What is the relationship between (i) and (ii)?
(ii) What is the relationship between (iii) and (iv)?
(iii) What is the coordination state of cobalt in the given compounds?
(iv) Give a chemical test to distinguish between (iii) and (iv) **(4marks)**

Question 6

(a) Give a chemical test to distinguish the following pair of organic compounds:

(i)



(ii)

$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CI_3$ and $CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CI_3$

(iii) CH_3CH_2COOH and CH_3CH_2COCl

(iv) $CH_3CH_2NH_2$ and CH_3NHCH_3

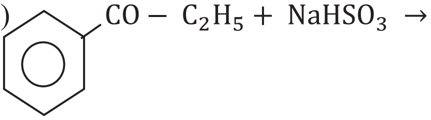
(6marks)

(b) Complete the following organic reactions;

(i) $CH_3COCH_3+NH_2-NH_2\xrightarrow{KOH(aq)}$

(ii) $CH_3\,CHO+HI\xrightarrow{\text{Red P},150°C}$

(iii)



$CO-C_2H_5+NaHSO_3\rightarrow$

(iv) $CH_3COOH+NH_3\xrightarrow[25°C]{}$

(v) $C_6H_5OH+CH_3COOH\overset{H^+}{\rightarrow}$

(6marks)

(c) A hydrocarbon R which has no geometrical isomers was found to contain 85.7% carbon and its vapour density was 28. R reacted with HCl acid to give compound S, which reacted with sodium hydroxide to give compound T. Compound T was easily oxidised by hot acidified by hot $KMnO_4$ solution to give compound U. Compound U has a positive iodoform test, it also reacted readily with Brady's reagent but was not able to reduce Fehling's solution or Tollens reagent. Identify the compounds T, R, S and U.

(8marks)

Examination Nine
CHEMISTRY 1E

SECTION A

Answer **all** questions in this section.

Question 1

(a) Provide the meaning for the following terms:
  (i) Quantum number
  (ii) Atomic spectrum
  (iii) Mass spectrometer

(1.5marks)

(b) Samples of pure silicon obtained from natural silicon ores, mined in different parts of the world, have slightly different relative atomic masses. Explain.

(2marks)

(c) Naturally occurring bromine consist of two isotopes, ^{79}Br and ^{81}Br. In determination of relative atomic mass of bromine, the following mass spectrum data was obtained, which showed peaks at masses 158, 160 and 162 a.m.u. The heights of the peaks were in the ratio of 6:1:5 respectively.
  (i) Sketch the mass spectrum data and label it properly
  (ii) Calculate the average atomic mass of bromine
  (iii) Why RAM of bromine is not a whole number
  (iv) Calculate the relative abundancies of ^{79}Br and ^{81}Br

(6.5marks)

Question 2

(a) According to octet rule, "Atoms combine together in order to attain the strong electronic configuration of noble gases". With examples, support and oppose the given statement.

(4 marks)

(b) Account for the following facts about metals:
  (i) Metals are commonly shiny coloured
  (ii) Metals are very ductile and malleable
  (iii) Metals are good conductors of electricity **(6 marks)**

Question 3

(a) Give qualitative explanation on how Boyle's law, Charles's law and Avogadro's law agree with kinetic molecular theory of gases.

(4.5 marks)

(b) From ideal gas equation, derive the relationship between density of a gas in grams per dm^3, the gas pressure in atmospheres, the temperature T in kelvin, the relative molecular mass of a gas (M_r) and the as constant, R.

(3marks)

(c) If 6.4g of CH_4 has pressure of 0.5 atm and volume of 2 litres. Find pressure of 9g of C_2H_6 having 1 litre volume under constant temperature.

(2.5 marks)

Question 4

(a) What do you understand by the following:
  (i) Colligative properties
  (ii) Freezing point
  (iii) Non-volatile solute
  (iv) Boiling point

(4marks)

(b) Briefly explain the following in terms of vapour pressure:
  (i) Boiling point of water rise due to addition of table salt.
  (ii) Freezing point of a solution is lower than that of a pure solvent.

(3marks)

(c) The freezing point depression of a 0.05molal solution of calcium nitrate in water was found to be 0.265°C. Calculate the degree of dissociation of the solute. (K_f for water $= 1.86°Cm^{-1}$)

(3marks)

Question 5

(a) Amphoteric hydroxides react with both acid and alkali.
  (i) Give an example of amphoteric hydroxide of metal.
  (ii) Write equations to show reaction between the metal hydroxide mentioned in (i) above with dilute nitric acid and with excess sodium hydroxide solution.

(3marks)

(b)
  (i) Compare solubility of carbonates and hydrogencarbonates in water.
  (ii) Describe with aid of chemical equation, how you can distinguish a hydrogencarbonate from a soluble carbonate.

(3marks)

(c) By using balanced chemical equation, show how the following chlorides may be prepared:
  (i) Iron (iii) chloride (by direct method)
  (ii) Iron (ii) chloride (by direct method)
  (iii) Potassium chloride (by indirect method)
  (iv) Calcium chloride (by indirect method)

(4marks)

Question 6

(a) Given that:

$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H^\theta = -393kJ/mol$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H^\theta = -285.6kJ/mol$

$6C(s) + 6H_2(g) \longrightarrow C_6H_{12}(l);\ \Delta H^\theta = -156kJ/mol$

Calculate the standard enthalpy of combustion of cyclohexane.

(3marks)

(b) Given the following bond enthalpies in kJ/mol;

$C-H\ 412;\ C-C\ 347;\ O-H\ 464;\ O=O\ 498;$

$C = O$ 805 (for CO_2 only); $C - O$ 358

Calculate theoretical enthalpy of combustion of cyclohexane, assuming all reactants and products are gases.

(3marks)

(c) If the enthalpy of vapourisation of water is +40.7kJ/mol and the enthalpy of vapourisation of cyclohexane is +30.0 kJ/mol, from your answer to (b), **recalculate** the enthalpy of combustion of cyclohexane.

(2marks)

(d) Compare and comment on your answers to (a), (b) and (c).

(2marks)

Question 7

(a) Concentrated sulphuric acid reacts with sodium chloride as follows: $H_2SO_4 + Cl^- \rightleftharpoons HCl + HSO_4^-$

(i) What would be observable result of this reaction?

(ii) Explain why this reaction goes almost completely to the right despite the hydrochloric and sulphuric acids are strong.

(2marks)

(b) Explain conditions applied to increase the yield of ammonia in the Haber process indicating numerical values of pressure, temperature applied and also the kind of catalyst to be used.

(5marks)

(c) Given with the equilibrium for the following reactions:

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g) \quad K_c = 10^2$$

$$2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g) \quad K_c = 10^3$$

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 10^4$$

Calculate the equilibrium constant for the following reaction

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

(3marks)

SECTION B

Answer **any two** questions from this section

Question 8

(a) Give the meaning of the following terms:

(i) Catenation

(ii) Electrophile

(iii) Carbocation

(iv) Electrophilic addition reaction

(2marks)

(b) Write structural formula for the following compounds:

(i) 4 – (1 – methylethyl)heptane

(ii) 4 – methylpent – 2 – ene

(iii) 4 – methyl – 4 – methylhex – 1 – yne

(iv) 2,2,4 − trimethylpentane

(4marks)

(c) Give a chemical test to distinguish the following pairs of organic compounds:

(i) Ethylbenzene and ethane
(ii) But-2-yne and but-1-yne

(2marks)

(d) In the bromination reaction of methane to yield halogenated methane, ethane is formed as one of the products. With the help of chemical equations, explain how the ethane is formed.

(3marks)

(e) An alcohol is prepared by the reaction between water and an alkene despite the fact that the two reagents are of the same type.
(i) Briefly explain the similarity between water and any named alkene with respect to organic reactions.
(ii) With the help of chemical equation(s) explain how the reaction for formation of alcohol from the two reagents in (d) above is made possible.

(4marks)

Question 9

(a) Indicate any reaction involving either side chain or the aromatic ring which occurs between phenylethene and
(i) H_2/Pt at 25℃
(ii) H_2/Pt at 200℃
Comment on the effect of unsaturated side chain in electrophilic substitution reaction of benzene ring.

(3marks)

(b) Explain the following:
(i) The treatment of alkyl chlorides with aqueous potassium hydroxide (KOH) leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major product.
(ii) Griginard reagents should be prepared under anhydrous conditions.
(iii) Silver nitrate solution does not precipitate the chloride in 1-chloropropene, but it does so in 1-chloropropane.
(iv) Bromine water reacts readily with hydroxybenzene but it has no reaction with benzene.

(6marks)

(c) Compound A is known to be aromatic and contains 66.4% carbon, 5.5% hydrogen and 28.1% chlorine by mass. The vapour density of pure A was found to be 63.
(i) Find the empirical formula of compound A
(ii) Find the molecular formula of compound A
(iii) Give the chemical structures of four isomers of compound A and their corresponding IUPAC names.
(iv) Which of the isomers of compound A will react with dilute KOH. Briefly explain your answer.

(6marks)

Question 10

(a) Give the meaning for the following terms as applied in soil.
  (i) Soil reaction
  (ii) Ion exchange
  (iii) Flocculation
  (iv) Soil colloids
  (v) Salinisation

(2.5marks)

(b) A certain soil contains the following cations, where all values are given in 100 gram of oven-dried soil

$Mg^{2+} = 20.0$
$Ca^{2+} = 38.0$
$Na^{+} = 4.0$
$K^{+} = 6.0$
$Mn^{2+} = 2.0$
$H^{+} = 24.0$ and
$Al^{3+} = 8.0$

If cation exchange capacity of the soil is 96meq in 100g of oven-dried soil, calculate:
  (i) The percentage base saturation of this soil
  (ii) The quantity of calcium in grams present in 100 grams of oven-dried soil

(6.5marks)

(c) With aid of chemical equations, describe how ozone layer is formed and depleted.

(6marks)

Examination Ten
CHEMISTRY 2E

Answer **five (5)** questions

Question 1

(a) Under what main condition does solution formed upon mixing two liquids **A** and **B** behave as ideal solution?

(1.5mark)

(b) Liquid **A** and **B** form an ideal solution when mixed together. If the boiling point of pure **A** is higher than the boiling point of pure **B** at 1 atmospheric pressure. Sketch:
- (i) A vapour- composition curve for the solution of liquid **A** and **B**
- (ii) A temperature –composition curve for the solution of liquids **A** and **B**
- (iii) Explain what will happen when an equimolar solution of mixture **A** and **B** is distilled at atmospheric pressure of 1atm.

(5.5marks)

(c) Steam is passed through a flask containing about 20g of chlorobenzene (C_6H_5Cl).The mixture is found to boil at 91°C at 760mmHg. The vapour of water at 91°C is 540mmHg. Calculate:
- (i) Mole composition of the distillate
- (ii) The mass composition of the distillate
- (iii) Total volume of the distillate obtained when 90% of chlorobenzene has been steam distilled. (Density of chlorobenzene is $1.1 g/cm^3$).

(6marks)

(d) Given the following result for the distribution of phenol between water and chloroform

Concentration of phenol in water (g/dm^3)	8.836	15.322	23.876
Concentration of phenol in chloroform (g/dm^3)	23.876	71.534	173.900

- (i) Use the above result to deduce whether phenol exists in normal state or dimerises in chloroform
- (ii) Describe clearly the reason for the state of phenol in chloroform deduced in (i) above

(7marks)

Question 2

(a) Give the meaning of the following terms:
- (i) Electrode
- (ii) Anode
- (iii) Transport number
- (iv) Conductance ratio

(2marks)

(b) A steady current of 0.27A passed for half an hour in a water voltameter liberated $56cm^3$ of hydrogen at s.t.p. Calculate:
- (i) The electrochemical equivalent of hydrogen

(ii) The electrochemical equivalent of aluminium

(4marks)

(c) Calculate the equilibrium constant for the Daniel cell at 25°C, if standard oxidation potential for Zn electrode is $+0.765$V and for copper electrode is -0.337 V.

(5marks)

(d) Consider the following reaction equation: $2HgCl_2(aq) + C_2O_4^{2-}(aq) \longrightarrow 2Cl^- + 2CO_2(g) + Hg_2Cl_2(aq)$

The equation for the reaction between mercuric chloride and oxalate ion in hot aqueous solution is shown above. The reaction rate may be determined by measuring the initial rate of formation of chloride ion, at constant temperature, for various initial concentrations of mercuric chloride and oxalate as shown in the following table.

Experiment	Initial $[HgCl_2]$	Initial$[C_2O_4^{2-}]$	Initial rate of formation of Cl^- in $molL^{-1}min^{-1}$
1	0.0836M	0.202M	0.52×10^{-4}
2	0.0836M	0.404M	2.08×10^{-4}
3	0.0418M	0.404M	1.06×10^{-4}
4	0.0316M	?	1.27×10^{-4}

(i) According to the data shown, what is the rate law for the reaction above?

(ii) On the basis of the rate law determined in part (a), calculate the specific rate constant specify the units.

(iii) What is the numerical value for the initial rate of disappearance of $C_2O_4^{2-}$ for experiment 1?

(iv) Calculate the initial oxalate ion concentration for experiment 4.

(9marks)

Question 3

(a)

(i) What is meant by the terms: solubility and solubility product?

(ii) Explain how the value of solubility product of sparingly soluble substance varies with temperature change.

(5marks)

(b) The solubility of AgBr in ammonia solution is not the same as it is in pure water. Suggest a reason for the difference.

(3marks)

(c) Below are data which can be used to compare solubility of AgBr in water and in ammonia solution.

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq);\ K_{sp} = 3.3 \times 10^{-13}$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq); K = 1.7 \times 10^{+7}$$

(i) How many grams of silver bromide, AgBr can be dissolved in 50 millilitres of water?

(ii) How many grams of silver bromide can be dissolved in 50millilitres of 10M$NH_3(aq)$?

(12marks)

Question 4

(a) What is the basic difference between Mendeleeff's periodic law and Modern periodic law?

(1mark)

(b) A neutral atom of a certain element has 17 electrons;

- (i) Write its ground state electronic configuration
- (ii) Classify the element into s,p,d or f block
- (iii) Determine whether it is diamagnetic or paramagnetic
- (iv) What is the principal oxidation number of the element?

(3marks)

(c) Study the following hypothetical elements placed in various group and periods of part of the periodic table and then answer the question that follow;

GROUP/PERIOD	I	II	III	IV	V	VI	VII	O
2	A	B	C	D	E	F	G	H
3	I	J	K	L	M	N	O	P

Giving reason (s) identify:

- (i) An element which is most likely to have highest electron affinity
- (ii) An element which is most likely to have highest electronegativity
- (iii) An element which is most likely to have least first ionisation energy
- (iv) A pair of elements which is most likely to form the strongest electrovalent bond
- (v) Two elements which are likely to have strongest reducing properties
- (vi) Two elements which form neither negative nor positive ions

(6marks)

(d) Assume you are mining manager of **Hopegen mining company Limited;** you have been assigned by board of directors of the Hopegen company to instruct the miners how to extract tin with very high purity so as to meet the demand of new order the company has received from one of its royal customer who need tin with almost 100% of purity. Show how you will organise your instruction under the following headings:

- (i) Chief ore of tin
- (ii) Concentration of the ore
- (iii) Roasting of the ore
- (iv) Leaching and washing
- (v) Smelting
- (vi) Purification

(10marks)

Question 5

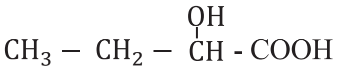
(a) Account for the following facts:

- (i) Solubility of benzyl alcohol in water is higher than that of phenol
- (ii) Although $LiAlH_4$ is very good reducing agent, it reduce alkene or alkyne to alkane
- (iii) Unlike water, alcohols are good antiseptic

(3 marks)

(b) Show how the following conversions may be achieved

- (i) $\mathrm{HO-CH_2-CH_2-HO}$ into $\mathrm{HO-CH_2-CH_2-CH_2-CH_2-OH}$

(ii) $CH_3 - CH_2 - CH_2 - OH$ into  $CH_3 - CH_2 - \overset{\overset{OH}{|}}{CH}\text{ - }COOH$

(iii) $CH_2 = CH_2$ into $CH_2 = CH - OH$

(4marks)

(c) Compound **A** is hydrocarbon with two carbon atoms. **A** undergoes hydrolysis to give compound **B**(C_2H_4O). **B** is unstable, it toutomerise to give more stable compound **C**. On reduction, **C** gives **D** (C_2H_6O). **C** also gives **E**$(C_2H_4O_2)$ on its oxidation. **D** and **E** reacts together to give compound **F**$(C_4H_8O_2)$ while **D** and **C** reacts to give **G**$(C_6H_{14}O_2)$.
(i) Identify A, B, C, D, E, F and G
(ii) Write an equation to show the hydrolysis of A to form C via B.
(iii) Write an equation to show the chemical reaction between C and D
(iv) Write a structure of at least one functional isomer for F and G

(13marks)

Question 6

(a) Define and give example of each of the following:
(i) Nucleophilic addition
(ii) Esterification
(iii) Ammonolysis
(iv) Hoffman's degradation reaction

(4marks)

(b) Give the structural formula of the following compounds:
(i) $1 - \text{chloro} - 3 - \text{Phenylpropan} - 2 - \text{one}$
(ii) $(1 - \text{bromoethyl})\text{ethanoate}$
(iii) $\text{Sodium } 3 - \text{methylbenzene carboxylate}$

(3marks)

(c) Complete the following reactions:
(i) $HCOONa + NaOH \xrightarrow[\Delta]{}$
(ii) $CH_3CH_2NC \xrightarrow{Na|CH_3CH_2OH}$
(iii) $C_6H_5OH + CH_3COOH \xrightarrow{H^+}$
(iv) $CH_3COCH_3 + N_2H_4 \xrightarrow{KOH(aq)}$
(v) $CH_3COH + CH_3C \equiv CH \rightarrow$
(vi) $CH_3O - COH + [Ag(NH_3)_2]NO_3 \rightarrow$

(6marks)

(d) Give a chemical test to distinguish the following pairs of organic compounds:
(i) Ethanoic acid and ethanedioic acid
(ii) Ethyl methanoate and ethyl ethanoate

(2marks)

(e) Two organic compounds, A and B, are all carbonyl compounds with molecular formula of C_3H_6O.
(i) Draw possible structural formula of A and B.

(ii) What type of structural isomerism do A and B exhibit?

(iii) Describe test (reagents, conditions and observations) that would show that A and B are carbonyl compounds.

(iv) Suggest class of another compound having the same molecular formula that is not carbonyl compounds. Give the structural formula of that compound and state what type of isomerism the compound exhibit with respect to compound A and B.

(5 marks)

Examination Eleven

CHEMISTRY 1F

SECTION A

Answer **all** questions in this section.

Question 1

(a) State the following:
  (i) Planck's quantum theory
  (ii) Heisenberg uncertainty principle
  (iii) Four shortcomings of Bohr's atomic theory

(4marks)

(b)
  (i) What is ionisation energy?
  (ii) By using Rydberg equation, calculate ionisation energy of hydrogen

(3marks)

(c) If the wavelength of the first line in the Balmer series in a hydrogen spectrum is $6863A^O$, calculate the wavelength of the first line in the Lyman series in the same spectrum.

(3marks)

Question 2

(a) Define **electrovalent bond** and give one example of it.

(1mark)

(b) Compare and contrast the following:
  (i) Covalent bonding and coordinate bonding
  (ii) Sigma (σ) bond and pi (π) bond

(2marks)

(c) Predict the hybridisation of the following:
  (i) PCl_5
  (ii) SF_6
  (iii) CO_2
  (iv) BCl_3 **(4marks)**

(d) Use VSEPR theory to predict the molecular geometry of the species:
PCl_3, NH_3 and PCl_5

(3marks)

Question 3

(a) What is the meaning of the following:
  (i) Molar volume of a gas at s.t.p.
  (ii) Dalton's la of partial pressure.

(1mark)

(b) From the fundamental gas equation derive the following:
  (i) Avogadro's law
  (ii) Ideal gas equation

(3marks)

(c) Two gas burettes, one containing $10cm^3$ of sulphur dioxide (SO_2) and the other containing $30cm^3$ of hydrogen sulphide (H_2S) both at 1 atmosphere and at 0°C are initially separated by a stop cork. The stop cork is then opened and the two gases are allowed to mix according to the reaction:

$$SO_2(g) + 2H_2S(g) \rightarrow 3S(s) + 2H_2O\ (l)$$

Calculate the final pressure (in atmospheres) after the reaction has ended and the apparatus has regained its temperature of 0°C. (Assume liquid water does not exert pressure).

(6marks)

Question 4

(a) Provide definition of the following:
  (i) Cryoscopy
  (ii) Ebullioscopy

(1mark)

(b) Arrange the following aqueous solution in order of increasing freezing point: $0.01MC_2H_5OH, 0.01MBa_3(PO_4)_2, 0.01MNa_2SO_4, 0.01MKCl, 0.01MLi_3PO_4$. Provide clear reason(s) for arrangement.

(2marks)

(c) Give a reason for each of the following:
  (i) Meat can be classified as fresh (not frozen) even though it is stored at −1 °C. Why wouldn't meat freeze at this temperature?
  (ii) One mole of sodium chloride depress the freezing point of 1kg of water almost twice as much as one mole of glycerine?

(2marks)

(d)
  (i) Calculate the freezing point of a solution of 22.5g of cane sugar ($C_{12}H_{22}O_{11}$) in 450g of water.
  (ii) If a solution of potassium chloride in water had a freezing point of $-0.048°C$, compare this value to the one obtained in (i) above and state from which solution will the ice first separate.
  (Use K_f for water $= 1.86°Ckgmol^{-1}$)

(5marks)

Question 5

(a) Explain the following chemical phenomena with the aid of chemical equation (s):
  (i) The passage of carbon dioxide through calcium hydroxide solution changes the latter into a precipitate which dissolves into clear solution in excess carbon dioxide.
  (ii) Aluminium nitrate cannot be prepared by reaction between aluminium and concentrated nitric acid.
  (iii) On heating magnesium nitrate produces brown fumes but potassium nitrate does not.
  (iv) Effervescence is observed when sodium bicarbonate is added to copper(II) sulphate solution.

(6marks)

(b) Under certain conditions, iron reacts with chlorine to give anhydrous iron(III) chloride.

(i) Why excess chlorine is used?
(ii) Why should moisture not allowed into apparatus during the reaction?

(2marks)

(c) Give four uses of metal chlorides.

(2marks)

Question 6

(a) State Hess's law of constant heat of summation

(1mark)

(b) Explain briefly what is wrong with each of the following definitions:

(i) **Standard enthalpy of combustion:** *Is the heat change when one mole of an element or compound is completely burned in oxygen under standard conditions of temperature and pressure.*

(ii) **Enthalpy of neutralisation:** *Is the heat evolved when a dilute solutions of acid and base reacts to give water under given conditions of temperature and pressure.*

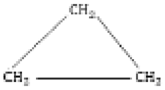
(iii) **Standard enthalpy of hydrogenation:** *Is the heat evolved when an unsaturated compound is converted to the corresponding saturated compound by the reaction with one mole of hydrogen under standard conditions of temperature and pressure.*

(iv) **Ionisation energy:** *Is the energy required to remove completely any valence electron each from one mole of gaseous atom or ion at given conditions of temperature and pressure.*

(4marks)

(c) The heat of combustion of carbon and hydrogen are 393.5kJ/mol and 286kJ/mol respectively. The enthalpy of sublimation of carbon is 720kJ/mol and dissociation energy of hydrogen is 432kJ/mol. Calculate the mean $\text{C}-\text{C}$ bond energy of cyclopropane given that the enthalpy of combustion of cyclopropane to be 2091kJ/mol and the mean $\text{C}-\text{H}$ bond bond energy is 414kJ/mol.

(5marks)



cyclopropane

Question 7

(a) In which scenarios the following factors do not affect position of chemical equilibrium?

(i) Temperature
(ii) Concentration
(iii) Pressure
(iv) Catalyst

(2marks)

(a) Consider the following reversible equilibrium:

$$2C_2H_6(g) + 7O_2(g) \rightleftharpoons 4CO_2(g) + 6H_2O(l)$$

(i) Write down the K_c and K_p expressions.
(ii) Derive the relationship between K_c and K_p.

(3marks)

(b)

(i) Explain why there is a constant pressure of carbon dioxide at a particular temperature over calcium carbonate undergoing thermal dissociation; $CaCO_{3(s)} \rightleftharpoons CaO_{(S)} + CO_{2(g)}$ and why a current air is blown through a lime kiln during production of quick lime CaO.

(ii) 20g Of $CaCO_3(s)$ were placed in a closed vessel, heated and maintained at 727℃ under equilibrium:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g);$$

And it is found that 75% of $CaCO_3$ was decomposed if the volume of the container was 15L, calculate the value of K_p.

(5marks)

SECTION B

Answer **any two** questions from this section

Question 8

(a) With the aid of an example in each case give the meaning of the following as applied to organic chemistry

(i) Isomerisation reaction

(ii) Metamers

(2marks)

(b) Compound **X** containing a carbon-carbon double bond, would react with the following reagents:

(i) **Y** to form 2-bromo-2-methylbutane.

(ii) **Z** to form $(CH_3)_2CH(OH)(CH_3)_2$.

(iii) **W** to form 2-chloro-2-methylbutane.

Name the compound **X** and the reagents **Y**, **Z** and **W**.

(5marks)

(c) Addition of bromine water to an unbranched alkene **A** (C_4H_8) gave compound **B**. Acid-catalysed dehydration of **B** yielded two isomeric bromoalkanes **C** and **D**. Cleavage of compound **C** with trioxygen with subsequent reductive hydrolysis resulted into ethanal being isolated as one of the products. Similar treatment of compound **D** yielded propanal rather than ethanal. Explain the observations described above and identify compound **A**, **B**, **C** and **D**.

(8marks)

Question 9

(a) Benzene can undergo chemical reactions with the following reagents:

- CH_3CH_2Br under presence of $AlCl_3$ to give **A.**
- $(CH_3)_2C = CH_2$, H^+ to give **E.**

A may undergo series of chemical reactions as follows:

- It (**A**) reacts with mixture of H_2SO_4 and HNO_3 to give **B.**
- **B** reacts with Cl_2 under presence of $AlCl_3$ to give **C.**
- **C** reacts with acidified potassium permanganate to give **D.**

E may undergo series of chemical reactions as follows:

- It (**E**) reacts with CH_3CH_2Br under presence of $AlCl_3$ to give **F.**
- **F** reacts with acidified potassium permanganate to give **G**

Give the structural formula of all aromatic compounds (**A** to **G)** which are formed in the above reactions.

(6marks)

(b) What is the product for chlorination of benzene and methylbenzene in the presence of:
  (i) A halogen carrier catalyst
  (ii) Ultra-violet light

(4marks)

(c) Many organic compounds which are used in daily life can be synthesized from haloalkanes ($R-X$).
  (i) With the aid of reaction equations, outline four different applications of haloalkanes in organic synthesis process.
  (ii) List at least two hazards associated with daily use of haloalkanes.

(5marks)

Question 10

(a) What is the meaning of the following terms?
  (i) Anion exchange
  (ii) Cation exchange capacity (CEC)
  (iii) Fertilizer
  (iv) Liming

(2marks)

(b) The exchangeable hydrogen from 5g of oven dry soil was neutralized with $100cm^3$ of 0.1M NaOH. If the total CEC of the soil is 25me/100g of the soil, calculate:
  (i) Percentage base saturation of the soil sample
  (ii) The concentration of H^+ ions (in meq) in 75g of the oven dry soil above
  (iii) Comment on the nature of soil in (i) above.

(8marks)

(c)
  (i) Briefly explain ozone layer.
  (ii) List down four effects of ozone layer depletion.

(5marks)

Examination Twelve
CHEMISTRY 2F

Answer **five (5)** questions

Question 1

(a) Raoult's law only really works for ideal solutions. An ideal solution is defined as one which obeys Raoult's law.
How do the following affect how ideal a solution is?
(i) The concentration of the solution.
(ii) The forces between the particles in the solution.

(2.5marks)

(b) Explain the following:
(i) The Van't Hoff factor for 0.05molal $FeCl_3$ solution is much smaller than 4, while that for the same concentration of NaCl is only slightly less than 2.
(ii) The Van't Hoff factor for a concentrated solution of NaCl is much less than 2, while that for a dilute solution is only slightly less than 2.
(iii) The addition of lead (II) ions to a solution of magnesium chloride leads to an increase in the vapour pressure of the solution.

(5marks)

(c) The vapour pressures of several solutions of water-propanol ($CH_3CH_2CH_2OH$) were determined at various
compositions, with the following data collected at 45°C:

X_{H_2O}	**Vapour pressure mmHg**
0	74.0
0.15	77.3
0.37	80.2
0.54	81.6
0.69	80.6
0.83	78.2
1.00	71.9

Based on the above data, answer the following questions:

(i) Are solution of water and propanol ideal? Explain.
(ii) Predict the sign of enthalpy of solution, ΔH_{soln}, for water-propanol solutions.
(iii) Are the interactive forces between propanol and water molecules weaker than, stronger than, or equal to the interactive forces between the pure substances? Explain.
(iv) Which of the solutions in the data would have the lowest normal boiling point? What special name is given for this solution?

(6marks)

(d) A solution is made by mixing 50.0 g acetone (CH_3COCH_3) and 50.0 g methanol (CH_3OH). At 25°C the vapour pressures of pure acetone and pure methanol are 271torr and 143torr respectively. Assume ideal solution and gas behaviour:
  (i) What is the vapour pressure of this solution at 25°C?
  (ii) What is the composition of the vapour expressed as a mole fraction?
  (iii) The actual vapour pressure of this solution is 161torr. Explain any discrepancies.

(6.5marks)

Question 2

(a) Define the following terms as applied in collision theory of reaction rate:
  (i) Collision frequency
  (ii) Effective collision
  (iii) Collision energy
  (iv) Activation energy

(2marks)

(b) The reaction of $NO(g)$ and $O_2(g)$ is represented by the equation: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

The rate of the reaction is given by the rate equation: Rate equation $= k[NO]^2[O_2]$

This reaction is proposed to follow the mechanism below:

$2NO(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$ (Fast)

$N_2O_2(g) + O_2(g) \overset{k_3}{\rightarrow} 2NO_2(g)$ (Slow)

$2NO(g) + O_2(g) \overset{?}{\rightarrow} 2NO_2(g)$ (Net)

Show that the proposed mechanism is consistence with the given rate equation.

(5marks)

(c) Giving reasons argue for or against the statement that, *"reactions with large equilibrium constants are very fast"*

(2marks)

(d) Briefly explain any two methods for rusting prevention.

(2marks)

(e) At 13°C, the specific conductivity of a saturated solution of AgCl in water was $2.4 \times 10^{-6}\ \Omega^{-1}cm^{-1}$ and that of water was $1.16 \times 10^{-6}\ \Omega^{-1}cm^{-1}$.

Given that:

$\Lambda_\infty(NaCl) = 110.3\Omega^{-1}cm^2mol^{-1}$, $\Lambda_\infty(AgNO_3) = 116.5\Omega^{-1}cm^2mol^{-1}$, $\Lambda_\infty(NaNO_3) = 105.2\Omega^{-1}cm^2mol^{-1}$.

Calculate the solubility, hence the solubility product of AgCl at this temperature.

(9marks)

Question 3

(a) What do you understand by the following terms:
  (i) Buffer solution
  (ii) Buffer capacity
  (iii) Buffer range

(iv) Limiting reagent

(4marks)

(b) Calculate concentration of calcium carbonate precipitate in gdm^{-3} if 0.1M of calcium chloride as added to equal volume of 0.1M of sodium carbonate solution. Given that: K_{sp} of $CaCO_3 = 1.69 \times 10^{-8}\ mol^2dm^{-6}$

(6marks)

(c) Calculate concentration of H_3O^+ present in 0.001M potassium methanoate. Given that: pK_a of methanoic acid $= 3.6198$

(3marks)

(d) Calculate the pH at neutralisation point for the reaction between $0.01MNH_4OH$ and $0.01MHCl$ solutions given that $K_a(NH_4^+) = 5.7 \times 10^{-10}mol/dm^3$

(7marks)

Question 4

(a) State the following as related to development of periodic table:
- (i) Mosley periodic law
- (ii) Newland's law of octaves
- (iii) Triad law

(3marks)

(b) Explain the general trends in physical properties of elements across and down the group by considering:
- (i) Atomic size
- (ii) Ionization energy
- (iii) Electronegativity
- (iv) Electron affinity

(8marks)

(c) Account for the following chemical phenomena:
- (i) Some lithium compounds are covalent while compounds of other elements in the same group are electrovalent.
- (ii) Anhydrous magnesium chloride ($MgCl_2$) cannot be obtained by heating the hydrated magnesium chloride ($MgCl_2 \bullet 6H_2O$).
- (iii) Effervescence of a colourless gas is obtained when sodium hydrogencarbonate is added to copper (II) sulphate solution.
- (iv) Li_2CO_3 decomposes readily on heating but Na_2CO_3 cannot.
- (v) Aluminium and magnesium are both found in period three of the periodic table but the first ionisation energy of aluminium is smaller than that of magnesium although aluminium is towards right of period three.
- (vi) It is not possible to prepare hydrogen iodide by the action of concentrated acid on potassium iodide.

(9marks)

Question 5

(a) Give the meaning of the following terms:
- (i) Coordination compounds

(ii) Cationic complexes

(1mark)

(b) Given the following complexes: $[Fe(SO_4)(NO)_2(CO)Br(OH)]$ and $[Ni(CN)(H_2O)(C_2O_4)(NH_3)(SO_3)]^{4-}$

Give the following for each complex:

(i) Coordination number

(ii) IUPAC name

(iii) Name of geometrical shape

(iv) Electronic configuration of the central atom/ion

(5marks)

(c) Briefly explain the following observations. Support your explanation with equation(s) where applicable:

(i) Lead (II) chloride is soluble in concentrated hydrochloric acid.

(ii) Addition of ammonia solution to aqueous copper (II) sulphate gives a pale blue precipitate initially and deep blue solution when more ammonia is used.

(iii) Solid aluminium hydroxide is soluble in aqueous solution of sodium hydroxide.

(iv) Iodine is sparingly soluble in water but readily soluble in a concentrated solution of potassium iodide.

(6marks)

(d) A hydrocarbon P does not react with chlorine in dark. When a mixture of P and chlorine is irradiated with ultraviolet light only two monochlorinated products Q and R are obtained. When Q and R are treated separately with warm aqueous sodium hydroxide solution and then with $KMnO_4$ solution, Q gives an acid S and T gives ketone, T.

(i) Identify P,Q,R,S and T

(ii) Write the chemical equations for reaction involved.

(8marks)

Question 6

(a) With one example in each case, define the following:

(i) Aldol-ketol condensation reaction

(ii) Cannizaro reaction

(2marks)

(b) An unbranched organic compound A (M.F C_8H_8O) reacts with sodium metal to give B and hydrogen gas. A also reacts with PCl_5 to give C and hydrogen chloride gas. C reacts with zinc/copper couple in alcohol to give D. C also reacts with magnesium in a dry ether to give E. E react with CO_2 to give $F(C_4H_7O_2MgCl)$ which when hydrolyses in acid gives G.

(i) Identify the compounds A, B, C, D, E, F and G. Give balanced equation for each reaction.

(ii) Give one isomer of A which will not react in the same way.

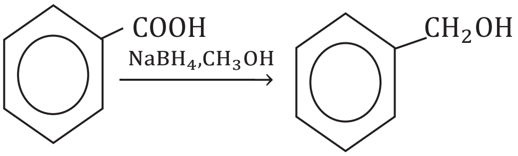
(8marks)

(c) In an examination paper, a student offered the suggestions given below for carrying out a series of conversions of organic compounds. Point out and explain the errors made by this student and offer suggestions by which the desired conversions could be carried out.

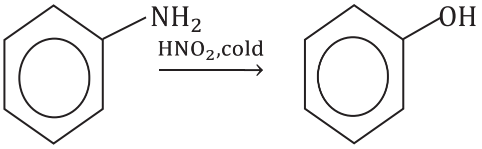
(i) $CH_3CH_2CHO \xrightarrow{KMnO_4|H^+} CH_3CH_2CH_2OH$

(ii) $CH_3CH_2COOH \xrightarrow{CH_3OH} CH_3CH_2COOCH_3$

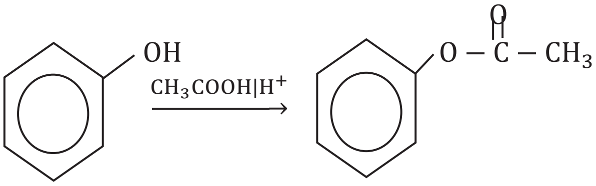
(iii)



(iv)



(v)



(10marks)

Examination Thirteen
CHEMISTRY 1G

SECTION A

Answer **all** questions in this section.

Question 1

(a) At different times scientists have proposed various descriptions or models of the atom to match experimental evidence available. The model that Thomson proposed was called the plum-pudding model.

(i) Why the model is known as plum-pudding model?

(ii) Describe the model.

(iii) List at least two advantages and two disadvantages of the model.

(5marks)

(b) What is the maximum number of orbitals with:

(i) $n = 2, l = 1$

(ii) $n = 2, l = 2$

(iii) $n = 3, l = 2$

(iv) $n = 5, l = 1, m_l = -1$ **(2marks)**

(c)

(i) When you charged a strip of plastic by rubbing it through your fingers or on cloth, you actually transferred electrons onto the plastic strip. Using the terms **"electrons"** and **"protons",** and **"negative"** and **"positive",** explain why the strip was attracted to your fingers or the cloth you rubbed it on.

(ii) When you rub a balloon on your hair, electrons are transferred onto the balloon. Using the terms **"electrons"** and **"protons",** and **"negative"** and **"positive",** explain why a rubbed balloon is attracted to and sticks to a wall even though you didn't rub the balloon on the wall. **(3marks)**

Question 2

(a)

(i) What is the difference between normal covalent bond and coordinate bond?

(ii) Out of sigma (σ) and pi (π) bonds, which one is stronger? Why?

(3marks)

(b)

(i) Describe the conditions necessary for the formation of hydrogen bond.

(ii) How does the described bond differ from other intermolecular forces?

(2.5marks)

(c) By using modern molecular theory complete the table on the following molecules:

Molecule	Geometrical structure	Name of the structure	Type of hybridisation
CO_2			
CH_2O			
PH_3			

(4.5marks)

Question 3

(a) State the following:
  (i) Boyle's law
  (ii) Grahm's law of diffusion

(1mark)

(b) State the postulates of kinetic theory of gases.

(2.5marks)

(c) Compressibility factor, **Z**, is used to test ideality and non-ideality of real gases:
  (i) Derive an expression for **Z**
  (ii) At what value of Z a real gas shows ideal behaviour, positive and negative deviation from ideality?

(3marks)

(d) When carbon dioxide gas is put in a sealed container at 701K and pressure of 10 atm and is heated to 1401K, some of the CO_2 decomposes to carbon monoxide and oxygen gas and the pressure rises to 22.5 atm. Calculate the mole percent of CO_2 that decomposes.

(3.5marks)

Question 4

(a) Colligative properties are very useful for experimental determination of molar masses of non-volatile solute.
  (i) Mention three colligative properties apart from osmotic pressure.
  (ii) State two methods which employ colligative properties in the molar mass determination.
  (iii) In the determination of molar mass, is it better to use diluted or concentrated solution? Explain.
  (iv) In the experiment of determining molar mass; it is better to employ osmotic pressure measurement than other ways like ebullioscopy and cryoscopy. Give one reason to oppose and two reasons to support this statement.

(5.5marks)

(b)

  (i) Calculate the boiling point and freezing point of a solution that is $3.725 m CaCl_2$ in ethanol from the following data:

Solvent	**Normal freezing point (°C)**	**Normal boiling point (°C)**	K_f **(°Ckgmol^{-1})**	K_b **(°Ckgmol^{-1})**
Ethanol	−117.3	78.5	1.99	1.22

  (ii) Do you expect the magnitude of practical values to be greater than or smaller than or the same as one calculated in (i) above? Explain.

(4.5marks)

Question 5

(a) Classify the following oxides as basic, acidic or amphoteric
$Mn_2O_7, ZnO, MgO, CrO_3, Al_2O_3, MnO_2$.

(1.5marks)

(b) Oxides of reactive metals are generally prepared by direct method.
- (i) How the direct method is done in preparing oxides?
- (ii) Although alkali metals are very reactive, only lithium oxide is commonly prepared by direct method. Explain.
- (iii) What alternative do chemists have in preparing normal oxides of other alkali metals in (ii) above? Use the preparation of K_2O as an example and give its corresponding chemical equation to justify your answer.

(3marks)

(c) Which of the following salts hydrolyse in water? In each case give the corresponding chemical equation for the reaction of salt with large amount of water.

$ZnSO_4, TiCl_2, K_2SO_4, AlCl_3$

(2marks)

(d) With vivid examples in each case, explain clearly uses of oxides of metals in:
- (i) Extraction of metals
- (ii) Soil liming

(3.5marks)

Question 6

(a) Define the following phrases as used in chemical energetic:
- (i) Enthalpy change
- (ii) Enthalpy of fusion
- (iii) Spontaneous reaction
- (iv) Exothermic reaction

(2marks)

(b) During chemical reactions, bond are broken (reactants) and formed (products), and the overall process may be exothermic or endothermic. Compare bond strengths in reactants and products if the overall reaction is:
- (i) Exothermic
- (ii) Endothermic

(1mark)

(c) Magnesium will displace copper from copper(II) sulphate according to the following equation:
$CuSO_4(aq) + Mg(s) \longrightarrow Cu(s) + MgSO_4(aq)$
When an excess of magnesium was added to $100cm^3$ of $1moldm^{-3}$ copper(II) sulphate, the temperature increased by $46.3°C$. It is known that density and specific heat capacity of the solution are $1gcm^{-3}$ and $4.18Jg^{-1}°C^{-1}$ respectively. Calculate:
- (i) The molar enthalpy change for the reaction.
- (ii) The minimum quantity of magnesium required.

(iii) The change in temperature if only 0.8g of magnesium was added.

(7marks)

Question 7

(a) Briefly explain the following phrases, giving one example for each:

(i) Heterogeneous chemical equilibrium

(ii) Reversible chemical reaction

(2marks)

(b) State the equilibrium law and provide the corresponding equation.

(1mark)

(c) The following dynamic equilibrium was established at temperature T in a closed container.

$P(g) + 2Q(g) \rightleftharpoons 2R(g);\ \Delta H^{\theta} = -50\ kJ/mol$

The value of K_c for the reaction was $68.0mol^{-1}dm^3$ when the equilibrium mixture contained 3.82mol of P and 5.24mol of R.

(i) Give the meaning of dynamic equilibrium.

(ii) Write an expression of K_c for this reaction.

(iii) The volume of container was $10dm^3$. Calculate the concentration in $moldm^{-3}$, of Q in the equilibrium mixture.

(iv) State the effect, if any, on the equilibrium amount of P, and on the value of K_c of increasing the temperature.

(v) State the effect, if any, on the equilibrium amount of P, and on the value of K_c of using a container of larger volume.

(vi) Deduce the value of the equilibrium constant, at temperature T, for the reaction;
$2R(g) \rightleftharpoons P(g) + 2Q(g)$

(7marks)

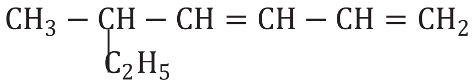
SECTION B

Answer **any two** questions from this section

Question 8

(a) Give IUPAC name of the following compounds:

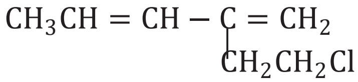
(i)



$CH_3-\underset{\substack{|\\ C_2H_5}}{CH}-CH=CH-CH=CH_2$

(ii) $CH_3CH=CH-CH_2-C\equiv CH$

(iii)



$CH_3CH=CH-\underset{\substack{|\\ CH_2CH_2Cl}}{C}=CH_2$

(iv) $CH_3CH=CH-CH=CH-C\equiv CH$

(2marks)

(b) The two isomers; n-butane and 2-methylpropane have different boiling point despite the fact that they have the same molecular mass. Explain this observation:

(1.5mark)

(c) Write the product of each of the following reactions:

(i) $CH_4 + Cl_2 \xrightarrow{UV}$

(ii) $CH_3CH = CH_2 + H_2SO_4 \xrightarrow[cold]{} \textbf{P} \xrightarrow{water+heat} \textbf{Q}$

(iii) $CH_3C \equiv CH + CuCl(aq) \xrightarrow{NH_3}$

(iv) $CaC_2 + H_2O \xrightarrow[heat]{}$

(2.5marks)

(d) You are provided with each of the following pairs of organic compounds; which one has higher boiling point in each pair? Give reason for your answer.

(i) Ethene and propene

(ii) Benzene and hexane

(iii) Pentane and 2,2-dimethylpropane

(iv) Ethane and ethyne

(v) Cis-2-butene and trans-2-butene

(5marks)

(e) A primary alkyl halide **A** (C_4H_9Br) reacted with alcoholic KOH to give compound **B**. Compound **B** reacted with HBr to give **C** which is an isomer of **A**. When **C** (in dry ether) reacted with Na metal, it gave compound **D** (C_8H_{18}).

(i) Give the structure of **A.**

(ii) Write equations of all reactions.

(4marks)

Question 9

(a) Provide the meaning for the following terms:

(i) Secondary haloalkane

(ii) Benzene

(iii) Aromatic compound

(iv) Resonance energy

(v) S_N1 mechanism

(2.5marks)

(b) With help of chemical equation(s) state what will happen when methylbenzene is:

(i) Refluxed with acidified potassium permanganate.

(ii) Treated with plenty amount of chlorine under presence of ultraviolet (UV) light.

(iii) Treated with chloromethane in presence of aluminium chloride

(iv) Burnt in excess oxygen.

(5marks)

(c) Explain the following:

(i) Silver nitrate solution does not precipitate the chloride in 1-chloropropene, but it does so in 3-chloropropene.

(ii) n-butyl chloride and t-butyl chloride undergoes different types of nucleophilic substitution reaction mechanism.

(iii) Toluene (methylbenzene) is more reactive than benzene.
(iv) Alkyl chlorides are not friendly to environment.
(v) Lewis acid is essential for electrophilic substitution reaction in benzene.

(7.5marks)

Question 10

(a) Give detailed explanation on any three methods of chemical treatment of sewages.

(6marks)

(b) **Cation exchange capacity (CEC)** is very important physical property of soil. Through CEC we can know quantity of the negatively charged sites on soil surfaces that can retain positively charged ions by electrostatic force.

(i) Define cation exchange capacity.
(ii) Outline three significances of CEC.
(iii) Five kilograms of soil is to be added for containerized planting. The current base saturation is 70% and the desired base saturation is 90%. How much pure $\mathrm{CaCO_3}$ is required if the CEC is $40\mathrm{meq}/100$ soil?

(9marks)

Examination Fourteen
CHEMISTRY 2G

Answer **five (5)** questions

Question 1

(a) A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.
  (i) What is the initial effect of the change on vapour pressure?
  (ii) How do rates of evaporation and condensation change initially?
  (iii) What happens when equilibrium is restored finally and what will be the final vapour pressure?

(6marks)

(b)
  (i) State Raoult's law of volatile liquids.
  (ii) Give any three examples of ideal solutions.
  (iii) Give two main assumptions for Raoult's law to be valid?

(4.5marks)

(c) The vapour pressure of pure liquid A and B are 450mmHg and 700mmHg respectively at 350K. If the total vapour pressure is 600mmHg; calculate the following:
  (i) Composition of liquid mixture
  (ii) Composition of the vapour phase

(5marks)

(d) During nuclear fuel reprocessing, solvent extraction with an organic solvent is used to recover uranium salts from aqueous solution. If the partition coefficient of a uranium salt between the organic solvent and acidified water has a value of 50, calculate the ratio of the total number of moles of uranium in the organic solvent layer to that in water layer after 500dm^3 of an aqueous solution of uranium salt has been extracted with 200dm^3 of organic solvent.

(4.5marks)

Question 2

(a) What do the following mean?
  (i) Cathode
  (ii) Anode
  (iii) Standard electrode potential
  (iv) Concentration cell

(2marks)

(b)
  (i) Briefly explain how voltaic cell differ from electrolytic cells.
  (ii) Why is it necessary to use a salt bridge in a galvanic cell?

(3marks)

(c) Given the following reduction potentials:

Half reaction	$\mathbf{E^{\theta}(V)}$
$Cl_2(g) + 2e \rightarrow 2Cl^-$	$+1.36$
$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$	$+1.33$
$Cr^{3+} + e \rightarrow Cr^{2+}$	-0.50
$Cr^{3+} + 3e \rightarrow Cr$	-0.73
$S_4O_6^{2-} + 2e \rightarrow 2S_2O_3^{2-}$	$+0.17$

(i) Determine the standard e.m.f of the following cell with the following cell reaction:
$Cr^{3+}(1M) + Cl_2(g) \rightleftharpoons Cr_2O_7^{2-}(1M) + Cl^-\ (1M)$

(ii) Sketch the galvanic cell based on the reaction in (i) above and show the direction of the electron flow

(iii) Calculate the equilibrium constant for the following reaction:
$S_4O_6^{2-}(aq) + Cr^{2+}(aq) \rightleftharpoons Cr^{3+}(aq) + S_2O_3^{2-}(aq)$

(iv) What conclusion can be made from the equilibrium constant obtained in (iii) above?

(9marks)

(d) The initial rate of reaction 2A + 2B → C + D is determined by different initial conditions with results listed in the following table:

Experiment	[A](M)	[B](M)	Initial rate (Ms^{-1})
1	0.185	0.133	3.5×10^{-4}
2	0.185	0.266	1.35×10^{-4}
3	0.370	0.133	6.75×10^{-4}
4	0.370	0.266	2.70×10^{-4}

(i) What is the order of reaction with respect to each reactant?

(ii) Calculate the value of rate constant

(6marks)

Question 3

(a) Classify the following species as Bronsted acid/Base. $S^{2-}, HCO_3^-, H_2O, NH_3$.

(2marks)

(b) Explain the two components of the buffer solution. **(3marks)**

(c)

(i) State whether a precipitate will form when $0.5dm^3$ of 2×10^{-3}M $BaCl_2$ is mixed with $1dm^3$ of 2×10^{-4}MNa_2SO_4 given that $K_{sp}(BaSO_4) = 1 \times 10^{10}mol^2dm^{-6}$

(ii) Calculate the mas of $Ca(OH)_2$ which is precipitated at 25°C when $500cm^3$ of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4M NaOH. $K_{sp}(Ca(OH)_2)$ at $25°C = 4.4 \times 10^{-5}mol^3dm^{-9}$.

(7marks)

(d) A solution prepared by mixing 150mL of 1×10^{-2}M $Mg(OH)_2$ and 250mL of 1×10^{-1}M NaF. Calculate the concentration of Mg^{2+} and F^- at equilibrium with solid MgF_2. (K_{sp} at 298K is 6.4×10^{-9} M^2).

(8marks)

Question 4

(a) Explain the meaning of the following:
  (i) Disproportionation reaction
  (ii) Polarising power
  (iii) Second electron affinity
  (iv) Per-hali compounds

(4marks)

(b) Explain each of the following phenomena and give balanced chemical equation where necessary
  (i) Nitrogen dioxide is paramagnetic but not dinitrogen tetraoxide.
  (ii) Silicon tetrachloride react vigorously with water, but carbon tetrachloride does not react with water.
  (iii) $HClO_4$ is stronger acid than HNO_3.
  (iv) Boron hydroxide is more acidic than aluminium hydroxide.
  (v) Aqueous solution of aluminium chloride is acidic while that of sodium acetate is basic.
  (vi) When magnesium metal is introduced into a beaker containing ammonium chloride solution, hydrogen gas is evolved.
  (vii) Action of concentrated sulphuric acid on calcium phosphate.
  (viii) Reaction of orange coloured potassium dichromate with hydrogen chloride.

(16marks)

Question 5

(a) Name the following:
  (i) $(NH_4)_3[Fe(SCN)_6]$
  (ii) $[Fe(ox)_3]^{3-}$
  (iii) $[CoCl(NH_3)_5]Br_2$
  (iv) $[Co(S_2O_3)_2(H_2O)_2]^{2-}$
  (v) $Na_2[MoCl_4O]$

(5marks)

(b) A solution containing 2.665g of $CrCl_3.6H_2O$ is passed through cation exchanger; the chloride ion obtained in solution was treated with excess of $AgNO_3$ to give 2.87g of AgCl, deduce the structure of the compound.

(5.5marks)

(c) Suggest suitable tests to distinguish the following compounds:
  (i) Methanol and ethanol
  (ii) Propanol and phenol

(2marks)

(d) Write a conversion to show how you would prepare propan-1-ol from:

(i) Propan-2-ol
(ii) Buan-1-ol (4 steps are required)

(3.5marks)

(e) An alcohol B reacts with concentrated H_2SO_4 at 170℃ to form alkene Q. Alcohol also reacts with hydrochloric acid in the presence of $ZnCl_2$ to form cloudness immediately. When Q reacts with ozone in the presence of zinc dust and water it gives propanone and ethanal. Deduce the structural formula of Q and B.

(**4marks**)

Question 6

(a) Name one carbonyl compound which is **commonly** used in:
(i) Manufacture of Bakelite
(ii) Nail polish remover
(iii) Silvering mirror
(iv) Providing mushroom flavour in food

(2marks)

(b) Give one example of each of the following:
(i) Hoffman's degradation reaction
(ii) Ketol condensation reaction
(iii) Carbylamine reaction
(iv) Cannizaro reaction

(3marks)

(c) **A** is a neutral compound containing four carbon atoms per molecule, with the percentage by mass: carbon 53.33%, hydrogen 11.11% and oxygen 35.56%. **A** reacts readily with metallic sodium to give hydrogen, and can also be oxidised to **B** (empirical formula C_2H_3O), which forms a condensation compound with 2,4-dinitrophenylhydrazine in acid and reduces Fehling's solution to copper (I) oxide. **B** can further be oxidised to a dicarboxylic acid **D,** the mono-bromo derivative of which, **X,** can be converted, by the loss of hydrogen bromide to another dicarboxylic acid **E** (emprical formula CHO), which exists in two forms. From the information given;
(i) Find the molecular of A, B and E
(ii) Giving full structural formulae of all five compounds, complete the reaction schemes:
$A \rightarrow B \rightarrow D$
$X \rightarrow E$
(iii) Draw another structure for **E** and explain why there are two forms of **E**

(**15marks**)

Examination Fifteen
CHEMISTRY 1H

SECTION A

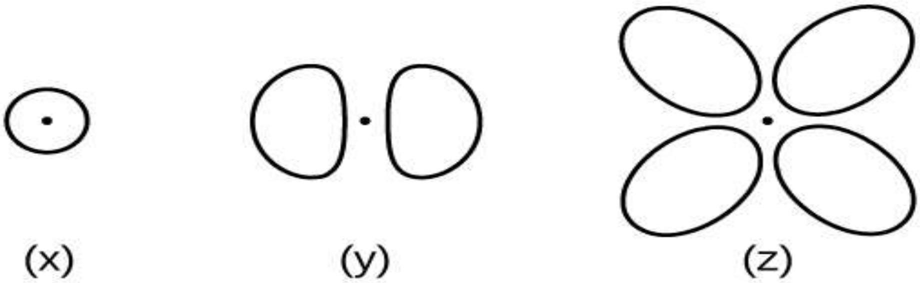
Answer **all** questions in this section.

Question 1

(a) Write down the meaning of the following:
   (i) Electronic configuration
   (ii) Azimuthal quantum number
   (iii) Stark effect
   (iv) Quantum number

(2marks)

(b) Consider orbitals shown in the figure below:



   (i) What is the maximum number of electrons contained in each of orbitals of type **Y**?
   (ii) How many orbitals of type **Z** are found in a shell with $n = 2$?
   (iii) An electron residing in a shell with principal quantum number of 3, in an orbital of type **X** is spinning in clockwise direction. Write set of all four quantum numbers for the electron.
   (iv) What is the smallest possible value of n for an orbital of type **Y**?
   (v) What are the possible l and m_l values for an orbital of type **Z**?

(3marks)

(c) An organic fertiliser was analysed using a mass spectrometer. The spectrum showed that the nitrogen in the fertiliser was made up of 95.12% ^{14}N and 4.88% ^{15}N.
   (i) Calculate the relative atomic mass of the nitrogen found in this organic fertiliser.
   (ii) In a mass spectrometer, under the same conditions, monopositive ions of ^{14}N and ^{15}N follow different paths.
   A: State the property of these ions that causes them to follow different paths.
   B: State **one** change in the operation of the mass spectrometer that will change the path of an ion.
   (iii) Organic fertilisers contain a higher proportion of ^{15}N atoms than are found in synthetic fertilisers. State and explain whether or not you would expect the chemical reactions of the nitrogen compounds in the synthetic fertiliser to be different from those in the organic fertiliser. (Assume that the nitrogen compounds in each fertiliser are the same).

(5marks)

Question 2

(a) What is the meaning of the following:
  (i) Intermolecular forces
  (ii) Ionic bonding
  (iii) Valence electrons
  (iv) Dispersion forces

(2marks)

(b) With help of sketches, briefly explain the following:
  (i) Ortho-nitrophenol has lower boiling point than para-nitrophenol.
  (ii) Molar mass of acetic acid in carbon tetrachloride is 120g/mol and not the expected 60g/mol.

(3marks)

(c)
  (i) Describe the hybridisation of central atom and shapes of the following molecules:

$$CH_4, BF_3 \text{ and } SCl_2$$

  (ii) Which among the above molecules has maximum bond angle?

(5marks)

Question 3

(a) State whether you agree or you disagree in each of the following statements. In each case, give brief explanation to support your answer.
  (i) According to Boyle's law, equal mass of hydrogen and oxygen kept in different containers of the same volume at the same temperature exerts the same pressure.
  (ii) According to Charles's law increasing the temperature of the gas from 10°C to 20°C doubles its volume.
  (iii) 2mol of oxygen gas in 5L container at 25°C shows greater deviation from ideal behaviour than 1mol of the oxygen gas in the container of the same volume at the same temperature.

(4.5marks)

(b) One eighth of a mole of a certain hydrated salt contains 11.2g of water. Calculate the number of molecules of water of crystallization of the salt.

(1.5marks)

(c) The atomic radius of sodium is 1.86×10^{-8}cm, and the molar volume of sodium is 23.68 cm^3. If 68.52% of this volume is the actual volume occupied by sodium atoms, calculate the Avogadro's constant. (Volume of one sodium atom $\frac{4}{3}\pi r^3$).

(4marks)

Question 4

(a) State the following:
  (i) Van't Hoff's law of osmotic pressure
  (ii) Blagden's law

(1.5marks)

(b) The Van't Hoff factor for a 0.05molal $FeCl_3$ solution is much smaller than 4, while that for the same concentration of NaCl is only slightly less than 2. Explain.

(1.5marks)

(c) Van't Hoff's factor may help us to determine degree of dissociation or association of non-volatile solute in the solution. Briefly explain the relationship between Van't Hoff's factor and concentration of the solution. **(2marks)**

(d) An aqueous solution is 1.0%NaCl by mass and has density of $1.071 gcm^{-3}$ at 25°C. The observed osmotic pressure of this solution is 7.83atm at 25°C.

(i) What fraction of the mole of NaCl in this solution exists as ion pair?
(ii) Calculate the freezing point of this solution.
Use K_f for water $= 1.86°Ckgmol^{-1}$

(5marks)

Question 5

(a) Write chemical equation(s) to show the reaction between:
(i) Boron oxide and water
(ii) Red lead oxide and nitric acid
(iii) Zinc oxide and sodium hydroxide
(iv) Calcium oxide and silicon dioxide

(2marks)

(b)
(i) What are salts of carbonic acids?
(ii) Explain two methods of preparing of salts of carbonic acids.
(iii) Outline three uses of salts of carbonic acids in daily life.

(8marks)

Question 6

(a) Write down the meaning of the following:
(i) Enthalpy of hydrogenation
(ii) Standard enthalpy of dissolution
(iii) Bond energy
(iv) Lattice energy

(2marks)

(b) Study carefully the information in the following table and then answer the questions that follow:

Process	$\Delta H^{\theta}(kJ/mol)$
$Na(s) \longrightarrow Na(g)$	$+108$
$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	$+121$
$Na(g) \longrightarrow Na^+(g) + e$	$+496$
$Cl(g) + e \longrightarrow Cl^-(g)$	-349
$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$	$+787$
$NaCl(s) + H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$	$+4$

(i) Calculate the standard enthalpy change for the process :
$2Cl(g) \longrightarrow Cl_2(g)$
(ii) Calculate the standard enthalpy change for the process:

$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow Na^+(g) + Cl^-(g)$

(iii) Compare the different between enthalpy change for the processes: $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$ and $NaCl(s) + H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$ and then comment on the difference.

(4marks)

(c) Some enthalpy change data are shown in the table below:

Process	**Enthalpy change (kJ/mol)**
$AgI(s) \longrightarrow Ag^+(aq) + I^-(aq)$	$+112$
$Ag^+(g) \longrightarrow Ag^+(aq)$	-464
$I^-(g) \longrightarrow I^-(aq)$	-293

(i) Use the data in above table to calculate the lattice energy of silver iodide.

(ii) A calculation of the lattice energy of silver iodide based on a perfect ionic model gives a smaller numerical value than the value calculated in (i) above. Explain this difference.

(4marks)

Question 7

(a) The following equilibrium is established between colourless dinitrogen tetraoxide gas (N_2O_4) and dark brown nitrogen dioxide gas (NO_2).

$$N_2O_4(g) \rightleftharpoons 2NO_2(g); \;\; \Delta H = +58kJ/mol$$

(i) Give two main features of reaction at equilibrium.

(ii) Use Le Chatelier's principle to explain why the mixture of gases becomes darker in colour when the mixture is heated at constant pressure.

(iii) Use Le Chatelier's principle to explain why the amount of NO_2 decreases when the pressure is increased at constant temperature.

(3marks)

(b) Ammonia is manufactured by the Haber process in which the following equilibrium is established.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) Why catalyst has no effect on position of this equilibrium?

(ii) At equilibrium, with a pressure of 35MPa and a temperature of 600K, the yield of ammonia is 65%.

A: State why industry uses a temperature higher than 600K.

B: State why industry uses a pressure lower than 35MPa

(2marks)

(c) 24.4g of ethanoic acid and 24.3g of ethanol were mixed in stoppered bottle and left for several days to reach equilibrium at room temperature. At the end of that time, the mixture was poured into pure water and made up to a total volume of $250cm^3$. A $25.0cm^3$ sample of this needed 26.5cm^3 of 0.400MNaOH to neutralise the remaining ethanoic acid. Calculate a value of K_c for the reaction:

$$CH_3COOH(l) + CH_3CH_2OH(l) \longrightarrow CH_3COOCH_2CH_3(l) + H_2O(l);$$

(5marks)

SECTION B

Answer **any two** questions from this section

Question 8

(a) What do you understand by the following:
  (i) Markonikoff's rule
  (ii) Saytzeff's rule

(2marks)

(b) Starting with less acidic, arrange the following compounds in of their acidic strength. Give an explanation to justify your arrangement.
Ethane, ethene, ethyne.

(2marks)

(c) Chlorine can react with dichloromethane (CH_2Cl_2) to form trichloromethane ($CHCl_3$)
  (i) Write an equation for each of the following steps in the mechanism for this reaction.
    - Initiation step
    - First propagation step
    - Second propagation step
  (ii) Give one essential condition for this reaction and name the type of mechanism.

(2.5marks)

(d) Compound **X** is shown below. It is a member of homologous series of hydrocarbons.
$CH_3CH = CHCH_3$
  (i) Give the general molecular formula of homologous series that contains **X**.
  (ii) Give the structure and IUPAC name of the position isomer of **X**.
  (iii) At high temperature, one molecule of $C_{15}H_{32}$ can be converted into two molecules of **X** and one molecule of another compound.
  A: Write an equation for this reaction.
  B: State the name of the process used to obtain a high yield of X from $C_{15}H_{32}$ and give one reason why this process is used in industry.
  C: State why high temperature are needed for this process.
  (iv) Compound X burns completely in oxygen. Write a balanced equation of this reaction and state how the products of this reaction may affect the environment.

(5.5marks)

(e) Compound X (in (d) above) can be converted into compound Y. Compound Y is shown below.
$CH_3CH_2CH_2CH_3$
  (i) Suggest reagent(s) that could be added to X in order to convert it to Y.
  (ii) Give one main use of Y.
  (iii) Write a balanced chemical equation to show the reaction of Y in a limited supply of air to produce a solid and water only.

(iv) Explain briefly one hazard associated the solid formed in (iii) above.

(3marks)

Question 9

(a) Complete the following reactions in words:

(i) $\text{Benzene} + \text{concentrated nitric acid} \xrightarrow{\text{conc } H_2SO_4, 50°C}$

(ii) $\text{Benzene} + \text{ozone} \xrightarrow{Zn, H_2O}$

(iii) $\text{Benzene} + 2 - \text{chloropropane} \xrightarrow{\text{Anhydrous } AlCl_3}$

(iv) $\text{Toluene} + \text{chloromethyl} \xrightarrow{\text{Anhydrous } AlCl_3}$

(v) $\text{Toluene} + \text{Mild oxidising agent} \longrightarrow$

(5marks)

(b) Arrange the following chloroalkanes in order of decreasing reactivity in S_N1 reaction:

(i) CH_3CH_2Br

(ii) $CH_3CH_2CH(CH_3)Br$

(iii) $CH_3CH_2CH_2CH_2Br$

(iv) $C(CH_3)_3Br$ **(2marks)**

(c) By indicating whether the reaction will involve side chain, aromatic ring or both, write chemical equations showing the reaction between phenylethene (styrene) and:

(i) Br_2

(ii) H_2, Pt at 20°C

(iii) H_2, Pt at 200°C

(3marks)

(d) For each pair of compounds below, provide a chemical test to distinguish between:

(i) Benzyl chloride and phenyl chloride

(ii) Bromoethane and chloroethane

(iii) Chloroform and carbon tetrachloride

(iv) Benzene and toluene

(v) t-butylbenzene and n-butylbenzene

(5marks)

Question 10

(a) Define the following terms as applied to soil:

(i) Soil reaction

(ii) Percentage base saturation

(1mark)

(b) Explain how microbial and microbial activity in the soil influence the quality of soil for agricultural production. **(1.5marks)**

(c) How do the following processes contribute to the changes in the soil pH?

(i) Microbial activity

(ii) Fertility

(iii) Leaching

(4.5marks)

(d) For healthy environment, sewages should be properly treated before damping. One of the methods employed to accomplish the sewage treatment is **thermal incineration**. The incineration is regarded as one of **thermal treatment** methods of sewage.

(i) Define thermal treatment as used above.

(ii) Explain clearly what is thermal incineration?

(iii) Outline four advantages of the thermal incineration to environment.

(iv) List down three disadvantages to environment associated with the employment of the incineration. **(8marks)**

Examination Sixteen
CHEMISTRY 2H

Answer **five (5)** questions

Question 1

(a) For each system, compare the intermolecular interactions in the pure liquids with those in the solution to decide whether the solution will be approximately ideal solution, non-ideal solution with positive deviation or non-ideal solution with negative deviation:

(i) cyclohexane and ethanol
(ii) methanol and acetone
(iii) n-hexane and isooctane

(6marks)

(b) The vapour pressure of water at 95℃ is 635mmHg. A water insoluble organic liquid **X**, of relative molecular mass 160, steam distills at 95℃ under atmospheric pressure of 760mmHg. Calculate the mass of the distillate during the collection of 40g of **X**.

(4marks)

(c)

(i) Derive Nernst's distribution law.
(ii) Give any four applications of Nernst's distribution law.

(5marks)

(d) If 10g of acid is dissolved in the mixture of 100cm^3 of water and 100cm^3 of ether. Calculate:

(i) The amount of acid extracted by 100cm^3 of ether in one extraction only
(ii) The amount of acid extracted by using four consecutive extractions of 25cm^3in each extraction

Given that: $\frac{\text{[Acid]in ether}}{\text{[Acid] in water}} = 5$

(5marks)

Question 2

(a) Using the following half reactions:

$\text{Au}^{3+} + 3\text{e} \rightarrow \text{Au} \qquad E^\theta = 1.5\text{V}$

$\text{NO}_3^- + 4\text{H}^+ + 3\text{e} \rightarrow \text{NO} + 2\text{H}_2\text{O} \quad E^\theta = 0.96\text{V}$

Predict whether 1MHNO_3 will dissolve gold metal to form 1MAu^{3+} solution or not.

(3.5marks)

(b) Account for the following chemical phenomena:

(i) Potassium manganate (VII) is not used as a primary reagent in volumetric analysis as potassium dichromate (VI) does.
(ii) Hydrochloric acid cannot be used as acidic medium during redox titration of potassium permanganate against iron (II) sulphate.
(iii) When acidified potassium dichromate reacts with sodium chloride, green colouration is observed.

(4.5marks)

(c) If the activation energy for a reaction is 83.14kJ/mol

   (i) What will be the approximate ratio of the rate constant of the reaction at $27°C$ to that at $37°C$?
   (ii) What will the ratio be for a reaction with an activation energy of $53.59 kJ/mol$?

(4.5marks)

(d) At $337°C, 0.01M$ of H_2 and $0.01M$ of iodine vapours are mixed together in a litre vessel and reaction proceeded as per the following equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$$

The initial rate of reaction was found to be $9 \times 10^{-8} Msec^{-1}$

   (i) What would be the expected trend of the reaction rate (increase or decrease) as time passes by?
   (ii) What would be the initial rate of reaction if pressure of the mixture was doubled?

(4marks)

(e) A certain first order reaction is 35% complete in 65 seconds. What are the rate constant and half-life of this reaction?

(3.5marks)

Question 3

(a) Give the meaning of the terms:
   (i) Solubility
   (ii) Solubility product
   (iii) Buffer capacity
   (iv) Fractional precipitation

(2marks)

(b) The solubility product of lead (II) chloride, $PbCl_2$, is $1.6 \times 10^{-5} mol^3 dm^{-9}$ at 298K. Calculate the solubility of $PbCl_2$ at this temperature in:
   (i) Water
   (ii) A solution of lead (II) nitrate, $Pb(NO_3)_2$ with the concentration of $0.10M$

(5marks)

(c) What will be the approximate pH if $1 cm^3$ of $0.1 M NaOH$ is added to $100\ cm^3$ of $0.001 M HCl$?

(3marks)

(d) Calculate the number of grams of sodium acetate (CH_3COONa) which are to be added to $500\ cm^3$ of 0.12M acetic acid (CH_3COOH) to give a buffer solution of pH 4.6. Assume the volume of the solution does not change on adding sodium acetate given that, $K_a(CH_3COOH) = 1.8 \times 10^{-5} moldm^{-3}$

(5marks)

(e) The dissociation constant, K_a for the reaction.
$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ is 4.8×10^{-12}. Calculate the pH of 0.01M calcium bicarbonate solution.

(5marks)

Question 4

(a) State any two merits and two demerits of each of the following:
   (i) Dobereiner's law of triads

(ii) Newland's law of octaves
(iii) Long form of the periodic table.

(6marks)

(b) The cyano (CN^-) has about the same size as Br$^-$. Hence CN^- is pseudo halide, resembling the halide in many aspects. List five ways in which cyanide ion resembles halide ions.

(5marks)

(c) Explain each of the following:
(i) Magnesium has higher melting point than phosphorous.
(ii) Potassium ion (K^+) is smaller than the chloride ion (Cl^-) even though they have the same number of electrons.
(iii) Electron affinity of fluorine is anomalous.
(iv) KCl is known and has been prepared while KCl_2 is not known and has never been prepared.
(v) The element with atomic number 36 has exceptional high ionisation energy
(vi) Common reductants are useless in the manufacture of aluminium from its ore.

(9marks)

Question 5

(a) What is the meaning of the following terms?
(i) A transition metal
(ii) A complex
(iii) Coordination sphere
(iv) Coordination number

(2marks)

(b) Name the following coordinate compounds:
(i) $[Co(H_2O)_6]^{3+}$
(ii) $[Cu(SO_4)(NH_3)_3(H_2O)_2]$
(iii) $[Fe(CN)_2(H_2O)_4]Cl$

(3marks)

(c) Explain the following chemical phenomena with the aid of chemical equation (s)
(i) Addition of aqueous solution of silver nitrate into dilute HCl produces white precipitate which dissolves in aqueous ammonia solution.
(ii) Zinc sulphide is not precipitated when hydrogen sulphide is passed through a solution to which dilute HCl is added.

(3marks)

(d)
(i) Define condensation reaction.
(ii) Explain how nylon-66 can be prepared and why is it called nylon-66?

(4marks)

(e) Explain how alcohol can be prepared by fermentation process.

(8marks)

Question 6

(a)

- (i) Write an equation for the formation of propylamine by the reaction of ammonia with $1-\text{bromopropane}$. In the equation, indicate necessary conditions for the reaction.
- (ii) Propylamine can also be prepared in two step synthesis starting from 1- bromoethane. Write an equation for each of the two steps in this synthesis.
- (iii) Explain why propylamine is a stronger base than ammonia
- (iv) Identify a substance that could be added to aqueous propylamine to produce a basic buffer solution.
- (v) Write five isomers of propylamine.

(8marks)

(b) With help of chemical equation, explain each of the following:

- (i) If one feels pain after receiving ant's bite and then quickly rub a baking soda on the afflicted skin surface, the pain are eliminated.
- (ii) If one mix fish with vinegar, fishy odour is reduced.
- (iii) Ethanal is useful in silvering of mirror.

(6marks)

(c) When alcohol A is heated with acid, it is slowly converted into two isomeric alkenes B and C of molecular formula C_5H_{10}. On ozonolysis, B gives ethanal and D which gives positive iodoform test and alkene C gives methanal and another product, E which responds positively to Benedict's solution test. Identify compounds A, B, C, D and E.

(6marks)

Examination Seventeen
CHEMISTRY 1I

SECTION A

Answer **all** questions in this section.

Question 1

(a) State the following:
  (i) Aufbau principle
  (ii) Paul's exclusion principle
  (iii) Hund's rule of maximum multiplicity
  (iv) Half-filled and full-filled orbital rule

(2marks)

(b) From Heisenberg equation; show that Heisenberg's uncertainty principle is true.

(1.5marks)

(c) The mass number of two atoms, **X** and **Y** with the same atomic number are 35 and 37 respectively. If **X** contains 18 neutrons in its nucleus, find the number of neutrons and electrons in **Y**.

(1.5marks)

(d) A diode laser emits a wavelength of 987nm. All of radiations it emits is measured with a total energy of 0.52J over a period of 32 seconds. Calculate the number of photons per second emitted by the laser.

(2marks)

(e) For each of the following statement, state whether you agree or disagree and give reason(s) to defend your answer:
  (i) If you know the atomic number of an element in the periodic table, you will also know the number of neutrons in any atom of that element.
  (ii) Different atoms of the same element can have different atomic masses.

(3marks)

Question 2

(a)
  (i) Define hydrogen bond.
  (ii) State any two effects hydrogen bonding.

(1.5marks)

(b) Identify intermolecular forces present in the following solids:
  (i) CH_3CH_2OH
  (ii) $CH_3CH_2CH_3$
  (iii) CH_3CH_2Cl

(2marks)

(a) Explain how a molecule that contains polar bond can be non-polar. Give an example of such molecule.

(1.5marks)

(d) **P, Q, R** and **S** represents elements of atomic numbers 11, 15, 17 and 29 respectively.

(i) Write electronic configuration of **P**, **Q**, **R** and **S**.
(ii) Predict the type of bonding which you would expect to occur between:

- **P** and **R**
- **Q** and **R**
- **P** and **S**
- Atoms of **R**
- Atoms of **S**

(5marks)

Question 3

(a)
(i) State the meaning of an ideal gas.
(ii) Derive an ideal gas equation.

(2marks)

(b) Comment on the following statements:
(i) The molecular attraction between gas molecules is high at low temperature.
(ii) In Van der Waals equation for real gases, the value of constant, **'a'** is larger for NH_3 gas than for N_2 gas but that of **'b'** is larger for N_2 gas.

(3marks)

(c) A compound of phosphorous (P) and Fluorine (F) was analysed as follows: Heating 0.2324g of the compound in a 378cm^3 container turn all of it to gas, which had a pressure of 97.3 mmHg at 77°C. Then the gas was mixed with calcium chloride solution which turned all of the F to 0.2631g of CaF_2. Determine the molecular formula of the compound.

(5marks)

Question 4

(a) A solute in a solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature occupying the same volume.
(i) Which theory is this statement based?
(ii) The theory stated in (i) above is useful in deducing number of laws. State them.

(3marks)

(b) As a solution freezes, the freezing temperature continues to decrease. Why is this so?

(1mark)

(c) The freezing point of t-butanol is 25.50°C and K_f is 9.1°°C/molal. Usually t-butanol absorbs water on exposure to air. If the freezing point of a 10.0g sample of t-butanol is 24.59°C, how many grams of water are present in the sample?

(2marks)

(d) 5.00g of an organic solid was dissolved in 100.0g of benzene. The boiling temperature of this solution was 82.3°C. The organic compound is 46.7% nitrogen, 6.67% hydrogen, 26.7% oxygen, and the remainder is carbon. Given that: the boiling temperature of pure benzene is 80.2°C; K_b for benzene $= 2.53°\text{C/m}$.
(i) Determine empirical formula of the organic solid.

(ii) Determine molecular formula of the organic solid.

(4marks)

Question 5

(a) Give one carbonate or bicarbonate which is commonly used:
  (i) In softening hard water
  (ii) In fire extinguisher
  (iii) In making glass
  (iv) As industrial base
  (v) In production of quick lime

(2.5marks)

(b) Soluble sulphates of metals may be prepared by **direct method** whereby metals are reacted with dilute sulphuric acid. This method is also known as **displacement method**.
  (i) Why the method is also known as displacement method?
  (ii) With help of chemical equations give two examples of sulphate which may be prepared by this method.
  (iii) Explain briefly three conditions for the displacement method to be effective.
  (iv) Can this method be used in preparing copper (II) sulphate? Explain.
  (v) In (iv) above, if the answer is **yes** give the corresponding equation for the justification and if it is **no** give an alternative method with its corresponding chemical equation for preparing the sulphate.

(7.5marks)

Question 6

(a) What do you understand by each of the following:
  (i) Dissociation energy
  (ii) Atomization energy
  (iii) Ionization energy
  (iv) Electron affinity
  (v) Enthalpy of solution
  (vi) Enthalpy of dilution

(3marks)

(b) State the types of enthalpies in each of the following thermochemical equations:
  (i) $AgI(s)+H_2O(l) \longrightarrow Ag^+(aq) + I^-(aq) \quad \Delta H = +112kJ/mol$
  (ii) $Na(s) \longrightarrow Na(g) \quad \Delta H^\theta = +108kJ/mol$
  (iii) $Cl(g) + e \longrightarrow Cl^-(g) \quad \Delta H = -349kJ/mol$
  (iv) $NaOH(aq) + HCl(aq) \longrightarrow NaCl + H_2O \quad \Delta H^\theta = -57kJ/mol$

(2marks)

(c) Two liquids; trichloromethane ($CHCl_3$) and ethoxyethane ($CH_3CH_2OCH_2CH_3$) form intermolecular hydrogen bonds when mixed. In a certain experiment, 0.05moles of trichloromethane and 0.3moles of ethoxyethane were weighed into the same calorimeter. When the temperature of both liquids had equalized, the liquids were mixed. The temperature increase of 5.4°C were recorded upon mixing. Assume that the heat capacity of calorimeter is negligible, while heat capacities of trichloromethane and ethoxyethane are $0.98Jg^{-1}°C^{-1}$ and $2.28Jg^{-1}°C^{-1}$ respectively. Calculate:

(i) Heat change in this experiment.
(ii) Enthalpy change of mixing one mole of trichloromethane with excess ethoxyethane.

(5marks)

Question 7

(a) By referring to Le-Chatelier's principle and behaviour of particles; explain clearly two advantages of using high pressure in Haber process.

(3marks)

(b) *Catalyst has no effect on chemical equilibrium.* What is wrong about this argument? Explain clearly.

(2marks)

(c) A mixture was prepared using 1.00mol of propanoic acid, 2.00mol of ethanol and 5.00mol of water. At a given temperature, the mixture was left to reach equilibrium according to the following equation:

$$CH_3CH_2COOH(l) + CH_3CH_2OH(l) \longrightarrow CH_3CH_2COOCH_2CH_3(l) + H_2O(l); \Delta H = -22kJ/mol$$

The equilibrium mixture contained 0.54mol of the ester, ethyl propanoate.

(i) Write an expression for the equilibrium constant, K_c, for this equilibrium.
(ii) Calculate the number of moles of water in the equilibrium mixture.
(iii) Calculate a value for K_c for this equilibrium at this temperature. Explain why this K_c value has no units.
(iv) For this equilibrium, predict the effect of an increase in temperature on each of the following:
A: The amount of ester at equilibrium.
B: The time taken to reach equilibrium.
C: The value of K_c

(5marks)

SECTION B

Answer **any two** questions from this section

Question 8

(a) Using one appropriate example in each case, give the meaning of the following:
(i) Functional group
(ii) Alkyl group

(1mark)

(b) **Rose** is your friend who study advanced chemistry. She was given a home – work of IUPAC naming of organic compounds but was unable to give correct names for five structures. The bad news is that, she had lost a question paper and there is no way of getting it and her teacher need correction of the exercise while **Rose** has no idea of doing correction without having structures of organic compounds she failed to name. Below are incorrect names given by **Rose** in the home – work exercise:

(i) 2 – methypent-4-ene
(ii) 4 – vinyheptane

(iii) 6 – vinylhepta – 1,4-diene
(iv) 4-isopropylhex-2-yne
(v) 1-buten-3-yne.

If **Rose** came to you and asks for your help in doing correction; what would be your help to her (includes drawings of missed structures).

(5marks)

(c) By indicating suitable reagents and conditions, show how the following molecules can be prepared by one step reaction:
(i) Ethene from ethanol
(ii) Propene from propyne
(iii) Butane from 1-bromobutane
(iv) Ethane from ethanal
(v) 1-butyne from 1-chloroethane

(5marks)

(d) A haloalkane **P** $(C_5H_{11}Br)$ reacts with aqueous sodium hydroxide to give **Q** $(C_5H_{12}O)$. Q reacts with concentrated sulphuric acid at $170°C$ to form **R** (C_5H_{10}) which decolourises bromine water. When **R** is reacted with ozone followed by hydrolysis, methanal and a branched aldehyde **S** is formed. Deduce the structural formula of **P**, **Q**, **R** and **S** by showing the chemical reactions involved.

(4marks)

Question 9

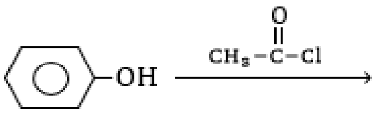
(a) Giving one example in each case, define the following:
(i) Elimination reaction
(ii) Electrophilic substitution reaction
(iii) Nucleophilic substitution reaction

(3marks)

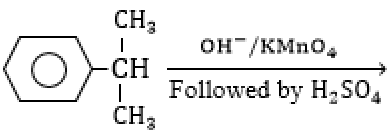
(b) Complete the following reactions:

(i) $BrCH_2CH_2CH_2CH_2Br + Na \xrightarrow{\text{Dry ether}}$

(ii)

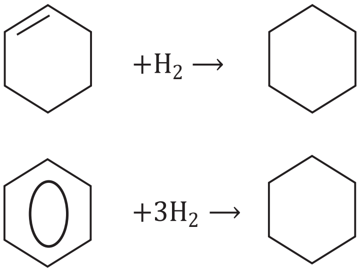


(iii)



(3marks)

(c) Data about the hydrogenation of cyclohexene and of benzene are given below:



$\Delta H^{\theta} = -120kJ/mol$

$\Delta H^{\theta} = -208kJ/mol$

Compare the stability of benzene with that of the hypothetical cyclohexa-1,3,5-triene molecule. (Use the given data above).

(3marks)

(d) The reaction mixture of hot concentrated ethanolic potassium hydroxide and 2-bromo-3-methylbutane forms two alkenes that are structural isomers of each other.
  (i) Name the mechanism of this reaction.
  (ii) Give the structure of 2-bromo-3-methylbutane
  (iii) Give the structure of major product of this reaction.
  (iv) Give the structural formula for the other isomer that is formed.
  (v) State the type of structural isomerism shown by these two alkenes.

(3marks)

(e) A small amount of another organic compound, **X**, can be detected in the reaction mixture in (d) above. Compound **X** has the molecular formula of $C_5H_{12}O$.
  (i) Give the structure of **X.**
  (ii) Suggest **three** changes to the reaction conditions that would increase the yield of **X**.
  (iii) Name the mechanism for the conversion of 2-bromo-3-methylbutane into **X.**

(3marks)

Question 10

(a) Below are some of common aerial pollutants:

- Sulphur dioxide
- Ground level ozone
- Particulate matter
- Lead

For each pollutant mentioned above state the following:

(i) Two sources.
(ii) Two harmful effects.

(8marks)

(b) A soil sample (20g) was analysed and found to contain 0.0015g of calcium. What concentration of calcium in the soil sample in milliequivalents per 100g soil?

(2marks)

(c) In soil, particles which are less than 0.001mm size possess colloidal properties and are known as **soil colloids.**

(i) Define soil colloids.
(ii) Explain briefly how soil colloids are formed.
(iii) Mention four major types of soil colloids.
(iv) Explain briefly how soil colloids facilitate plant nutrition.

(5marks)

Examination Eighteen
CHEMISTRY 2I

Answer **five (5)** questions

Question 1

(a) For each of the following liquid mixture; classify the mixture as ideal solution, non-ideal solution with positive deviation or non-ideal solution with negative deviation:
   (i) Benzene and n-hexane
   (ii) Trichloromethane and acetone
   (iii) Ethylene glycol and carbon tetrachloride
   (iv) Acetic acid and propanol

(2marks)

(b) Alcohol dissolves in water to give a solution that boils at a lower temperature than pure water while table salt dissolves in water to give a solution that boils at a higher temperature than pure water. Explain this fact in terms of vapour pressure.

(2marks)

(c) If a solute, **X**, is shaken with two immiscible solvents, **Y** and **Z**, at constant temperature, it is found that: $\frac{(\text{Concentration of } \mathbf{X} \text{ in } \mathbf{Y})}{(\text{Concentration of } \mathbf{X} \text{ in } \mathbf{Z})} = \text{a constant}$
   (i) What name is given to the constant.
   (ii) For $\mathbf{X} =$ phenylamine, $\mathbf{Y}$ = water and $\mathbf{Z} =$ ethoxyethane the value of the constant is 0.20. Calculate the mass of phenylamine extracted into the ethoxyethane layer when 100cm^3 of water containing 20g of phenylamine per dm^3 is treated with 100cm^3 of ethoxyethane.
   (iii) How could the efficiency of extraction of phenyl amine have been improved using the same total volume of ethoxyethane?

(6marks)

(d) Benzene and toluene form a nearly ideal solution. At 80°C, the vapour pressure of pure benzene (Mwt = 78g/mol) is 753torr and that of toluene (Mwt = 92g/mol) is 290torr. The following questions refer to a solution that contains equal weight of the two liquids.
   (i) Calculate the partial pressure of each component that would be in equilibrium with the solution at 80°C.
   (ii) At what atmospheric pressure will this solution boil at 80°C?
   (iii) What will be the composition of the liquid that condenses when this vapour is cooled?

(6marks)

Question 2

(a) What is meant by:
   (i) Activated complex
   (ii) Rate law
   (iii) Molecularity
   (iv) Order of reaction

(2marks)

(b) Arrhenius equation may be written as; $k = (pz)e^{-\frac{Ea}{RT}}$:

(i) Explain the meaning of symbols ‘p’ and ‘z’?

(ii) What is the name given to the product ‘pz’? What is its significance?

(iii) Based on the above Arrhenius equation, explain two ways of which catalyst may affect the value of k.

(6marks)

(c) The decomposition of N_2O_5 proceeds according to the equation:

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

If the rate of decomposition of N_2O_5 at particular instant in a reaction vessel is $4.2 \times 10^{-7} molsec^{-1}$, what is the rate of appearance of:

(i) NO_2

(ii) O_2

(3marks)

(d) The rate of decomposition of hydrogen peroxide was studied by titrating known volumes of the reaction mixture with potassium permanganate at different intervals and the result obtained were tabulated below:

Volume of $KMnO_4$ used (cm^3)	70	47	30	13	7.20
Time (minutes)	00	06	09	20	29

(i) Show that the reaction is the first order

(ii) Find the rate constant

(9marks)

Question 3

(a) Lead (II) sulphate is used as a white pigment in paints and as a key component in a common lead-acid battery. Its solubility in water at 25°C is $4.25 \times 10^{-3} g/100mL$ solution. What is the solubility product of $PbSO_4$?

(3marks)

(b)

(i) Define pH

(ii) Is it possible for neutral solution to have pH of less than 7? Explain your answer.

(iii) Calculate the pH of 0.05M aqueous solution of dimethylamine given that the degree of dissociation of the base is 4.37×10^{-5}.

(3marks)

(c) If the dissociation constant for NaF and NH_3 are 1.5×10^{-11} and 1.77×10^{-5} respectively. Find the pH of:

(i) A 0.25M solution of NaF

(ii) A 0.01M solution of NH_3

(6marks)

(d) An ethanoic acid/sodium ethanoate buffer containing 1.00M CH_3COOH has pH of 4.742; calculate the following given that, $K_a(CH_3COOH) = 1.8 \times 10^{-5} moldm^{-3}$

(i) Concentration of sodium ethanoate in the given buffer

(ii) pH of the resulting solution after 0.01 mole of HCl solution has been added in 1dm^3 of the buffer solution
(iii) pH of the resulting solution after 0.01 mole of NaOH is added in 1dm^3 of the buffer solution
(iv) pH when 0.01mole of NaOH is added to 1dm^3 of pure water.

(8marks)

Question 4

(a) Write a balanced chemical equation and expected observation for each of the following:
(i) Magnesium nitride is dissolved in water.
(ii) Chlorine gas is bubbled through a beaker containing solution of NaBr.
(iii) Solid ammonium chloride is heated.
(iv) Dilute hydrochloric acid is added to powder egg shells.
(v) Calcium nitrate is heated.
(vi) Carbon dioxide is added to a beaker containing solution of calcium hydroxide.

(6marks)

(b) Consider the reactions:

$$2S_2O_3^{2-}(aq) + I_2(s) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$
$$S_2O_3^{2-}(aq) + 2Br_2(s) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$$

Why does the same reductant, thiosulphate react differently with iodine and bromine?

(2marks)

(c) With the help of chemical equation(s), explain each of the following:
(i) Concentrated sulphuric acid should not be used to dry hydrogen sulphide gas.
(ii) When binary compound of Aluminium and carbon is hydrolysed, methane is formed.
(iii) Magnesium is recovered from sea water by liming.
(iv) A reaction between aqueous sodium hydroxide and carbon dioxide gas cannot be used as a chemical test of CO_2.
(v) Hard water becomes soft when washing soda ($Na_2CO_3.10H_2O$) is added.
(vi) When water is sprayed into dry mixture of sulphur dioxide and hydrogen sulphide, a yellow solid is formed.

(12marks)

Question 5

(a) Provide the meaning for the terms:
(i) Coordinate bond
(ii) Coordination number

(1mark)

(b) $[CoBr(NH_3)_5]SO_4$ and $[Co(SO_4)(NH_3)_5]Br$ are isomers:
(i) Which ions will these isomers yield in solution?
(ii) What is the coordination number of cobalt in each isomer?
(iii) Give two chemical tests that could be used to distinguish between them

(4marks)

(c) Consider the complex $[Co(NH_3)_6]Cl_3$

(i) What is the oxidation state of cobalt in the compound?
(ii) Explain why chloride ions are not considered to be acting as ligands in this complex?
(iii) Give the formula of a complex ion of cobalt which does not contain chloride ions acting as ligands.
(iv) Deduce the structural formula of the complex compound $CoCl_3.4NH_3$, in which cobalt has the same oxidation state and coordination number as in $[Co(NH_3)_6]Cl_3$.

(5marks)

(d) Compound **A** gives white precipitate of sulphide when its solution is mixed with hydrogen sulphide in the presence of dilute hydrochloric acid. When a solution of potassium cyanide (KCN) is added to the sulphide precipitate, the precipitate appears to dissolve. However the precipitate does not dissolve when excess ammonia is added to it. When the solution of **A** is mixed with solution of $BaCl_2$, white precipitate is observed. When hydrochloric acid solution is added to the precipitate, the precipitate appears to dissolve without evolvement of any gas. Identify cation and anion present in the compound **A** and hence name the compound.

(10marks)

Question 6

(a) More than 90 million organic compounds are known to man today. In the table below the letter A to E represent a few of these compounds

	COMPOUND
A	$CH_3CH_2CH_2COOH$
B	Trimethylamine
C	$CH_3 - CH(OH) - CH_3$
D	$6 - \text{Methyl} - 1 - \text{heptene}$
E	$CH_3CONHCH_3$

(i) Write down IUPAC name of compound C
(ii) Write down structural formula of compound D
(iii) To which homologous series does compound E belongs?
(iv) Write down the IUPAC name of function isomer of A
(v) Compound B is one of the substances responsible for the fish odour (smell) of fish. Explain why serving lemon slices with fish reduces the odour.

(4marks)

(b) Soap is manufactured by the hydrolysis of naturally- occurring compounds using sodium hydroxide. Name the type of compound present in soap and draws the structure of the organic by – product formed when these naturally occurring compounds are hydrolysed to produce soap. **(1mark)**

(c) Arrange the following compounds in order of increasing of their reactivity towards nucleophilic addition reaction.

$$HCHO, CH_3CHO, CH_3COCH_3$$

(1mark)

(d) (Phenylmethyl)amine,$C_6H_5CH_2NH_2$, can be prepared from (bromomethyl)benzene, $C_6H_5CH_2Br$ and also from benzenecarbonitrile, C_6H_5CN.

(i) Write an equation for the conversion of (bromomethyl)benzene into (phenylmethyl)amine. Name the type of reaction taking place and explain why a low yield of product is obtained.

(ii) Name the type of reaction involved in the conversion of benzenecarbonitrile into(phenylmethyl)amine. Write an equation for this reaction and suggest a suitable reagent or a combination of reagent and catalyst. Explain why this method of preparation gives a high yield of product.

(iii) State which of the two amines, (phenylmethyl)amine and phenylamine,$C_6H_5NH_{2,}$is the weaker base, and explain your choice.

(6marks)

(e) Organic compound P, C_8H_8O, gave iodoform reaction and on vigorous oxidation yielded, Q, $C_7H_6O_2$, which was sparingly soluble in cold water after neutralisation. Q gives a buff precipitate with aqueous iron (III) chloride. Treatment of Q with phosphorous pentachloride gave R which reacted with concentrated aqueous ammonia to give a precipitate of S, C_7H_7ON.Prolonged treatment of S with phosphorous (V) oxide gave T which could be reduced to U, C_7H_9N. On reduction with alcohol under presence of sodium amalgam, P gave V, $C_8H_{10}O$. v gave positive iodoform test but did not give colouration with aqueous iron (III) chloride.

Write the structural formula of substances P to V

(8marks)

Examination Nineteen
CHEMISTRY 1J

SECTION A

Answer **all** questions in this section.

Question 1

(a) Give the meaning of the following:
  (i) Mass number
  (ii) Relative atomic mass

(1mark)

(b) Clearly state four postulates of Planck's quantum theory as derived from black body radiation. **(3marks)**

(c) Indium is in Group IIIA in the Periodic Table and exists as a mixture of the isotopes: $\text{In}-113$ and $\text{In}-115$. A sample of indium must be ionised before it can be analysed in a mass spectrometer.
  (i) State what is used to ionise a sample of indium in a mass spectrometer.
  (ii) Write an equation, including state symbols, for the ionisation of indium that requires the minimum energy.
  (iii) State why more than the minimum energy is **not** used to ionise the sample of indium.
  (iv) Give two reasons why the sample of indium must be ionised.
  (v) By reference to the relevant part of the mass spectrometer, explain how the abundance of an isotope in a sample of indium is determined.
  (vi) A mass spectrum of a sample of indium showed two peaks at $m/z = 113$ and $m/z = 115$. The relative atomic mass of this sample of indium is 114.5. Calculate the percentage abundances of the two isotopes.

(6marks)

Question 2

(a) What is the meaning of the following terms?
  (i) Polar covalent bond
  (ii) Dipole moment
  (iii) Polar covalent molecule

(1.5marks)

(b)
  (i) Explain clearly the relationship between terms defined in (a) above.
  (ii) If the molecule $\mathbf{X}F_3$ has a dipole moment. Is **X** boron or phosphorous? Give a reason.

(3marks)

(c) The melting point of $H_2O(s)$ is 0°C. Would you expect the melting point of $H_2S(s)$ to be −85°C, 0°C, or 185°C? Briefly, explain your answer.

(1.5marks)

(d) When H^+ reacts with H_2O molecules, H_3O^+ ions are formed.
  (i) Name the type of bond formed when H^+ reacts with H_2O.
  (ii) Explain how this type of bond is formed in H_3O^+ ion.

(iii) Draw and name the shape of the H_3O^+ ion.
(iv) Suggest a value for the bond angle in the H_3O^+ ion.
(v) Identify one molecule with the same number of atoms, the same number of electrons and the same shape as the H_3O^+ ion.

(4marks)

Question 3

(a) State the following gas laws. In each case give their corresponding mathematical equation.
(i) Gay-Lussac's law
(ii) Combined gas law
(iii) Ideal gas law
(iv) Avogadro's law

(3marks)

(b)
(i) Real gases are those which disobey gas laws. Outline two assumptions of kinetic theory of gases which must be modified for gas to behave ideally.
(ii) Calculate the root mean square velocity for the atoms in a sample of helium gas at 25°C?

(3.5marks)

(c) Two glass bulbs of equal volumes joined by a narrow tube of negligible volume are containing gas at s.t.p. When one of the bulbs is lowered into a container containing melting ice and other kept in hot water, the new pressure in the bulb is 877.6mmHg. Determine the temperature of the water.

(3.5marks)

Question 4

(a) Colligative properties are very useful in determination of molar mass of non-volatile solutes.
(i) What is the non-volatile solute?
(ii) Explain why osmotic pressure is more preferred in the determination of molar mass of substance with large molar mass like protein than freezing point depression or boiling point elevation?

(2marks)

(b) A solution is prepared by mixing 50.0g glucose ($C_6H_{12}O_6$) with 600.0g water. What is the vapour pressure of this solution at 25°C? (At 25°C the vapour pressure of pure water is 23.8torr)

(2marks)

(c) Consider the following solutions:
$0.010mNa_3PO_4$ in water
$0.020mCaBr_2$ in water
0.020mKCl in water
0.020MHF in water
(i) Complete the following table for the above solutions:

Solution	Van't Hoff factor, i	Effective molality of solute, m
$0.010mNa_3PO_4$		
$0.020mCaBr_2$		
$0.020mKCl$		
$0.020mHF$		

(ii) Which solution(s) would have the same boiling point as $0.040mC_6H_{12}O_6$ in water?
(iii) Which solution(s) would have the lowest freezing point?
(iv) Which solution(s) would have highest vapour pressure 30°C?
(v) Which solution(s) would have nearly the same osmotic pressure as $0.020mC_6H_{12}O_6$ in water? **(6marks)**

Question 5

(a) With at least one example in each case, define the following:
  (i) Neutral oxide
  (ii) Compound oxide
  (iii) Oxoacid

(3marks)

(b) With help of chemical equation in each case, suggest three different ways of which indirect method may be employed in the preparation of metallic oxides. **(3marks)**

(c) Both carbonates and bicarbonates can prepared by neutralisation method by passing carbon dioxide to alkaline solution.
  (i) With help of ionic equation state the condition which favour the formation of each, carbonate and bicarbonate.
  (ii) What is the alternative method for preparing carbonates?
  (iii) Is the method mentioned in (ii) above suitable for preparing bicarbonates? Explain.

(4marks)

Question 6

(a) Anhydrous magnesium chloride, $MgCl_2$, can absorb water to form the hydrated salt, $MgCl_2.4H_2O$.

$$MgCl_2(s) + 4H_2O(l) \longrightarrow MgCl_2.4H_2O(s)$$

  (i) Suggest **one** reason why the enthalpy change for this reaction cannot be determined directly by calorimetry.
  (ii) Some enthalpies of solution are shown in the table below:

Salt	Enthalpy of solution (kJ/mol)
$MgCl_2(s)$	-155
$MgCl_2.4H_2O(s)$	-39

Calculate the enthalpy change for the absorption of water by $MgCl_2(s)$ to form $MgCl_2.4H_2O(s)$. **(4marks)**

(b) Given the standard enthalpy of combustion (ΔH_c^θ) of the following substances:

$$\text{Hydrogen, } \Delta H_c^\theta = -286\text{kJ/mol}$$
$$\text{Carbon, } \Delta H_c^\theta = -394\text{kJ/mol}$$
$$\text{Methane, } \Delta H_c^\theta = -890\text{kJ/mol}$$
$$\text{Ethene, } \Delta H_c^\theta = -1390\text{kJ/mol}$$

Given that heat of formation of ethanol is -276kJ/mol; calculate in kJ/mol the heat change:

(i) Of formation of methane.
(ii) Of formation of ethene.
(iii) For the reaction $CH_2 = CH_2(g) + H_2O(l) \longrightarrow CH_3CH_2OH(l)$
(iv) Of combustion of 4.48dm^3 of ethene.

(6marks)

Question 7

(a) When 3-methylbutanoic acid reacts with ethanol in the presence of an acid catalyst, an **equilibrium** is established. The organic product is a pleasant-smelling ester.

$$(CH_3)_2CHCH_2COOH + CH_3CH_2OH \rightleftharpoons \underset{\textbf{Ester}}{(CH_3)_2CHCH_2COOCH_2CH_3} + H_2O$$

The carboxylic acid is very expensive and ethanol is inexpensive. In the manufacture of this ester, the mole ratio of carboxylic acid to ethanol used is 1 to 10 rather than theoretical ratio of 1 to 1.

(i) By referring to the reaction between the 3-methylbutanoic acid and ethanol above; explain clearly the meaning of the term **equilibrium**.
(ii) Explain why 1 to 10 mole ratio is used and not the theoretical one. (You should **not** refer to cost).
(iii) Explain the effect of catalyst in the equilibrium.

(4marks)

(b) The equilibrium constant for the reaction; $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at 986°C is 0.63. A mixture of 1.0 mole of water vapour and 3.0 mole of CO is allowed to come to equilibrium. The equilibrium pressure is 2.0atm.

(i) Calculate the number of moles of H_2 present at equilibrium.
(ii) Calculate the partial pressure of gases at equilibrium mixture.

(6marks)

SECTION B

Answer **any two** questions from this section

Question 8

(a) Using one example in each case, give the meaning of the following:

(i) Homologous series
(ii) Carbenium ion
(iii) Free radical
(iv) Hydrocarbon

(2marks)

(b) Hexane (C_6H_{14}) is a member of the homologous series of alkanes.

- (i) Name the raw material from which hexane is obtained.
- (ii) Name the process used to obtain hexane from this raw material.
- (iii) State **one** main type of structural isomerism shown by the isomers of C_6H_{14}. Give two isomers to illustrate your answer.
- (iv) One molecule of an alkane **X** can be cracked to form one molecule of hexane and two molecules of propene. Deduce the molecular formula of **X**.
- (v) State the type of cracking that produces a high percentage of alkenes. State the conditions needed for this type of cracking.
- (vi) Hexane can react with chlorine under certain conditions as shown in the following equation:

$$C_6H_{14} + Cl_2 \longrightarrow C_6H_{13}Cl + HCl$$

A: State the type of this reaction.

B: Both the products of this reaction are hazardous. The organic product would be labelled 'flammable'. Suggest more suitable hazard warning for the other product.

C: Presence of ultra-violet light (UV) is essential for this reaction to take place. However reaction was undertaken in absence of sunlight. Suggest possible alternative condition applied to enable this reaction.

(6marks)

(c) Butan-2-ol reacts with concentrated sulphuric acid to form a mixture of three isomeric alkenes. Two of the alkenes are stereoisomers.

- (i) Define the type of chemical reaction involved in this reaction.
- (ii) Draw the skeletal formula of each of the three isomeric alkenes formed by the reaction of butan-2-ol with concentrated sulphuric acid. Give the full IUPAC name of each isomer.

(4marks)

(d) A by-product of the reaction of butan-2-ol with concentrated sulphuric acid in (b) above has the molecular formula of C_4H_8O.

- (i) Give the structure and name of this by-product.
- (ii) To what homologous series does this by-product belong?
- (iii) State the role of the sulphuric acid in the formation of by-product.
- (iv) Suggest the name of a method that could be used to separate the products of this reaction (Main product in (b) and by-product in (c)).

(3marks)

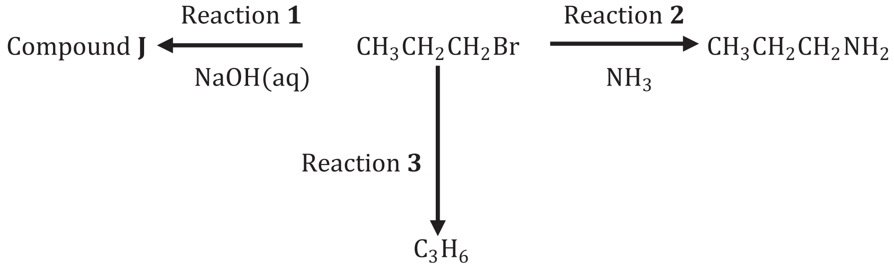
Question 9

(a) Arrange the following set of compounds in order of decreasing of reactivity toward methenium ion (H_3C^+):

- (i) Benzene, 4-nitrotoluene, 4-chlorophenol.
- (ii) Chlorobenzene, 2,4-dinitrobenzene, 4-nitrochlorobenzene.
- (iii) Isopropylbenzene, carboxybenzene, chlorobenzene.
- (iv) Methylbenzene, 4-nitromethylbenzene, 2,4-dinitromethylbenzene.

(3marks)

(b) Reaction scheme below shows some compounds made from a haloalkane.



- (i) Draw **displayed formula** of compound **J**.
- (ii) Name the mechanism for Reaction **2** and explain clearly essential condition(s) used to ensure that $CH_3CH_2CH_2CH_2NH_2$ is the major product.
- (iii) When Reaction **2** is carried out under different conditions, a compound with molecular formula $C_9H_{21}N$ is produced. Give structural formula of the compound and identify the functional group in the compound including its classification.
- (iv) Identify reagents and conditions used in the Reaction **3**. What type of reaction is this?
- (v) Show mechanism of appropriate mechanism of Reaction **3**.

(6marks)

(c) Explain the following:

- (i) Alkyl chlorides are readily attacked by nucleophile in the reactions.
- (ii) Nitration of aminobenzene gives significant amount of meta product although the amino group in benzene is ortho-para director.
- (iii) Hydrogenation in benzene occurs at higher temperature than in hexene.
- (iv) Alcohol is formed when bromoethane is mixed with a solution of sodium carbonate.

(6marks)

Question 10

(a) Soil pH is very useful physical property of soil. From measured soil pH it is possible to determine soil fertility, type of crops that can be grown on the particular soil, etc.

- (i) Define soil pH
- (ii) Write briefly notes on the effect of prolonged use of ammonium sulphate fertilizer on soil pH.
- (iii) Write brief notes on the five factors that influence soil pH

(10marks)

(b) State the main negative impact(s) to environment of each of the following substances:

- (i) Hot water
- (ii) chlorofluorocarbons (CFCs)
- (iii) sulphur dioxide
- (iv) Lead
- (v) DDT

(5marks)

Examination Twenty
CHEMISTRY 2J

Answer **five (5)** questions

Question 1

(a) What is wrong with each of the following statements:
 (i) When polar liquids are mixed together, the resulting mixture is always ideal solution.
 (ii) Boiling point of any solution containing two volatile liquids always lies between boiling points of the pure liquids.
 (iii) Solution containing alcohol and water is appropriately separated into its pure components by simple fractional distillation.

(4.5marks)

(b) When two volatile liquids are mixed to form solution, the heat change for the process may be either be zero, positive or negative. Explain clearly each of the three scenarios.

(4.5marks)

(c) 18g of compound **X** distribute themselves between water and equal volume of an immiscible solvent **Y** so that 2g of **X** are in water. Calculate to the nearest integer, the percentages **X** left in $1000cm^3$ of water containing 1g of **X** are extracted by one Litre of **Y**.

(5marks)

(d) Steam is passed through a flask containing about 20g of Chlorobenzene (C_6H_5Cl).The mixture is found to boil at 91°C at 760mmHg. The vapour of water at 91°C is 540mmHg. Calculate:
 (i) Mole composition of the distillate.
 (ii) The mass composition of the distillate.
 (iii) Total volume of the distillate obtained when 90% of Chlorobenzene has been steam distilled. (Density of chlorobenzene is $1.1 g/cm^3$).

(6marks)

Question 2

(a)
 (i) State Kohlrausch's law of independent ionic mobility.
 (ii) Differentiate between an electronic conductors and electrolytic conductors.

(3marks)

(b) A conductivity cell with electrodes $2\ cm^3$ in area and 1 cm apart has a resistance of 7.25Ω when filled with 5% potassium chloride solution;
 (i) Calculate the cell constant
 (ii) Determine the conductivity of potassium chloride solution
 (iii) If the cell was filled with 0.02M KCl, with resistivity of $361\Omega cm$, what would the cell resistance be?

(5marks)

(c) The standard electrode potential for Zn^{2+}/Zn is $-0.76V$ and for Cu^{2+}/Cu is $+0.34V$
 (i) Draw a cell diagram of a cell that can be formed from Cu and Zn electrodes

(ii) Write the cell reaction and calculate its e.m.f under standard conditions
(iii) Calculate the equilibrium constant for the reaction

(6marks)

(d)

(i) Isolation of an acid from aqueous solution gave crystals **C** of molecular formula $C_2H_2O_4 \bullet xH_2O$. The acid can be oxidised quantitatively to carbon dioxide and water by acidified aqueous manganate (VII) above 60°C. This reaction can be represented by the equation:

$$2MnO_4^-(aq) + 5\,C_2H_2O_4 \bullet xH_2O(aq) + 6H^+ \rightarrow 2Mn^{2+}(aq) + (8 + 5x)H_2O(l) + 10CO_2(g)$$

Given that 0.126g of **C** required $20.00\ cm^3$ of aqueous manganate (VII) of concentration 0.02M for complete reaction, calculate the value of x in $C_2H_2O_4 \bullet xH_2O$

(ii) Give reason(s) for using the temperature which is above 60°C.

(6marks)

Question 3

(a) According to Bronsted-Lowry theory, HSO_3^- (aq) ion behave as an acid in the following reaction:

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq)$$

(i) Explain in terms of Bronsted-Lowry theory how HSO_3^- is acting as an acid
(ii) Write the formula for the conjugate base
(iii) Illustrate with an equation, how HSO_3^- ion can also act as a base

(4marks)

(b) The solubility product of lead (II) chloride ($PbCl_2$) has a value of $1.6 \times 10^{-5} mol^3dm^{-9}$ at 298K;

(i) Explain what is meant by this statement.
(ii) Calculate the solubility of lead (II) chloride in water at 298K.
(iii) Calculate the solubility of the above compound in 0.1M solution of lead (II) nitrate at the same conditions.

(6marks)

(c) The pH of a solution **A,** 0.15M solution of weak monoprotic acid, Hx is 2.69

(i) Calculate $[H^+]$ in solution **A** and hence determine the value of K_a for Hx
(ii) A 25 cm^3 sample of A is titrated with 0.25M NaOH. Calculate the pH of the titrated solution when Hx is exactly half neutralized and $[Hx] = [x^-]$
(iii) Which indicator is suitable for the titration (in (ii) above)? Give reason (s) for your answer.

(10marks)

Question 4

(a) Mendeleeff's was successful in arranging the elements according to his law in the form of a table. However the table produced some defects which, he could not explain. Explain the defects of Mendeleeff's periodic table under the following headings:
  (i) Position of isotope
  (ii) Position of isobars
  (iii) Anomalous pairs
  (iv) Position of lanthanides and actinides
  (v) Superfluous relationship

(7.5marks)

(b) Consider the reactions:

$$3H_2SO_4(conc) + 2NaBr \longrightarrow 2NaHSO_4 + Br_2 + SO_2 + 2H_2O$$

$$9H_2SO_4(conc) + 8NaI \longrightarrow 8NaHSO_4 + 4I_2 + H_2S + 4H_2O$$

Why does the same compound, sulphuric acid react differently with NaBr and NaI?

(2marks)

(c) With the help of chemical equation where applicable, explain each of the following:
  (i) Molten NaCl conduct electricity while molten $AlCl_3$ does not.
  (ii) Unlike other halogens, fluorine liberat.es oxygen from cold water.
  (iii) Alkali metals are good reducing agents.
  (iv) Effervescence of colourless gas is obtained when ammonium chloride solution is added to a warm aqueous solution of sodium nitrite.
  (v) PCl_3 is covalent liquid but in aqueous solution it conducts electricity.

(10.5marks)

Question 5

(a)
  (i) What is stable oxidation state?
  (ii) Mention three compounds in which the oxidation state of manganese is $+7, +6$ and $+4$ respectively.

(2marks)

(b) With the aid of balanced chemical equation where applicable, explain the following observations:
  (i) In aqueous solution, copper (II) ions are blue but turn green when excess hydrochloric acid is added to it.
  (ii) The addition of aqueous alkali to aqueous solution of iron (III) ions, give gelatinous reddish brown precipitate.
  (iii) The addition of aqueous ammonia solution to the solution of nickel (II) ions, gives green precipitate which dissolves to form blue solution when excess ammonia is added.
  (iv) Concentrated nitric acid has no practical reaction with iron.

(6marks)

(c) Identify and write structural formula of compounds B, C, D, E and F.

(i) $CH_3CH_2OH \xrightarrow{PCl_5} B \xrightarrow{Mg,Dry\ ether} C \xrightarrow{CH_2O,H_2O,H^+} D + Mg(OH)Br$

(ii) $C_2H_5Br \xrightarrow{KOH(aq)} E \xrightarrow{Cu,\Delta} F + H_2$

(5marks)

(d) A condensation polymer **A** has a repeating unit of $(C_7H_{12}O_2)$. **A** was heated with aqueous sodium hydroxide (NaOH) to give compound **B** $(C_7H_{13}O_3Na)$. When **B** was heated with soda lime, unbranched compound **C** $(C_6H_{14}O)$ was formed. When **C** was treated with dilute alkaline $KMnO_4$ on gentle warming and after acidification, compound **D** $(C_6H_{12}O_2)$ was formed. Identify compound **C** and **D** and hence deduce possible structures of compound **B** and **A**. Explain your reasoning and give equations from the reactions leading to the formation of compound **B** and **D**.

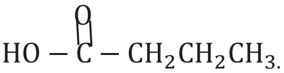
(7marks)

Question 6

(a) Consider the following pair of isomers.

$H-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_3$

C



$HO-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3.$

D

(i) Name the compound C
(ii) To which family do compound C and D belong?
(iii) Identify a reagent which could be used in a test-tube reaction to distinguish between C and D . In each case, state what you would observe.

(3marks)

(b) Classify the type of reaction and give the structure of the organic products of the reaction of propanal with;

(i) Sodium tetrahydridoborate (III)
(ii) Fehling's solution
(iii) Hydrogen cyanide

(3marks)

(c) Show how you can bring about the following conversions in not more than four (4) steps.

(i) $CH_3OH \longrightarrow CH_3CO_2H$
(ii) $CH_3CO_2H \longrightarrow (CH_3CO)_2O$
(iii) $C_6H_6 \longrightarrow C_6H_5NH_2$

(6marks)

(d) An organic compound **A** on treatment with ethyl alcohol gives carboxylic acid **B** and compound **C**. Hydrolysis of **C** under acidic conditions gives **B** and **D**. Oxidation of **D** with potassium permanganate gives **B**. **B** on heating with calcium oxide gives **E** with molecular formula C_3H_6O. **E** does not give positive result with Tollen's reagent and does not reduce Fehling's solution but forms 2,4-DNP hydrazone with Brady's reagent. Identify **A**, **B**, **C**, **D** and **E**.

(8marks)

Necta 2020
CHEMISTRY 1

SECTION A

Answer **all** questions in this section.

Question 1

(a) By using chemical equations, describe the following:
  (i) Amphoteric oxides
  (ii) Basic oxides **(4 marks)**

(b) With the aid of chemical equation(s), explain how you can prepare soluble chlorides. **(4 marks)**

(c) A student suggested a methodology to prepare aluminium trichloride ($AlCl_3$) by following stepS; (i)-(iv) as follows:
  (i) Add sodium hydroxide solution to aluminium sulphate solution.
  (ii) Filter off the precipitate
  (iii) Convert the hydroxide into a chloride by adding hydrochloric acid.
  (iv) Evaporate the solution to leave crystals of $AlCl_3$
  Could this process work? Justify. **(2 marks)**

Question 2

(a) Explain two detrimental effects of excessive salts in the soil. **(2 marks)**

(b) Give four advantages of adding organic manures in the soil. **(4 marks)**

(c) 20g of a soil sample was shaken with $40cm^3$ of 0.1MHCl solution. After filtering and washing the soil, the filtrate required $27cm^3$ of 0.1MNaOH solution for complete neutralization. The total Cation Exchange Capacity (CEC) of the soil is 29 milli. Eq. per 100g of the soil sample. Calculate the Percentage Base Saturation (PBS) of the soil sample. **(4 marks)**

Question 3

(a)
  (i) Name two natural sources of organic compounds. **(1 mark)**
  (ii) Briefly, explain three properties of carbon element that makes it able to form a large number of compounds. **(3 marks)**

(b) A form six student gave the following names for various substituted aliphatic hydrocarbons:
  (i) 2-methyl-3-bromobutane.
  (ii) 3,3-dimethyl-2chlorobutane.
  (iii) 4-chloro-3-bromo-2-pentene.
  (iv) 2-methyl-4-butyne.

  The names indicate the formulae of the substituted aliphatic hydrocarbons but do not strictly obey IUPAC rules. Draw the structure suggested by the incorrect names and assign the correct names for each compound. **(4 marks)**

(c) Explain each of the following observations:

(i) Methylpropane has a lower boiling point than butane although both have the same molecular mass.

(ii) Ignition sources such as smoking are not allowed at petrol stations.

(2 marks)

Question 4

(a) Diborane (B_2H_6) is very reactive such that it was once considered as a possible rocket fuel for U.S space programs. The overall equation for the synthesis of diborane is:

$$2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$$

Use the following data to calculate the enthalpy change of formation of B_2H_6 from its elements:

$2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s)$ $\Delta H = -1273kJ$

$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$ $\Delta H = -2035kJ$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286kJ$

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H = -286kJ$

(2 marks)

(b) When $100\ cm^3$ of 1MKOH and $100\ cm^3$ of 1MHCl were mixed in a calorimeter, temperature rose by 6.25 K. Given that heat capacity of the calorimeter was 95 J/K and specific heat capacity of the solution mixture was 4.2 J/gK, calculate the standard enthalpy of neutralization. Assume that, the density of the solution is equal to the density of water. **(5 marks)**

Question 5

(a)

(i) State four postulates of Dalton's atomic theory. **(2 marks)**

(ii) Why different atoms have different chemical properties? Briefly explain.

(1 mark)

(b) Write the chemical symbol $\left({}^{Z}_{A}X\right)$ and orbital electronic configuration for the atoms described in the following table:

SN	Number of Neutrons	Number of Electrons
(i)	13	11
(ii)	7	8
(iii)	17	18
(iv)	16	16

(4 marks)

(c) Calculate the minimum energy required to remove an electron from the hydrogen atom in its ground state. **(3 marks)**

Question 6

(a) Differentiate:

(i) Electrovalent bond from octet rule.
(ii) Lone pair from bonding pair of electrons. **(2 marks)**

(b) Using sketches, briefly explain three possible overlaps that can occur during sigma bond formation. **(3 marks)**

(c) Give two reasons for the observed difference in bond strength between sigma and pi bonds in compounds. **(2 marks)**

(d) Predict the geometry of ammonia, basing on the Valence Shell Electron Pair Repulsion (VSEPR) theory. **(3 marks)**

Question 7

(a) A 0.25 moles of air has entered a diesel engine at a pressure of 1.05×10^5 Pa and a temperature of 27°C. Assuming that the air is ideal, calculate:
(i) The volume it occupies. **(3 marks)**
(ii) Its temperature, immediately after compression to one twentieth of its original volume where the pressure rises to 7.0×10^6 Pa.

(b) A 42g of nitrogen gas and 8g of hydrogen gas are mixed in a 10 litre vessel at 20°C. Calculate the partial pressure of each gas and the total pressure of the gas mixture. **(4 marks)**

SECTION B

Answer **two (2)** questions from this section.

Question 8

(a)
(i) Differentiate between cryoscopic constant and ebullioscopic constant. **(2 marks)**
(ii) Derive an expression relating the Van't Hoff factor (i) and the degree of dissociation. **(2 marks)**
(iii) Briefly, explain the effect of degree of dissociation of a solute on the boiling point of solution. **(1 mark)**

(b) What mass of ethylene glycol, $C_2H_6O_2$, the main component of anti-freezing agent which mass is added to a 10.0L of water to produce a solution for use in a car radiator, that freezes at -23.3°C. Assume that the density of water is exactly 1 g/mL and cryscopic constant is 1.86 °Ckg/mol. **(4 marks)**

(c) A 0.120g of haemoglobin, the protein which carries oxygen in the blood was dissolved to 200cm^3 of benzene at 20 °C. The solution exerted an osmotic pressure of 25.6Pa. Find the relative molecular mass of haemoglobin. **(3 marks)**

(d) A 1% solution of sodium chloride freezes at -0.604 °C. Calculate the deree of dissociation of the sodium chloride if the molal freezing point depression constant for water is 1.86 °Ckg/mol. **(3 marks)**

Question 9

(a) (i) Briefly, explain the effect of change of pressure to a system at equilibrium. **(2 marks)**
(ii) Why a Coca cola soda fizzes out when its bottle is opened? Give a reason. **(1 mark)**

(b) Consider the following equilibrium:

$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$

Yellow Orange

What would be observed when:

(i) Dilute NaOH is added to the equilibrium mixture?

(ii) Dilute HCl is added to the equilibrium mixture? **(4 marks)**

(c) The following equilibrium was established during the preparation of phosphorous pentachloride:

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \quad \Delta H = -92.5kJ$

Explain what will happen on the amount of $PCl_3(g)$ if the temperature is:

(i) Raised

(ii) Lowered

(d) The following reaction occurs during the Haber process:

$N_2(g) + H_2(g) \rightleftharpoons 2NH_3(g)$

(i) Calculate the equilibrium constant for this reaction at $127°C$ if the equilibrium concentrations observed at this temperature were $0.031 mol/L$ for ammonia, $0.85 mol/L$ for nitrogen and $0.031 mol/L$ for hydrogen.

(ii) Using the same equilibrium concentrations in (d) (i), calculate the equilibrium constant at $127°C$ for the equilibrium:

$2NH_3(g) \rightleftharpoons N_2(g) + H_2(g)$ **(6 marks)**

Question 10

(a) Why benzene though highly unsaturated, it does not undergo addition reactions? Briefly explain. **(4 marks)**

(b) Name two examples in each of the following chemical groups:

(i) *Ortho-para* directors.

(ii) *Meta* directors. **(2 marks)**

(c) Why *ortho-para* directing groups are called activating groups and *meta-directing* groups are called deactivating groups? Briefly explain. **(4 marks)**

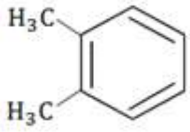
(d) Determine the structural formulae of the following compounds:

(i) 1,3,5-trimethylbenzene

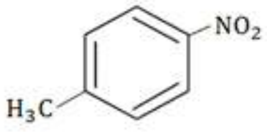
(ii) (1-methylethyl)benzene **(2 marks)**

(e) Give the IUPAC names of the following aromatic compounds:

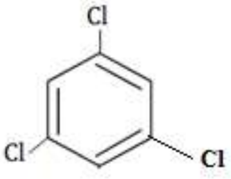
(i)



(ii)



(iii)



(3 marks)

Necta 2020
CHEMISTRY 2

Answer **five (5)** questions

Question 1

(a) Ethanol and water form an azeotropic mixture which boils at 78.01°C and contains 95.6% ethanol at standard pressure. If the boiling points of pure water and ethanol are 100°C and 78.4°C, respectively.

(i) Draw and label a temperature versus mole fraction phase-diagram of ethanol and water solution. **(4 marks)**

(ii) What happens when a dilute ethanol solution of less than 50% is boiled and condensed several times? **(4 marks)**

(iii) How would you increase the percentage of ethanol after obtaining a 95.6% ethanol-water mixture? **(4 marks)**

(b) When 500cm^3 of an aqueous solution containing 4g of a solute G per litre was shaken with 100cm^3 of pentan-1-ol, 1.5g of the solute G was extracted. Assuming the molecular state of the solute remained the same in both solvents, calculate:

(i) Partition coefficient of the solute G between pentan-1-ol and water. **(4 marks)**

(ii) Mass of the solute G which remained in the aqueous solution after a further shaking with $100\ \text{cm}^3$ of pentan-1-ol. **(4 marks)**

(c) Write two practical applications of the partition law. **(2 marks)**

Question 2

(a)

(i) What are the effects of a catalyst on the activation energy of a reaction? **(2 marks)**

(ii) Describe how temperature, concentration, light, pressure and surface area can affect the rate of a chemical reaction. **(5 marks)**

(b) The decomposition of a hydrogen peroxide at 25°C was studied by titrating portions of the reaction mixture with a standard potassium permanganate solution at different time intervals. The results obtained were tabulated as follows:

Volume of $KMnO_4(\text{cm}^3)$	75	47	30	13	7.20
Time (min)	0	6	9	20	29

(i) Show that the reaction is a first order.

(ii) Without using a graph, calculate the rate constant at given temperature. **(9 marks)**

(c) The reaction, $NH_4NO_2(aq) \rightarrow N_2O(g) + H_2O(l)$ is a first order with $k = 2.2 \times 10^{-5}\ \text{sec}^{-1}$

(i) Find the percentage of NH_4NO_2 that would decompose on heating at 310°C for 90 minutes.

(ii) If the rate of reaction triples when the temperature is raised from 20 to 50°C, calculate the activation energy of the reaction in kJ/mol. **(4 marks)**

Question 3

(a) Calculate the pH of a solution obtained when:
  (i) 1.0 cm^3 of 0.1MNaOH is added to 100 cm^3 of 0.001 M HCl.
  (ii) 1.0 cm^3 of 1.0MHCl is added to a 1000 cm^3 of a solution mixture prepared by dissolving 0.04moles of CH_3COOH. Use $K_a(CH_3COOH) = 1.84 \times 10^{-5}$.
(10 marks)

(b) How does Bronsted-Lowry concept account for the relative strength of acid-base conjugate pairs? **(4 marks)**

(c) Indicate the acid-base conjugate pairs in each of the following equilibria:
  (i) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
  (ii) $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$
  (iii) $AH + H_2O \rightleftharpoons A^- + H_3O^+$ **(6 marks)**

Question 4

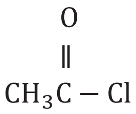
(a) Describe four characteristics of s-block elements. **(4 marks)**

(b) (i) What do you understand by the word electronegativity?
  (ii) Explain three factors that affect the size of electronegativity. **(6 marks)**

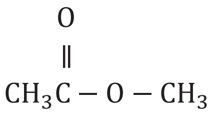
(c) Briefly, explain how hydrides of period 2 react with water, acids and bases. Support your answers with reaction equations. **(10 marks)**

Question 5

(a) With the aid of chemical equations, show how dimethylamine reacts with the following compounds:

(i) 

$CH_3C(=O)-Cl$

(ii) 

$CH_3C(=O)-O-CH_3$ **(3 marks)**

(b) Give the structural formula of the following compounds:
  (i) tripropylamine
  (ii) dipentlyamine
  (iii) 2,4-dimethyl-3-hexanamine **(3 marks)**

(c)
  (i) Show how you can carry out the conversion starting from propanoyl chloride to dipropylamine.
  (ii) Write the equation to show the reaction between benzaldehyde (C_7H_6O) and warm phenylamine.
  (iii) Write the general formula and functional group of secondary amine and tertiary amine.
  (iv) Write the equation for the equilibrium that exists when diethylamine dissolves in water. **(8 marks)**

(d) Give the structural formula for compounds B through E, which undergo the following sequence of reactions:

$$B(C_7H_8) \xrightarrow{Cl_2/light} C(C_7H_7Cl) + HCl$$

$$C \xrightarrow{NH_3} D(C_7H_{10}NCl) \xrightarrow{OH^-} E(C_7H_9N) + Cl^- + H_2O$$ **(6 marks)**

Question 6

(a) Briefly, explain the following and give one example for each:
  (i) Thermoplastic polymers
  (ii) Thermosetting polymers
  (iii) Natural polymers **(4 marks)**

(b) Write the monomers used in synthesis of the following polymers:
  (i) Polyvinylchloride (PVC)
  (ii) Teflon
  (iii) Bakelite **(3 marks)**

(c)
  (i) Why cationic polymerization is more favoured than anionic polymerization when vinylic monomers contain an electron donating group?
  (ii) Why styrene undergo anionic polymerization easily? Briefly explain.
  (iii) Differentiate addition from condensation polymers basing on the mode of polymerization. Give one example for each type. **(4 marks)**

(d) With reasons, write down the use of following polymers:
  (iv) Butyl-rubber
  (v) Polyacrylonitriles
  (vi) Polyhaloalkene **(6 marks)**

Necta 2021
CHEMISTRY 1

SECTION A

Answer **all** questions in this section.

Question 1

(a) Differentiate the following terms:
  (i) Isotopy from isotopes **(1 mark)**
  (ii) Atomic spectrum from photon. **(1 mark)**
  (iii) Continuous spectrum from line spectrum. **(1 mark)**

(b) Calculate the frequency of a wave in a visible region formed following the emission of energy by an electron falling from energy level $n = 4$ to the ground level. **(5 marks)**

(c) List two uses of mass spectrometer. **(2 marks)**

Question 2

(a) Identify a more energetically stable compound among the following pairs:
  (i) $NaBr$ and $NaBr_2$
  (ii) ClO_4 and ClO_4^-
  (iii) OF_4 and SeF_4
  (iv) SO_4 and XeO_4

(4 marks)

(b) Although the Valency Shell Electron Pair Repulsion theory (VSEPR) predict the CH_4 and NH_3 molecular geometries (or shapes), it does not account for the differences in (H-C-H) and (H-N-H) bonds whose angles are $109.5°$ and $107.3°$, respectively. Give reasons for the deviations. **(4marks)**

(c) Giving a reason, classify the type of bond involved in each of the following chemical equations:
  (i) $Ca + 2Cl \rightarrow Ca^{2+}(Cl^-)_2$
  (ii) $H^+ + F^- \rightarrow HF$

(2 marks)

Question 3

(a) Calculate the partial vapour pressure of water in a mixture of 36g of water and 32g of methanol at 298K, if the vapour pressure of pure water at 298 is 3.2kPa. **(4 marks)**

(b) A candle wax is approximately a non-volatile organic compound with molecular formula $C_{22}H_{46}$ and soluble in carbon tetrachloride. Calculate the vapour pressure of a solution made by dissolving 10g of the wax in 40g of carbon tetrachloride at 23°C, if the carbon tetrachloride has a vapour pressure of 100 mmHg at 23°C. **(4 marks)**

(c) Comment on the observation that, further dilution of 0.1 M KCl solution causes the observed relative molecular mass to approach the theoretical value 37.3. **(2 marks)**

Question 4

(a) Using the following chemical equations and values provided for each, calculate the enthalpy of formation of $Ca(OH)_2$.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\ \Delta H = -68.3kCal$$
$$Ca(s) + H_2O(l) \rightarrow Ca(OH)_2(s);\ \Delta H = -15.3kCal$$
$$Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s);\ \Delta H = -151.8kCal$$

(5marks)

(b) Diborane,(B_2H_6) is synthesized in the laboratory according to the equation:
$2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$.
Calculate the heat change for the synthesis of diborane from its elements, using the enthalpies provided in the following table:

S/N	Reaction	ΔHkJ
1	$2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s)$	−1273
2	$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$	−2035
3	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	−286
4	$H_2O(l) \rightarrow H_2O(g)$	44

(5marks)

NECTA 2021 - QNS P1

Question 5

(a) Justify on the following facts:
  (i) Ion exchange in the soil system is a reversible process.
  (ii) All calcium or magnesium compounds can be liming materials.
  (iii) Aluminium contributes to soil acidity.

(6 marks)

(b) Rungwe high school farm soil requires 100kg of nitrogen to fulfil the plant requirements of nitrogen per hectare. If the farm has 60 hectares, calculate the number of bags of ammonium sulphate,$(NH_4)_2SO_4$ fertilizer required to meet this demand. (One bag of fertilizer weights 25kg). **(4 marks)**

Question 6

(a) When dilute hydrochloric acid is added to a yellow solution of potassium chromate, an orange solution of dichromate is produced. Briefly, explain what would be observed as a result of:
  (i) Adding more hydrochloric
  (ii) Adding dilute sodium hydroxide solution
  (iii) Adding anhydrous calcium chloride.

(6 marks)

(b) Briefly explain the following:
  (i) Hydrogen gas is evolved when magnesium is introduced into a beaker containing aqueous solution of ammonium chloride.

(ii) $AlCl_3$ reacts chemically with water while NaCl does not.

(4marks)

Question 7

(a)

(i) What are the properties that makes organic compounds suitable source of fuel? **(2 marks)**

(ii) Compressed natural gas methane, (CH_4) is a fossil fuel found in a large quantities in our country, Tanzania. Due to its several advantages, compressed natural gas is considered the most promising vehicles' fuel and thus it should be promoted as the main fuel in our country. State four benefits offered by the compressed natural gas over conventional fuel like gasoline and diesel. **(4 marks)**

(b) Suggest suitable chemical test to distinguish between the following compound:

(i) Butane and 1-butene

(ii) Propyne and propene

(iii) Pent-1-yne and pent-2-yne

(iv) Propane and 1-bromopropane

(4 marks)

SECTION B

Answer **two (2)** questions from this section

Question 8

(a)

(i) State Le Chatelier's principle. **(1mark)**

(ii) How does homogeneous equilibrium differ from heterogeneous equilibrium as applied in Chemistry? **(1mark)**

(b) Predict the direction of the net reaction for each of the following equilibrium reactions when the pressure of the system is doubled at constant temperature. Give one reason for each case.

(i) $2Pb(s) + 3O_2(g) \rightleftharpoons 2PbO(s) + 2O_2(g)$ **(1 mark)**

(ii) $PCl_5(g) \rightleftharpoons PCl_3(s) + Cl_2(g)$ **(1 mark)**

(iii) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ **(1 mark)**

(c) Hydrogen iodide gas was synthesized from hydrogen gas and iodine vapour at $450°C$ in a 2.0litres vessel. The value of the equilibrium constant, K_c for the reaction was found to be 50.5. If 1.0×10^{-2} moles of hydrogen gas, 3.0×10^{-2} moles of iodine vapour and 2.0×10^{-2} moles of hydrogen iodine were placed in a vessel at the stated temperature;

(i) Write a balanced equilibrium reaction equation for the synthesis of hydrogen iodide gas. **(1 mark)**

(ii) Calculate the reaction quotient (Q) for the reaction. **(3 marks)**

(iii) State whether the reaction will proceed to the right or left of the equation. Give a reason. **(2 marks)**

(iv) With a reason, comment on a possible effect regarding the equilibrium position, if the pressure of the reaction system is increased. **(1 mark)**

(d) Consider the reaction; $K_2 + N_2 \rightleftharpoons 2KN$; $\Delta H = -20\,Jmol^{-1}$ which has an equilibrium constant, $K_c = 10$ at $25°C$. Calculate equilibrium constant in terms of partial pressure, (K_p) at the same temperature. **(3 marks)**

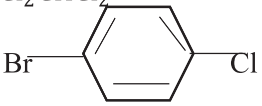
Question 9

(a) Write the IUPAC name of the following organic compounds:

(i) CCl_3CH_3

(ii) $CHCl_2CCl_2CHCl_2$

(iii)



(iv) $CCl_3CH_2CCl_3$

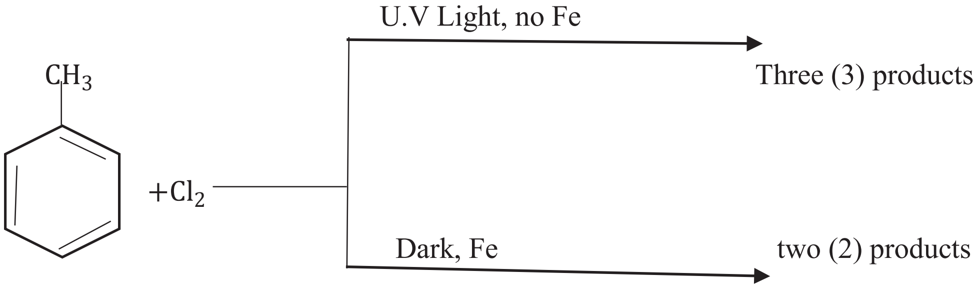
(2 marks)

(b) With the aid of a chemical equation (no reaction mechanism is needed), give a reason for the position occupied by bromide atom when bromine reacts with:

i) Phenol. **(1 mark)**

ii) Benzene carbaldehyde. **(1 mark)**

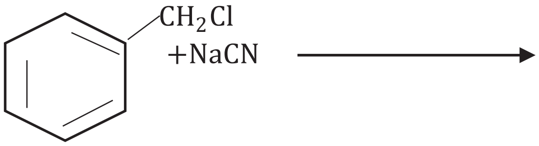
(c) Write the structures and the name of five products in the following reaction:



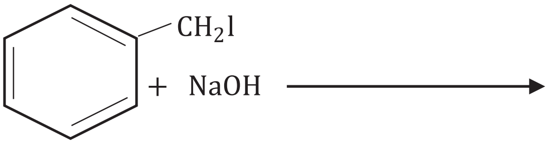
(5marks)

(d) Write the product of each of the following nucleophilic substitution reactions:

(i)



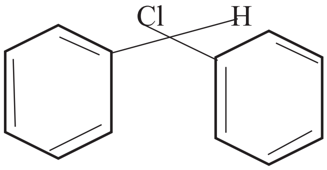
(ii)



(2marks)

(e) Write a chemical test to distinguish the following chemical compounds.

(i) Bromobenzene from

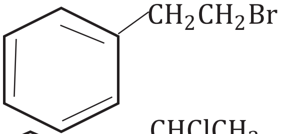


(ii) Vinyl bromide from p-chlorobenzene.

(2 marks)

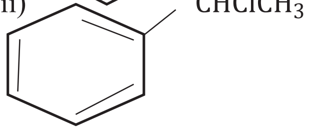
(f) Using chemical equations, show step-wise conversion of 2-phenol into each of the following organic compounds:

(i)



(1 mark)

(ii)



(1 mark)

Question 10

(a) Show how Boyle's and Charles's law are special cases of the ideal gas law.

(3 marks)

(b)

(i) Theoretically, ideal gasses cooled to temperature of $-273.15°C$ will occupy zero (0) volume. With reasons(s) comment on whether gases practically occupy zero volume at such temperature.

(2 marks)

(ii) Molecule A is twice as heavy as molecule B. Which of these has higher kinetic energy at any temperature? Give a reason.

(1 mark)

(c) Briefly explain the following:

(i) Liquid ammonia bottle is cooled before opening the seal.

(ii) The tyre of an automobile is inflated to a slightly lower pressure in summer than in winter.

(2marks)

(d) A 1.0 litre sample of dry air at25°C and 786mmHg contains o.925g of nitrogen gas (N_2) and other gas. Considering dry air to behave ideally, calculate the:

i) Mole fraction of (N_2) in the gas sample. **(3 marks)**

ii) Partial pressure of (N_2) in the gas sample (in mmHg). **(1 mark)**

(e) The volume of $200cm^3$ of oxygen gas required 250 seconds to diffuse through a porous membrane. Under the identical conditions, $200cm^3$ of gas 'Z' diffused in 177 seconds. Calculate the relative molecular mass of gas 'Z'. **(3marks)**

Necta 2021
CHEMISTRY 2

Answer **five (5)** questions

Question 1

(a)

(i) Distinguish between an electrolytic cell and a galvanic cell. **(1 mark)**

(ii) Lead rods are placed in each of the following solutions: $AgNO_3, CuSO_4, FeSO_4$ and $ZnSO_4$. In which solution would you expect a coating of one metal on lead rod? Give a reason.

(Given: $E^{\theta}(Zn^{2+}/Zn) = -0.76V, E^{\theta}(Pb^{2+}/Pb) = -0.13V, E^{\theta}(Cu^{2+}/Cu) = +0.34V, E^{\theta}(Ag^{2+}/Ag) = +0.81V$ and $E^{\theta}(Fe^{2+}/Fe) = -0.44V$)

(3 marks)

(b) Why the Kohlrausch's law of independent migration of ions applies at infinite dilution of electrolytes? Briefly explain.

(1 mark)

(c) Show that for the cell reaction

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ with different cell concentrations and the temperature 298K, the cell potential is given by;

$$E = E^{\theta}_{cell} - 0.0295\log\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$$

(7 marks)

(d) A galvanic cell consists of metallic zinc and lead plates immersed in 0.1 M $Zn(NO_3)_2$ and
$0.02M\ Pb(NO_3)_2$ solution.

(i) Write the chemical equations for the electrode reactions.

(ii) Write the cell notation for the reaction.

(iii) Calculate the e.m.f of the cell.

(8 marks)

Question 2

(a) Write a mathematical expression for distribution law.

(2 marks)

(b) Compound **P** has a partition coefficient of 4.00 between ethoxyethane and water. Given that 2.0g of **P** is obtained in solution, in $50cm^3$ of water, calculate the mass of **P** that can be extracted from the aqueous solution by:

(i) $50cm^3$ of ethoxyethane.

(ii) Two successive extractions of $25cm^3$ of ethoxyethane each.

(8 marks)

(c) Comment on the variation of the amount extracted in (b) (i) and (ii)

(2 marks)

(d) When $500cm^3$ of an aqueous solution containing 4g of a solute **G** per litre was shaken with $100cm^3$ of pentan-1-o1, 1.5g of the solute **G** was extracted. Assuming a molecular state of the solute remains the same in both solvents, calculate:

(i) The partition coefficient of the solute **G** between pentan-1-o1 and water.

(ii) Mass of the solute **G** which will remain in the aqueous solution after a further shaking with 100cm^3 of pentan-1-o1.

(8 marks)

Question 3

(a) To a solution containing $0.1\mathrm{MCl^-}$ and $0.01\mathrm{M\ CrO_4^{2-}}$, a solution of $\mathrm{AgNO_3}$ is added slowly.

(i) Which salt will precipitate first between AgCl and $\mathrm{Ag_2CrO_4}$? Show clearly how you arrived to your answer.

(ii) Find the concentration of the ion that will precipitate first at the time the second ion will start precipitating. Use $\mathrm{K_{sp}}(\mathrm{AgCl}) = 2.72 \times 10^{-10}$ and$\mathrm{K_{sp}}\ (\mathrm{Ag_2CrO_4}) = 2.4 \times 10^{-12}$

(8 marks)

(b) Calculate the solubility of $\mathrm{Ag_2CrO_4}$ in water if the value of solubility product $\mathrm{K_{sp}}$ is $1.3\times 10^{-11}\ (\mathrm{mol/L})^3$. **(4 marks)**

(c) A standard solution of $\mathrm{AgCl(aq)}$ at $36°\mathrm{C}$ has a conductivity of $1.32 \times 10^{-6}\Omega^{-1}\mathrm{cm^{-1}mol^{-1}}$. If its molar conductivity at infinite dilution is $\Omega^{-1}\mathrm{cm^2mol^{-1}}$, calculate

(i) The solubility of AgCl in $\mathrm{g/dm^3}$

(ii) The solubility product of AgCl at the given temperature.

(8 marks)

Question 4

(a) State the reason(s) for the following facts;

(i) Although $\mathrm{Na^+}, \mathrm{Mg^{2+}}$ and $\mathrm{Al^{3+}}$ ions have the same electronic configuration, they have different radii.

(ii) At ordinary temperature, phosphorous pentachloride($\mathrm{PCl_5}$) is a white solid with unexpected high melting point.

(iii) Sodium chloride (NaCl) and anhydrous aluminium chloride ($\mathrm{AlCl_3}$) are both chlorides of metals of period (III). Molten sodium chloride can be electrolyzed while molten anhydrous aluminium chloride cannot.

(iv) The first ionization energy increases from left to right across a period but the first ionization energy of magnesium is larger than that of aluminium.

(v) Lithium and potassium are metals of group (I). In aqueous solution, lithium is a poor conductor of electricity while potassium is a good conductor.

(vi) Boiling point of water ($\mathrm{H_2O}$) is higher than that of hydrogen sulphide ($\mathrm{H_2S}$). All are hydrides of group (IV) elements.

(11 marks)

(b)

(i) Which factors are used to classify elements in the periodic system of elements?

(ii) Account for the fact that the third period of the periodic system of elements has only eight elements and not eighteen as expected.

(3 marks)

(c) Ammonia, $\mathrm{NH_3}$ and phosphine, $\mathrm{PH_3}$, are hydrides of the first two elements in group VA. Some physical properties of ammonia and phosphine are given in the following table:

Compound	Boiling point(℃)	Solubility in water(Mol/ dm^3)
Ammonia, NH_3	-33	31.1
Phosphene,PH_3	-88	8.88×10^{-4}

(i) Suggest one reason for the difference in boiling temperature.
(ii) Why ammonia is more soluble in water than phosphene? Give a reason.

(2 marks)

(d) Why do elements exhibit diagonal relations? Briefly explain by giving two examples.

(4marks)

Question 5

(a) From the knowledge you have on hydroxyl group, write the chemical reaction equations with their IUPAC names showing what happen when propan-1-o1 is treated with;

(i) Excess HBr under reflux.
(ii) A small amount of concentrated H_2SO_4
(iii) Acidified $KMnO_4$
(iv) Ethanol acid in the presence of concentrated H_2SO_4
(v) $SOCl_2$

(10 marks)

(b) Compound **A** ($C_{10}H_{12}O$) gives off oxygen on treatment with sodium metal and also decolorizes Br_2 in CCl_4 to give organic compound **B**. Compound **A** on treatment with I_2 in NaOH gives iodoform and a salt **C** which after acidification gives a white solid **D** ($C_7H_6O_2$). Using knowledge of organic chemistry, identify structures **A**, **B**, **C** and **D**.

(10marks)

Question 6

(a) How can you distinguish the following? Support your answer with chemical equation.

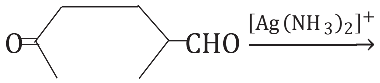
(i) Propanal and propanone.
(ii) Ethanal and benzaldehyde.
(iii) Pentanal and pentan-2-one.
(iv) 3-pentanone and 2-pentanone.

(8 marks)

(b) An organic compound **A** which has a characteristics odour is treated with 50% NaOH to give **B**(C_7H_8O) and **C** which is a sodium salt of an organic acid. Oxidation of **B** gives back **A**. Heating **C** with soda lime yields an aromatic hydrocarbon **D**. Deduce the structures **A**, **B**, **C** and **D**.

(8marks)

(c) Complete the following equations by giving the missing reagents/products;

(i) 

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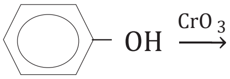
(ii) 

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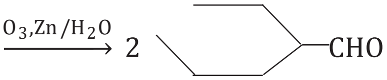
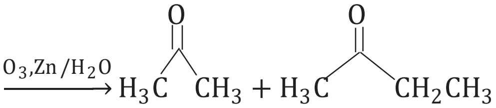
(iii) … . … … 

(iv) … … … … … … … … 

(4 marks)

Necta 2022
CHEMISTRY 1

SECTION A

Answer **all** questions in this section.

Question 1

(a) Energy of an electron in hydrogen atom is given by the expression,

$$E_n = \frac{-1.312 \times 10^6}{n^2} J/mol.$$

(i) Calculate the amount of energy required to promote an electron from the first energy level to the third energy level.

(ii) Why an electron in its ground state possesses energy less than zero?

(3 marks)

(b)

(i) The elements **X**, **Y** and **Z** have the following electronic configurations:

X: $1s^2 2s^2 2p^6 3s^2 3p^6$

Y: $1s^2 2s^2 2p^6 3s^2$

Z: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

The first ionization energies of the three elements (not in the same order) are 420, 740 and 1500kJ/mol and the atomic radii are 1.60, 0.94 and1.97A°. Identify the three elements and match the appropriate ionization energy and atomic radius to each configuration.

(3 marks)

(ii) Excited sodium atoms may emit radiation with the frequency of $5.09 \times 10^{14}/s$. What is the energy of the photons associated with this radiation?

(2 marks)

(c) Briefly, differentiate the following terms:

(i) Line from continuous spectrum.

(ii) Absorption from emission spectrum.

(2 marks)

Question 2

(a) Consider the following reaction that takes place in a fixed volume of a container:

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$; $\Delta H^\theta = -104kJ/mol$. How each of the changes affect the quantity of the reactants, products and equilibrium constant (K_c)? Answer by writing 'Increase', 'Decrease' or 'No change' appropriately, in a tabular form:

Change	**H_2**	**Br_2**	**HBr**	**K_c value**
Addition of some H_2				
Removal of some HBr				
Raise in temperature				
Increase in pressure				

(8 marks)

(b) When the reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ was studied at $25°C$, the partial pressures at equilibrium were found to be 1.2atm for NOCl, 5.0×10^{-2}atm for NO and 0.3atm for Cl_2. What would the K_p value for this reaction at 25°C?

(2 marks)

Question 3

(a) If the vapour pressure of water at $20°C$ is 17.5mmHg and lowering of vapour pressure of a sugar solution is 0.061mmHg, calculate;

(i) The relative lowering of vapour pressure.

(ii) The vapour pressure of the solution.

(iii) The mole fraction of sugar and water.

(4 marks)

(b) Ethanoic acid had a freezing point of $16.63°C$. When 2.5g of an organic solute was added to 40g of the acid, the freezing point was lowered to $14.48°C$. Calculate the relative molecular mass of the solute (Given K_f for ethanoic acid $3.9°C/m$).

(3 marks)

(c) An aqueous solution freezes at 272.07K while pure water freezes at 273K. Calculate the molality and boiling point of this solution (Given K_f for water $= 1.86K/m, K_b = 0.512K/m$) **(3 marks)**

Question 4

(a)

(i) Predict whether a chemical bond will be covalent or ionic basing on the charge and the relative size of the cations and anions as follows:

Cation/anion	**Ionic radium(nm)**	**Chemical bond**
C^{4+}	0.015	
1^{-}	0.216	
Na^{+}	0.095	
F^{-}	0.136	

(ii) "Intermolecular hydrogen bonding and dative covalent bonding are among the type of bonds exhibited by a number of molecules." Justify this statement by drawing a structure of a molecule for each type of the bonds aforementioned.

(4 marks)

(b) Briefly, comment of the following observations:

(i) Fluorine, chlorine and bromine form hydrides, but the hydride of fluorine forms hydrogen bond, whereas those of chlorine and bromine do not.

(ii) When molecules of hydrogen chloride are placed together, they do not show induced dipole interactions but they do so when placed with molecules of argon.

(2 marks)

(c)

(i) What is the difference between sp^2 and sp hybridization?

(ii) Which bond is stronger than the other in each of the following pairs? Give a reason for your choice.

$$C \equiv O \text{ or } C = O; C - N \text{ or } C - O; C - C \text{ or } C = C$$

(4 marks)

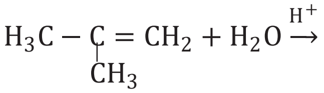
Question 5

(a) A certain chemical industry in Tanzania got an order to supply some reagents for research purposes. However, the requested reagents were not in the stock at the moment though enough starting materials shown in each case were present. What synthetic route(s) will you device in each case to meet the order required? Confine your reactions in not more than four steps.

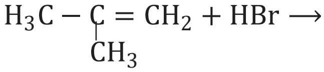
(i) Propan-1,2-diol from propene
(ii) Acetone from 2-methylpropene
(iii) Ethanol from propane
(iv) Ethyne from calcium carbide

(5 marks)

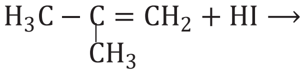
(b) Use Markovnikov's rule to predict the products of the following reactions:

(i) 

$H_3C - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2 + H_2O \xrightarrow{H^+}$

(ii) 

$H_3C - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2 + HBr \longrightarrow$

(iii) 

$H_3C - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2 + HI \longrightarrow$

(3 marks)

(c) "Wurtz synthesis is not suitable for preparation of an asymmetrical alkane." Briefly, justify this statement while supporting your answer with a chemical equation.

(2 marks)

Question 6

(a)

(i) Give that, the heat of formation of $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are $-393.5, -121.31$ and $-241.8 kJ/mol$, respectively. Calculate the enthalpy change ($\Delta H°$) for the reaction

$$CO_2(g), + H_2(g) \rightarrow CO(g) + H_2O(g)$$

(4 marks)

(ii) What are the four factors affecting the quantity of heat evolved or absorbed during a physical or chemical transformation?

(2 marks)

(b) Determine the heat of formation of ethyne basing on the following information given by the reactions **A-D**

A: $C(s)+O_2(g) \rightarrow CO_2(g); \Delta H_f = -393mol^{-1}$
B: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \Delta H_f = -286kJmol^{-1}$
C: $6C(s)+ 3H_2(g) \rightarrow C_6H_6(g); \Delta H_f = +50.2kJmol^{-1}$
D: $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l);\ \Delta H_f = -1323kJmol^{-1}$

(4 marks)

Question 7

(a) Suppose you are employed by the National Environment Management Council (NEMC), an institution which has a mandate to oversee the environmental management issue in Tanzania; what are the four possible intervention measure of environmental degradation you can address to the community.

(4marks)

(b) "Most of the greenhouse gases are produced from anthropogenic activities." Justify this statement by giving two reasons while supporting your answer with appropriate chemical equation in each case.

(2marks)

(c) Acid rain is formed as a result of excessive dissolution of gases in the atmosphere to produce acids with pH less than 5.6. What are the four chemical reactions that take place during the formation of an acidic rain?

(4marks)

SECTION B

Answer **two (2)** questions from this section

Question 8

(a)

(i) While pumping air into a ball, the volume as well as the pressure increase. Does the Boyles's law applicable here? Briefly, explain.

(ii) Hot air balloons are being used in the Serengeti National Park by tourists. Why hot air is more preferred in filling these balloons than cold air? Briefly, explain.

(iii) It is said that "Dalton's law of partial pressure cannot hold true for a mixture of SO_2 and O_2 gases. Briefly, explain the truth of this argument.

(iv) What would have happened to the gate pressure if the molecular collisions were not elastic?

(4 marks)

(b) The density of a gas at $27°C$ and $1520mmHg$ pressure was found to be $5.46 \times 10^{-3} g/cm^3$. What will be its density in g/cm^3 at **s.t.p.**?

(4 marks)

(c)

(i) Relative densities of carbon dioxide and oxygen are 22 and 16, respectively. If $25cm^3$ of carbon dioxide diffuses in 75 seconds, what volume of oxygen gas will diffuse in 96 seconds under similar conditions?

(5 marks)

(i) What are the two significances of Graham's law of diffusion in our daily life?

(2 marks)

Question 9

(a) Briefly, explain five uses of metal oxides in daily life.

(5 marks)

(b) When a dilute nitric acid was added to a green solid **P**, a blue solution **Q** was formed and a gas **R** that formed a white precipitate with lime water was evolved. When the blue solution was evaporated to dryness by heating it in crucible, a black solid **S**, brown fumes of gas **T** and a gas that relighted a glowing splint were formed.

(i) Identify solid **P** and **S**, and gases **R** and **T**.

(ii) Write an equation for the reaction between solid **P** and dilute nitric acid.

(6 marks)

(c) What is the importance of the following metal compounds in everyday life?

(i) Lime stone

(ii) Plaster of Paris.

(4 marks)

Question 10

(a) Briefly, explain the following concepts:

(i) Concentrated sulphuric acid is necessary for nitration of benzene.

(ii) Bromination of benzene takes place in the presence of Lewis acid, while that of hydroxybenzene does not require the presence of Lewis acid.

(iii) Despite chlorine atom being an electron withdrawing group, it directs an incoming group to the ortho or para positions in electrophilic aromatic substituting reactions.

(3marks)

(b) During one of the practical sessions in a school, a student wanted to differentiate a set of reagents. Briefly, advise the student on how to differentiate the given sets of reagents while supporting your answer with a chemical equation:

(i) Benzene and ethane

(ii) 3-chloro-2-methylpent-2-ene and 1-chloropropane

(iii) Bromobenzene and bromomethane.

(6 marks)

(c) Briefly, explain the following concepts:

(i) $(CH_3)_2CHBr$ Undergoes SN_1 mechanism, while $CH_3CH_2CH_2Br$ undergoes SN_2 mechanism when they react with aqueous alkalis.

(ii) Haloalkanes undergo nucleophilic substituting reactions, while halobenzenes undergo electrophilic substitution reactions.

(4 marks)

(d) Two isomeric hydrocarbons **K** and **L** have the molecular formula C_9H_{12}. On oxidation, **K** gives a monocarboxylic acid which when heated with excess soda lime yields benzene. When **L** is oxidized, it gives tricarboxylic acid, which can undergo nitration to give a monoderivative. What are the structural formulae of **K** and **L**?

(2 marks)

Necta 2022
CHEMISTRY 2

Answer **five (5)** questions

Question 1

(a)

(i) A solid Y is added to a mixture of benzene and water. After shaking well and allowing the mixture to equilibrate, 10cm^3 of the benzene layer was found to contain 0.13g of Y while 10cm^3 of the aqueous layer contained 0.22g of Y. Calculate the value of the distribution coefficient of Y between benzene and water.

(ii) Comment on the solubility of Y in benzene and water with respect to the distribution coefficient you have obtained in 1(a) (i).

(8 marks)

(b)

(i) What are the two applications of fractional distillation? Explain briefly.

(ii) Calculate the percentage by mass of bromobenzene (C_6H_5Br) in the distillate when a mixture of bromobenzene and water distills in steam at 95°C. The vapour pressure of bromobenzene and water at 95°C are 1.59×10^4 and $8.50 \times 10^4\ \text{Nm}^{-2}$ respectively.

(6 marks)

(c) Heptane (C_7H_{16}) and octane (C_8H_{18}) form an ideal solution. At 373 K, the vapour pressures of pure heptane and octane were 105.2 kPa respectively. Calculate the vapour pressure of the mixture of 26.0g of heptane and 35.0g of octane.

(6marks)

Question 2

(a) Calculate the pH of a sample of pure water at 25°C.
Given $\text{Kw} = 10^{-14} mol^2/dm^6$ at 25°C. **(4 marks)**

(b) A 500cm^3 of 0.1M aqueous solution of CH_3COOH(acetic acid) were mixed with 500cm^3 of 0.1M HCl solution. If 3g of NaOH are added to the mixture, calculate the pH of mixture before and after addition of NaOH, assuming that no change in volume occurs on mixing.

(6 marks)

(c)

(i) Although lead (II) chloride is sparingly soluble in pure water, it is soluble in concentrated hydrochloric acid. Explain briefly.

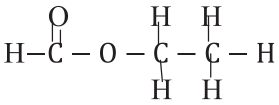
(ii) A chemist wanted to separate Al^{3+} and Zn^{2+} using fractional precipitation method. In the first experiment, NH_4OH was added and both Al^{3+} and Zn^{2+} precipitated. In the second experiment, NH_4OH was added followed by addition of NH_4Cl and only Al^{3+} precipitated. Comment briefly on the results obtained in the second experiment.

(5 marks)

(d) Equal volumes of $0.025\ \text{mol/dm}^3$ barium nitrate and $0.010\ \text{mol/dm}^3$ sodium fluoride were mixed together. Show whether the solution is saturated, supersaturated or unsaturated. (K_{sp} value of BaF_2 is $1.7 \times 10^{-6}\text{mol}^3/\text{dm}^9$). **(5 marks)**

Question 3

(a) Compound Q is commonly added to foods to give them rum flavor. It has the following structure formula:



$$H-\overset{\overset{O}{\|}}{C}-O-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H$$

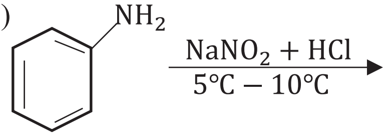
(i) To which class of organic compounds does the compound Q belongs?
(ii) How would you synthesize compound Q from ethanoic acid and methanol and any other suitable inorganic reagent?
(iii) What is the IUPAC name of compound Q?
(iv) Compound Q can react with NaOH in presence of heat. How can you represent this reaction using a chemical equation?

(8 marks)

(b) Briefly, comment on the following observations:
(i) The boiling point of ethanoic acid is higher than that of ethanol.
(ii) Methylamine is a stronger base than ammonia.
(iii) Trimethylamine and n-propylamine have the same molecular mass but the former boils at a lower temperature(276K) than the later (322K).

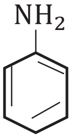
(6 marks)

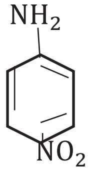
(c) Complete the following organic reactions:
(i)

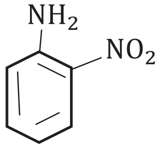


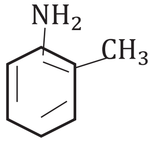
(ii) $CH_3CH_2NH_2 + CHCl_3 + KOH \xrightarrow{\text{alcohol}}$

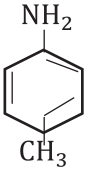
(d) Arrange the following organic compounds in order of increasing their basic strength.











(2 marks)

Question 4

(a) During a tour to one of the emerging local industries in Tanzania, it was noticed that some of the machine parts made up of iron were corroding. What do you think would be the factors affecting the extent of corrosion? Briefly, explain three factors only.

(6 marks)

(b) By using half-reaction method, balance the following redox reaction if it takes place in an acidic medium:

$$O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+} + NO_3^-(aq).$$

(4 marks)

(c) Ethanedioc acid crystal, $H_2C_2O_4.\ 2H_2O$, weighing 0.95g was dissolved in a 0.25 dm^3 of distilled water. A 0.25 cm^3 of the resulting solution required 33.0 cm^3 of potassium permanganate (VII) solution for complete reaction during a titration experiment. Calculate the concentration of potassium permanganate (VII) solution.

(6 marks)

(d) With a reason, predict if the reaction will occur when iodine and bromine are added to a solution containing ions of iodide and bromide at 1M. The electrode potential for the reactions are given as follows:

$I_2 + 2e \rightarrow I^-, E^\theta = +0.54V$

$Br_2 + 2e \rightarrow 2Br^-, E^\theta = +1.08V$

(4 marks)

Question 5

(a)

(i) What is the difference between periodicity and diagonal relationship?

(ii) How is tin reduced by thermal method in the reverberator furnace? Explain briefly while supporting your answer with appropriate chemical equations.

(4 marks)

(b) 'Lithium and magnesium relate diagonally in a periodic table of elements' By giving three reasons, briefly justify this statement.

(6 marks)

(c) The metallic characters of the elements change across the period. Illustrate this concept with reference to chlorides and hydrides of the elements of period 3.

(10 marks)

Question 6

(a) By giving a reason, arrange the following complex compounds in order of increasing their magnetic properties.

$[MnCl_4]^{2-}, [FeF_6]^{4-}, [Fe(CN)_6]^{4-}$

(2marks)

(b) Briefly explain the following:

(i) A concentrated aqueous copper(II) chloride solution is bright green in color but changes to light blue when diluted with water.

(ii) The d orbitals for both zinc and copper contain paired electrons, but copper is considered a transition element while zinc is not.

(4 marks)

(c) You have been employed as a chemist in a chemical industry which plan to use transition elements as catalysts in their production. Briefly, explain four applications/uses of transition elements as catalysts. Support your answer with one chemical equation in each case. **(4 marks)**

(d)

(i) With an example in each case, explain two types of polymers based on physical properties.

(ii) Why Tanzania government banned the use of polymers obtained from ethylene monomers? Briefly, explain.

(iii) How does the structural differences of High Density Polythene (HDP) and Low Density Polythene (LDP) account for their differences in behavior and nature?

(10marks)

Necta 2023
CHEMISTRY 1

SECTION A

Answer **all** questions in this section.

Question 1

(a) A person swallowed a drop of liquid oxygen, o_2(l),which has a density of $1.149 g/cm^3$ Assuming the drop has a volume of $0.050 cm^3$,calculate the volume of a gas that will be produced in the person's stomach at body temperature (37°C) and a pressure of one (1) atmosphere.

(3 marks)

(b) A compound contains only nitrogen and hydrogen and is 87.4% nitrogen by mass. A gaseous sample of the compound has a density of 0.977g/L at 710 mmHg and 100°C.Determine the molecular formular of the compound

(4 marks)

(c) A total volume of $2.50\times 10^2 cm^3$ chlorine gas was collected over water at 20°C and a total pressure of 1 atm. Calculate the mass of chlorine collected at this temperature if the vapour pressure of water was 17.5mmHg.

(3 marks)

Question 2

(a) Comment briefly on the following observation:

(i) Sodium chloride solution freezes at a lower temperature than that of pure water but boils at higher temperature than pure water.

(ii) A driver adds ethylene glycol to water in a car radiator during winter season.

(iii) The blood cells which are isotonic with 0.9% sodium chloride solution are placed in 1.2% sodium chloride solution

(iv) When dehydrated fruits and vegetables are placed in water, they slowly swell and return to the original forms.

(4 marks)

(b)

(i) Eighteen grams (18g) of glucose $C_6H_{12}O_6$ (molar mass = 18 g/mol) are dissolved in 1kg of water in a sauce pan. At what temperature will this solution boil? Given the k_b for water = 0.52 kg/mol.

(3 marks)

(ii) Calculate the elevation in boiling point that is expected for an alcohol when 5g of urea (molar mass 60g/mol) are dissolved in 75g of it. Given the moral elevation constant for the alcohol = 1.15K/m

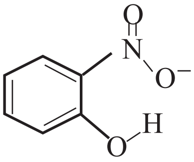
(3 marks)

Question 3

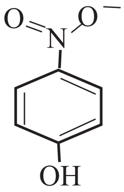
(a) What are the two condition necessary for the formation of hydrogen bond? Briefly explain

(2 marks)

(b) Study the chemical structure of composition **I** and **II** and answer the questions that follow while giving one reason in each case



I



II

(i) What type of hydrogen bonding is exhibited in each compound?
(ii) Which of the two compounds is expected to have higher melting point than the other?
(iii) Which compound is likely to be more soluble in polar solvent? **(4 marks)**

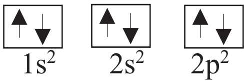
(c) Indicate the types of bonds present in NH_4NO_3 and the mode of hybridization of the N atom in the NO_3^- ion **(4 marks)**

Question 4

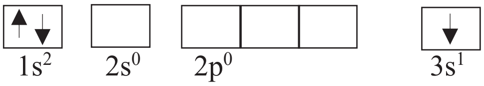
(a) All radiations associated with wave nature and differ from one another in terms of wavelength, frequency, velocity and energy. Give the relationship between the following:
(i) Frequency and Wavelength
(ii) Wavelength and Wavenumber
(iii) Energy and frequency
(iv) Energy and Wavelength **(4marks)**

(b) Indicate whether the following electronic configurations are possible or impossible. For the Impossible ones, specify the rules which have been violated.

(i)



(ii)



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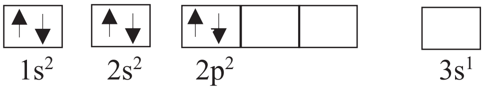

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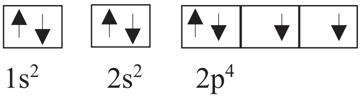
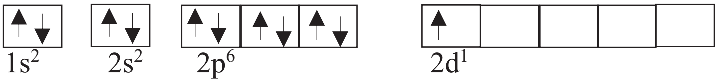


(v)



(5 marks)

(c) How many orbitals are there in each of the following Sub-shells?
(i) 2p
(ii) 3d **(1 marks)**

Question 5

(a) In the process of manufacturing chemicals, in one of the emerging chemical industries in Tanzania, a chemist performed the following activities:

(i) Exposed sodium metal to air followed by addition of water.
(ii) Burned sodium metal in air followed by addition of water. Briefly, explain the chemicals process that took place while supporting your answers with balanced chemical equations in each case.

(4 marks)

(b) Using balanced chemical equations, describe the reaction between the oxide of lead, aluminum and calcium with dilute;
(i) Sulphuric acid
(ii) Nitric acid

(6 marks)

Question 6

(a) Differentiate between the following terms:
(i) Born-Haber cycle and enthalpy of formation
(ii) Heat of neutralization and heat of solution

(3 marks)

(b) You are given an equation representing the hydrogenation of ethene as $C_2H_4(g) + H_2(g) \rightarrow CH_3CH_3(g)$. What would be the value for standard enthalpy of Hydrogenation of ethene (in KJ) if the bond enthalpies were C-H=416; C=C=612; C-C=348 and H-H=436?

(7 marks)

Question 7

(a) Using one chemical test, distinguish the following organic reactions:
(i) $CH_3C \equiv CH_2$ and $CH_3CH_2CH_3$
(ii) $CH_3 \equiv CCCH_3$ and $CH_3CH_2C \equiv CH$

(4 marks)

(b) Predict the major product in each of the following organic reactions:
(i) $CH_3C \equiv CCH_3(g) + H_2O(g) \xrightarrow[\text{Hg/H2SO4}]{\text{H2SO4}}$
(ii) $CH_3CH_2Br + Na \xrightarrow{\text{Dry ether}}$
(iii) $CH_3CH_3 + \text{Conc.}HNO_3 \xrightarrow{\text{heat}}$
(iv) $CH_3CH = CH_2 + Br_2 \xrightarrow{\text{U.V light}}$

(4 marks)

(c) A form six student wanted to arrange the following organic compounds in order of increasing acidity of their terminal hydrogen atoms. $CH \equiv CH$; $CH_3C \equiv CH$; $(CH_3)_3CC \equiv CH$; $CIC \equiv CH$; $NO_2C \equiv CH$; Suggest a correct sequence required by the student and give two reasons for your choices of arrangement

(2 marks)

SECTION B

Answer **two (2)** questions from this section.

Question 8

(a)

(i) "A chemical system at equilibrium is dynamic "Explain briefly the meaning of this statement.

(1 marks)

(ii) The equilibrium constant, k_p for the reaction $CCl_4(g) \rightarrow C(s) + 2Cl_2(g)$ is 0.76 atm at 978 K. Calculate the initial pressure of carbon tetrachloride that will produce a total equilibrium pressure of 1.2 atm at 978 K.

(4 marks)

(b)

(i) Why the solubility of CO_2 in soft drinks like Coca-Cola decreases with rise in temperature? Briefly, explain

(ii) What happens to equilibrium in a reversal reaction if a catalyst is added to it? Explain briefly

(iii) What happens to equilibrium constant of an exothermic reaction if temperature is raised? Explain briefly.

(3 marks)

(c) When a yellow solution of iron (III) chloride and a colorless solution of potassium thiocyanate (KSCN) are mixed in a test tube, a red color appears according to the following equilibrium

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons \underset{\text{Red solution}}{[Fe(SCN)]^{2+}(aq)}$$

(i) What would be the effect on Fe^{3+} ions upon addition of KSCN to the equilibrium

(ii) What would happen to the equilibrium position when the pressure of the system was to be doubled? Briefly, explain.

(iii) The red colour faded when the test tube containing the equilibrium mixture was placed in an ice-water bath. Briefly explain whether the value of K_c for the reaction is high or low and weather the reaction is exothermic or endothermic

(7 marks)

Question 9

(a) After a successful completion of your secondary educations farmers in your area of residence invite you to give a talk as afar as the concept of soil chemistry is concerned. Briefly explain each of the following terms while citing one example in each case;

(i) Soil reaction

(ii) Soil colloids

(iii) Liming

(iv) Organic fertilizers

(v) Artificial fertilizers **(5 marks)**

(b) Why is it necessary to measure soil pH? Explain by giving two reasons.

(4 marks)

(c) A farmer was advised to supply 200kg of nitrogen the paddy farm. What would be the mass of a fertilizer with 60% by mass $Ca(NO3)_2$ which the farmer has to buy in order to meet the nitrogen requirements for the farm?

(6 marks)

Question 10

(a)

(i) What are the two effects of substituent groups on the reactivity of benzene ring? Briefly explain.

(8 marks)

(ii) By giving one example in each case, briefly justify the statement "Despite the fact that both benzene and alkenes are unsaturated hydrocarbons, benzene undergoes electrophilic substitution reaction whereas alkenes undergo electrophilic addition reactions"

(3 marks)

(b) Why do activators when attached to benzenes ring direct the incoming electrophile to ortho and para positions? Briefly explain

(2 marks)

(c) Why are the products of nitrogen of methylbenzene obtained at a shorter time than those of sulphonation of benzene? Explain briefly supporting your answer with a chemical equation in each case.

(2 marks)

Necta 2023

CHEMISTRY 2

Answer **five (5)** questions

Question 1

(a)

(i) Can azeotropic mixtures be separated by distillation? Briefly explain

(ii) Mixing of acetone with chloroform takes place with reduction in volume. Identify the type of deviation from Raoult's law

(4 marks)

(b) Two liquids **M** and **N** are mixed to form an ideal solution the vapor pressure of the solution containing 3 moles of **M** and 1 mole of **N** is 550mmHg, when 4 moles of **M** and 1 mole of **N** are mixed, the vapour pressure of the solution formed is 560mmHg.What will be the vapour pressure of the pure **M** and pure **N** at this temperature?

(6 marks)

(c)

(i) Briefly explain five conditions that govern the distribution law.

(ii) The experiment was set to assess the solubility of succinic acid in water and ether at 15°C, it was found that, 20cm^3 of the ether layer contained 0.092g of the acid. If the distribution coefficient for succinic acid between ether and water was 5.2, find the weight of the acid which was present in 50cm^3 of the aqueous solution when the experiment was left at equilibrium

(10 marks)

Question 2

(a) Comment briefly on the following statements;

(i) Lewis's concept of acids and bases overruled Arrhenius concepts of acids and bases.

(ii) HSOB_4 is an amphiprotic

(iii) When rain is accompanied by a thunderstorm, the collected rain water will have a pH value slightly lower than that of rain water without thunderstorm

(6 marks)

(b)

(i) Calculate the pH of a mixture when $1cm^3$ of a0.5M H_2SO_4 is mixed with $2cm^3$ of 0.1M HCl, provide that no reaction occurs in the mixture.

(ii) A 0.1 M ethanoic acid solution contains 0.001MH_3O^+, What would be the K_a for this acid?

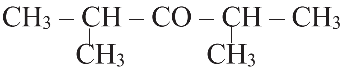
(8 marks)

(c) How much volume of a 0.1M HCN should be added to a $50cm^3$ of 0.2M NaCN solution to prepare a buffer solution with a pH value of 4.91? (pK_a of HCN IS 4.76).

(6 marks)

Question 3

(a) Write the IUPAC name of each of the following organic compounds;

(i) 
$CH_3-CH(CH_3)-CO-CH(CH_3)-CH_3$

(ii) 
$C_6H_5-CH=CH-CHO$

(2 marks)

(b)

(i) An organic compound E with molecular formula $C_9H_{10}O$ forms 2,4 dinitrophenylhydrazine (2,4-DNP) Derivative. Also, it reduces Tollen's reagent and undergoes Cannizzaro's reaction. Upon vigorous oxidation, Compound **E** gives 1,4-benzene dicarboxylic acid Determine the chemical structure of Compound **E.**

(ii) Why aldehydes and ketones have lower boiling points then their corresponding alcohols and carboxylic acid. Explain briefly,

(iii) A compound **B** (C_2H_4O) on oxidation gives C ($C_2H_4O_2$) compound **B** undergoes haloform reaction. On treatment with HCN, compound B forms a product **Z** which on hydrolysis, gives 2-hdroxypropanoic acid. Write the equation for all the reactions involved.

(8 marks)

(c) Briefly explain the following observations:

(i) Methylamine has lower boiling point than methanol

(ii) Aniline does not undergo Friedel-Crafts alkylation

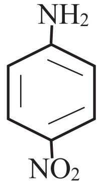
(4 marks)

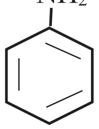
(d)

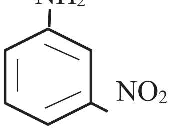
(i) Identify the structure of compound A, B, C and D in the following sequential conversions.

$$\mathbf{A}\xrightarrow[0-5^\circ C]{NaNO_2/HCl} CH_3OH \xrightarrow{SOCl_2} \mathbf{B} \xrightarrow{KCN} \mathbf{C} \xrightarrow{LiAlH_4} \mathbf{D}$$

(ii) Giving reasons, arrange the following organic compounds in decreasing order of basic strengths



, 

, CH_3NH_2 , NH_3 and 

(iii) How ethylamine can be prepared from propionic acid? Give two steps **(6 marks)**

Question 4

(a) Given the following compound $K_3[Fe(NH_3)]_6$;

(i) Give the IUPAC name of the compound

(ii) What is the number of electrons in the d-orbital in the central metal atom?

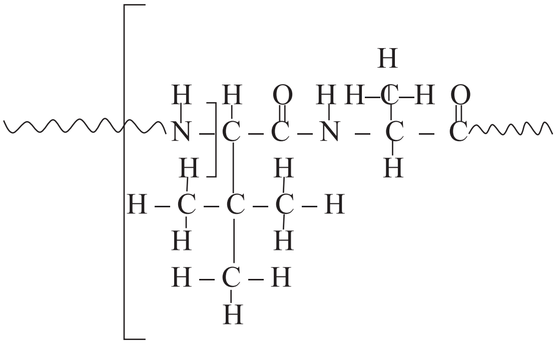
(iii) Give the geometric structure and hybridization of the complex.
(iv) Is the complex cationic, anionic or neutral? Briefly explain

(4 marks)

(b) Briefly, comment on the following statements:
(i) Silver nitrate can react with $[Cu(NH_3)_5Cl]$ Cl but not with $[Cu(NH_3)_4Cl_2]$
(ii) The complex compounds of cobalt have different Colors; $[Co(CN)_6]^{3-}$is yellow, ; $[Co(NH_3)_6]^{3+}$is orange while ; $[Co(H_2O)_6]^{3+}$is blue

(5 marks)

(c) Protein is the polymer of amino acid produced naturally by plants and has the formula



(i) Name the polymer
(ii) Suggest two monomers which might have been used to synthesize this polymer,
(iii) Is this an addition polymer or condensation polymer? Give reasons for your answer.
(iv) Write the reaction equation to show this polymer is formed

(6 marks)

(d)
(i) Suppose you are a chemist in one of the synthetic industries and you are required to synthesize a polymer using acrylonitrile(CH_2=CH-CN) monomers. What type of polymerization process will you comply in order to synthesize the required polymer? Give a reason for your answer.
(ii) With an example in each, distinguished homopolymer from co-polymer

(5 marks)

Question 5

(a) Briefly describe four characteristics of p-block elements

(4 marks)

(b) In four ways, briefly explain the factors affecting ionization energy

(4 marks)

(c) How do oxides of period 3 elements react with water? Explain briefly and support your answer with appropriate chemical equations

(8 marks)

(d) You have been asked to extract sodium metal from sea water through electrolysis. What will be the draw back and how would you overcome it? Explain briefly and support your answer with appropriate chemical equations.

(4 marks)

Question 6

(a) The decomposition of dinitrogen pentoxide is of first order being governed by the reaction equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. When this reaction was allowed to proceed at 40°C.the following data were collected;

$[N_2O_5]$(M)	Time(min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

Calculate

(i) The rate constant at the given temperature without using graph,
(ii) The concentration of $\mathbf{N_2O_5}$ after 10 minutes,

(10 marks)

(b) In the ARRHENIUS equation for a certain reaction the values of A and $\boldsymbol{E_a}$ are 4×10^{23}/s and 98.6 KJ mol^{-1} respectively if the reaction is of first order, Calculate the temperature at which its half- life period will be 10 min.

(05 marks)

(c) The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at constant volume, $SO_2Cl_2 \overset{\Delta}{\rightarrow} SO_2(g) + Cl_2(g)$.

Experiment	Time (s-1)	Total pressure/atom
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atmosphere

(05 marks)

MARKING SCHEMES
AND
MODEL SOLUTIONS
FOR
NECTA 2020-2023

Solutions Examination One

CHEMISTRY 1A

Question 1

(a) (i) Is the rule which govern the arrangement of electrons in an orbital which instructs that maximum number of electrons in the orbital is two and the two electrons must have opposite spin. (**1**)

(ii) Is the rule which govern the arrangement of electrons in degenerated orbitals which restricts pairing of electrons in degenerated orbitals until each orbital is singly occupied with electron spinning in parallel direction.(**1**)

(iii) Represents wavelength of energy emitted when excited electron return to lower energy excited state or to ground state. (**1**)

(iv) Is the level used to specify the main energy level in which electron is placed. It is usually represented by using whole numbers whereby greater value of the number means higher energy level. (**1**)

Remark: To get full score examinee must give relevant explanation to reflect his/her understanding and **not** just giving the definition or stating the law.

(b) (i) $2s - \text{orbital}$ (**0.5**) (ii) $1s - \text{orbital}$ (**0.5**) (iii) $3d - \text{orbitals}$ (**0.5**) (iv) $4P_x - \text{orbital}$ (**0.5**)

(c) (i) K,L,M and N stands for $n = 1, n = 2, n = 3$ and $n = 4$ principal numbers respectively. Thus the full configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$ (**1**)

Remarks:

- It is acceptable to write $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$
- It is acceptable to use boxes and arrows electronic configuration (in full)
- Examinee must give full (complete) electronic configuration. Shorthand (abbreviated) electronic configuration ($[Ar]\ 3d^5 4s^2$ or $[Ar] 4s^2\ 3d^5$) is **not** acceptable.

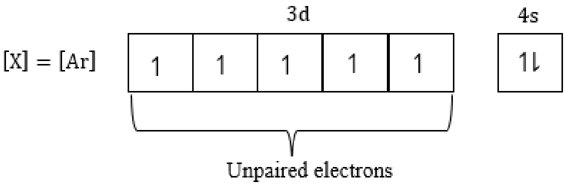
(ii) Atomic number of X is the total number of electrons in the atom. That is $Z = 2 + 8 + 13 + 2 = 25$

Hence the atomic number is 25 (**0.5**)

(iii) **Four** principle quantum numbers (represented by letters: K, L, M and N). (**0.5**)

(iv) Sublevels with electrons are $1s, 2s, 2p, 3s, 3p, 3d$ and $4s$. Hence there are **seven** sublevels with electrons. (**0.5**)

(v) The sublevel with unpaired electrons is 3d-sublevel as illustrated below:



Hence the total number of unpaired electrons is **five (1)**

(vi) The block letter, is the letter representing sublevel with highest energy which is 3d-sublevel. Hence the element belongs to **d-block. (0.5)**

Question 2

(a)(i) Hybrid bonds are covalent bonds whose bonding orbitals are resulted from hybridisation of atomic orbitals. **(0.5)**

(ii) sp^3d and sp^3d^2 Hybridized orbitals. **(0.5)**

Reason:

Elements in the second period have outermost energy level of n = 2 which has no d sub-energy level to enable such hybridisation. **(1)**

Remark: It is **not** acceptable to write dsp^3 instead of sp^3d and d^2sp^3 instead of sp^3d^2.

(b) (i) Ice has four bonded electron pairs without any lone pair around oxygen atom making its shape tetrahedral with bond angle of 109° unlike in liquid water where there are two lone pairs decreasing the bond angle to 104°. **(1)**

Remark: The reason must base on participation of lone pairs in affecting the bond angle.

(ii) Since the two elements have the same electronic structure with 18 electrons in each, they have the same strength of Van der Waals dispersion forces and hence similar boiling point. **(1)**

Remark: The reason must base on the strength of Van der Waals dispersion forces (London dispersion forces) as related to the number of electrons (**not** molecular mass/weight).

(c) (i) Atomic orbital is the region around the nucleus of an atom where there is a high probability of finding electrons while molecular orbital is the intersectional region with high electron density formed after overlapping of adjacent atomic orbitals where covalent bonded (shared) electrons are more likely to be found. **(1)**

(ii) Sigma bond is strong covalent bond formed by maximum overlap of two atomic orbitals to make molecular orbital through head to head (end to end) overlapping while pi bond is the weak covalent bond formed by minimum overlap of two atomic orbitals to make molecular orbital through the side way (lateral) overlapping. **(1)**

(iii) Since N in NH_3 is more strong electronegative than P in PH_3 , NH_3 is capable of forming strong intermolecular hydrogen bond with water and hence unlike PH_3, NH_3 becomes soluble in water. **(2)**

Remark: The explanation must base on hydrogen bonding formation ability as result of electronegative difference between N and P.

(d) (i) Geometrical structure: Trigonal planar **(0.5)** Example: BF_3 **(0.5)**

(ii) Geometrical structure: Octahedral **(0.5)** Example: $[Co(NH_3)_6]^{3+}$ **(0.5)**

Remark: Octahedral compounds like SF_6 and $[CoF_6]^{3-}$ which fall in sp^3d^2 (not d^2sp^3) are **not** acceptable.

Question 3

(a) (i) The law is Dalton's law of partial pressure **(0.25)**

It states that: The total pressure exerted in the container of the mixture of two or more gases is equal to the summation of their partial pressure provided that the gases do not react. **(0.75)**

(ii) From kinetic equation of gases:

$PV = \frac{Nmc^2}{3}$ or $P = \frac{Nmc^2}{3V}$ **(0.5)**

For mixture of gases, say three gases A,B and C with their respective number of molecules N_A, N_B and N_C and the total pressure excited by gaseous mixture, P_T:

$P_T = \left(\frac{N_A+N_B+N_C}{3V}\right)mc^2$ **(0.5)**

$= \frac{N_Amc^2}{3V} + \frac{N_Bmc^2}{3V} + \frac{N_Cmc^2}{3V}$

But $\frac{N_Amc^2}{3V} = P_A, \frac{N_Bmc^2}{3V} = P_B$ and $\frac{N_Cmc^2}{3V} = P_C$ **(0.5)**

Where P_A, P_B and P_C are partial pressures of A, B and C respectively.

Hence $P_T = P_A + P_B + P_C$ which is Dalton's law of partial pressure. **(0.5)**

(b) (i) It is completely **elastic.** **(0.5)**

(ii) Pressure **(0.5)**

(iii) Under presence of intermolecular forces, the collision will not be elastic. This is because, the intermolecular forces lowers speed as well as kinetic energy making the collision inelastic as some kinetic energy are transformed into intermolecular energy.**(1)**

Also the intermolecular forces, lowers the observed pressure. This is because as result of decrease in speed, both collision frequency and collision force (intensity) are decreased resulting to decrease in pressure of the gas. **(1)**

(c) (i) Low temperature (**0.5**) and high pressure (**0.5**)

(ii) **a** is the coefficient of attraction reflecting the strength of intermolecular force of attraction between gas particles (molecules). (**0.5**)

b is the effective volume reflecting the molecular size of the gas. (**0.5**)

(d) From Grahm's law: $\frac{R_{Ne}}{R_{He}} = \sqrt{\frac{M_{He}}{M_{Ne}}}$ (**0.5**)

But $R_{Ne} = \frac{V_{Ne\ diffused}}{t_{Ne}} = \frac{\frac{1}{2}V_{Ne}}{t_{Ne}}$ (Volume of Ne diffused is half of its original volume)

And $R_{He} = \frac{V_{He}\ diffused}{t_{He}} = \frac{\frac{2}{3}V_{He}}{t_{He}}$ (Volume of He shrinked to $\frac{1}{3}$ of original volume meaning $\frac{2}{3}$ of the original volume effused).

Then $\frac{\frac{\frac{1}{2}V_{Ne}}{t_{Ne}}}{\frac{\frac{2}{3}V_{He}}{t_{He}}} = \sqrt{\frac{M_{He}}{M_{Ne}}}$ (**0.5**)

But $V_{Ne} = V_{He}$ (balloon was the same)

Substituting: $\frac{3\times t_{He}}{4\times 22hr} = \sqrt{\frac{4}{20}}$ (**0.5**) $t_{He} = 13.12$ hours

Hence the time is 13.12 hours (**0.5**)

Question 4

(a) (i) Boiling point of a liquid is the temperature at which vapour pressure of the liquid is equal to the atmospheric (external) pressure. **(0.5)**

(ii) Increase in external pressure increases boiling point and vice versa. **(0.5)**

(b) (i) Colligative properties are properties of solution which depend on the relative amount of solute and solvent and not on the nature of the solute. **(0.5)**

These are: lowering of vapour pressure, boiling point elevation, freezing point depression and osmotic pressure.**(0.5)**

Remark: To get full score the examinee must do both give the meaning and mention colligative properties (the question asked 'what').

(ii) Colligative properties are not observed when:

1. The solute is volatile **(0.5)**
2. The solution is concentrated (is not very dilute) **(0.5)**

(iii) If the soft drink is cooled to temperature that is below the freezing point of pure water, then the dissolved CO_2 lowered the freezing point of the soft drink so that it was still liquid. **(1)**

But when the bottle is opened, the dissolved CO_2 escape from the solution, decreasing concentration of dissolved solute (gas) and thus raising the freezing point to the temperature above the temperature of solution and hence the solution (soft drink) freeze.**(1)**

(c) (i) From Raoult's law of relative lowering in vapour pressure: $X_{su} = \frac{\Delta P}{P^0_{SV}}$ **(0.5)**

But $X_{su} = \frac{n_{su}}{n_{su}+n_{sv}}$ (**0.5**)

And for dilute solution; $n_{su} + n_{sv} \approx n_{sv}$ (**0.5**)

Thence $\frac{n_{su}}{n_{sv}} = \frac{\Delta P}{P^0_{SV}}$

But $n_{su} = \frac{m_{su}}{M_{su}}$ and $n_{sv} = \frac{m_{sv}}{M_{sv}}$

Thus $\frac{M_{sv} \times m_{su}}{M_{su} \times m_{sv}} = \frac{\Delta P}{P^0_{SV}}$; Whence $M_{su} = \frac{P^0_{SV} \times M_{sv} \times m_{su}}{\Delta P \times m_{sv}}$ (**0.5**)

Where the solute (su) is sulphur and the solvent (sv) is CS_2

But

$\Delta P = P^0_{SV} - P_{soln} = (5333 - 5223)\text{Pa} = 110\text{Pa}$(**0.5**)

$m_{sv} = \rho_{sv} \times V_{sv} = 1.27\text{g}/\cancel{\text{cm}^3} \times 63\cancel{\text{cm}^3} = 80.01\text{g}$ (**0.5**)

$M_{sv} = 76\ \text{g/mol}$

Then substituting; $M_{su} = \frac{5.5\cancel{\text{g}} \times 76\text{g/mol} \times 5333\cancel{\text{Pa}}}{110\cancel{\text{Pa}} \times 80.01\cancel{\text{g}}} = 253\ \text{g/mol}$ (**0.5**)

Hence the R.M.M is 253 (**0.5**)

Remarks:

- The examinee should give the answer with no unit (R.M.M has no unit).
- **Deduct** 0.5 mark if g/mol is used as unit for the answer.
- **Allow** if a.m.u is used as unit for the answer.

(ii) Let the molecular formula of sulphur be S_n

Then $32n = M_r(S_n) = 253; n = 8$ (**0.5**)

Hence the molecular formula is S_8 (**0.5**)

Question 5

(a) (i) Indirect method **(0.5)**

$MgCl_2(aq) + 2KOH(aq) \longrightarrow Mg(OH)_2(s) + 2KCl(aq)$ **(0.5)**

(ii) Direct method **(0.5)**

$Ba(s) + H_2O(l) \longrightarrow Ba(OH)_2(aq) + H_2(g)$ **(0.5)**

(iii) Direct method **(0.5)**

$Na(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$ **(0.5)**

(iv) Indirect method **(0.5)**

$FeCl_2(aq) + 2NaOH(aq) \longrightarrow Fe(OH)_2(s) + 2NaCl(aq)$ **(0.5)**

Remark: For (i) and (iii) the reactants **must** be soluble compounds (award zero score for equation if at least one of reactants is insoluble).

(b) (i) Precipitation method **(0.5)**

$Ca(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow CaSO_4(s) + 2NaNO_3(aq)$ **(0.5)**

Remarks:

- The term **double decomposition method** is acceptable.
- The reactants **must** be soluble (award zero score for equation if at least one of reactants is insoluble).

(ii) Direct method **(0.5)**

$Zn(s) + H_2SO_4(dil) \rightarrow ZnSO_4(aq) + H_2(g)$ **(0.5)**

Remark: The term **displacement method** or **excess metal method** is acceptable.

(iii) Neutralisation method **(0.5)**

$2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O$ **(0.5)**

Remark: Instead of KOH; K_2O, K_2CO_3 or $KHCO_3$ may be used.

(c)

1. Manufacture of soap **(0.5)**
   NaOH and KOH are commonly used for this purpose by employing saponification reaction. **(0.5)**
2. Soil liming **(0.5)**

   Calcium hydroxide is a cheap alkali which is commonly used in large quantities to treat acid soils through employment of acid-base neutralisation reaction. **(0.5)**
3. Extraction of metals **(0.5)**

   Sodium hydroxide is used in extraction of aluminium from bauxite. **(0.5)**
4. Manufacture of bleach **(0.5)**

   Sodium hydroxide and calcium hydroxide are commonly used for this purpose. **(0.5)**
5. Softening of hard water **(0.5)**

   Calcium hydroxide is used in the softening of temporary hard water. **(0.5)**
   Remark: The examinee must **outline** any relevant **three** uses to get **maximum** of 3marks.

Question 6

(a) (i) Is the **normal molecular state** and **physical state** of a substance at **room temperature and pressure** (25°C and 1 atm). **(1)**

(ii) Is the **enthalpy diagram** used in calculation (indirectly determination) of **lattice energy** during the **ionic compound** formation/ Is the enthalpy diagram which shows all steps involved in the formation of ionic compound. **(1)**

(iii) Is the heat **evolved** when dilute solutions of **acid** and **base** reacts to give **one mole of water** under **standard conditions** (25°C and 1 atm). **(1)**
Remark: Heat change instead of heat evolved is **not** acceptable.

(iv) Is the **energy required** to **break one mole of molecules** to their corresponding **gaseous atoms** under **standard conditions** (25°C and 1atm). **(1)**
Remark: Energy change instead of energy required is **not** acceptable.

(b) Because both strong acid and strong base ionises completely (to give $H^+$and OH^- respectively) it easier for neutralisation reaction to take place between them than if one of them would be weak as weak acid and base tend to ionise only partially. Easier for $H^+$and OH^- to combine means more heat is evolved and hence greater enthalpy of neutralisation between strong acid and strong base. (**1.5**)

(c) Reaction equation: $NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$ (**0.5**)

Incorrect determination:

$n_{NaOH} = \frac{100}{1000}\cancel{dm^3} \times 0.3\ mol\cancel{dm^{-3}} = 0.03mol$

$n_{HNO_3} = \frac{115}{1000}\cancel{dm^3} \times 0.305\ mol\cancel{dm^{-3}} = 0.030575mol$

Since $n_{HNO_3} > n_{NaOH}$ and the mole ratio of the reaction equation is 1:1, HNO_3 was in excess and limited reactant is NaOH. (**0.5**)

Thus $n_{NaOH} = n_{H_2O}$ produced $= 0.03mol$

Using $\Delta H = mc\Delta T$; Where $m = \rho V$ and

Heat released in the reaction, $\Delta H = -\rho VC\Delta T$ (**0.5**)

Where: $\rho = 1gcm^{-3}$; $V = (100 + 115)cm^3 = 215cm^3$;$C = 4.2Jg^{-1}C^{-1}$; $\Delta T = (39 - 35)°C = 4°C$

Then $\Delta H = -1\cancel{gcm^{-3}} \times 215\cancel{cm^3} \times 4.24.2J\cancel{g^{-1}C^{-1}} \times 4\cancel{^{\circ}C} = -43612J = -3.612kJ$ (**0.5**)

Then using $\Delta H_n = \frac{\Delta H}{n_{H_2O}} = \frac{-3.612kJ}{0.03\ mol} = -120.4\ kJ/mol$ (**0.5**)

Hence incorrectly determined enthalpy of neutralisation is $-120.4\ kJ/mol$.

Correct determination:

Adding water to the container with NaOH does not change the number of moles of NaOH (n_{NaOH})

So n_{NaOH} and hence n_{H_2O} produced remained to be 0.03 mol. The only variable that will change is, V (**0.5**)

That is correct $V = (100 + 115 + 20)cm^3 = 235cm^3$

(The temperature rise of 4°C occurred in $235cm^3$ of solution and not in $215cm^3$).

Correct $\Delta H = -1\cancel{gcm^{-3}} \times 235\cancel{cm^3} \times 4.2J\cancel{g^{-1}C^{-1}} \times 4\cancel{^{\circ}C} = -3948J = -3.948kJ$. (**0.5**)

Then correct $\Delta H_n = -\frac{3.948kJ}{0.03\ mol} = -131.6kJ/mol$ (**0.5**)

Absolute error = $(131.6 - 120.4) = 11.2kJ/mol$

Percentage error = $\left(\frac{\text{Absolute error}}{\text{Real value}}\right) \times 100\% = \frac{11.2}{131.6} \times 100\% = 8.5\%$

Hence the percentage error is 8.5% . (**0.5**)

Question 7

(a) (i) Is the principle which explains effect of different factors on the position of chemical equilibrium.**(0.5)**

(ii) Is the chemical reaction which can proceed in both forward and backward direction.**(0.5)**

(iii) Is the law which express the relationship between concentration of reactants and that of products when the chemical system of reversible reaction is allowed to attain the equilibrium. **(0.5)**

(iv) Is the substance that alters the rate of chemical reaction but itself remain unchanged at the end of chemical reaction. **(0.5)**

(b) $[Ag(NH_3)_2]^+$ is more stable **(0.5)**

Reason: Large value of K_c implies that the position of equilibrium lies to the $[Ag(NH_3)_2]^+$ side (right hand side) **(1.5)**

(c) By adding hydrogen gas **(0.5)**

Explanation:

Decreasing volume of the container has no effect on the position of chemical equilibrium. This is because the decrease in volume will increase the total pressure of the system and since the reaction is not accompanied with change in number of gas molecules, the change in pressure has no effect on the position of equilibrium and thus no effect on the yield of HI too. However according to Le-Chatelier's principle, the increase in concentration of hydrogen gas shift the position of equilibrium to HI side and therefore increasing the yield of HI. **(2.5)**

Distribute:

- **0.5 mark** for mentioning 'decrease in volume has no effect on the position of chemical equilibrium'
- **1 mark** for explaining why the decrease in volume will not affect the yield of HI
- **1 mark** for explaining how the increase in concentration will increase the yield of HI

(d) (i) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$ (**0.5**) (ii) $K_p = \frac{(NO_2)^2}{(N_2O_4)}$ (**0.5**)

(iii) $K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(P_{NO_2})^2}{2.71\text{atm}} = 0.133\text{atm}$ **(1)**

$$(P_{NO_2})^2 = 0.36043\text{atm}^2;\ P_{NO_2} = \sqrt{0.36043\text{atm}^2} = 0.6\text{atm}$$

Equilibrium pressure of NO_2 is 0.6atm **(1)**

Question 8

(a) (i) Is an organic reaction whereby atom (or group of atoms) is replaced from organic compound by free radical. (**0.5**)

(ii) Is an electron-poor specie with tendency to accept an electron **pair** from electron-rich specie called nucleophile to form new covalent bond. (**0.5**)

(iii) Are group of atoms or bonds which determine characteristics chemical reactions of organic compounds.**(0.5)**

(iv) Is the existence of organic compounds with the same molecular formula, the same functional group but differ in their parent chain. **(0.5)**

(b) (i) Hydrocarbons are **very abundant, easily combustible** and **large amount of heat energy is evolved,** in their combustion and hence they are good fuel. **(1)**

Remark: To get full score examinee must mention at least two points (bolded words) including the point of *'large amount of heat evolved in combustion'*. **Deduct 1 mark** if the compulsory point is not mentioned.

(ii) Alkanes commonly exhibit position and chain isomerism, all of them needing branch (attached group) formation. And because it needs more than three carbons to form alkyl group branches, it is impossible for first three members of alkane to exhibit isomerism.**(1)**
Remark: The explanation must base on the ability to form alkyl group branches.

(iii) When 2-bromobuutane is formed, the intermediate carbenium ion is secondary which is more stable than primary carbenium ion found as an intermediate in the formation of 1-bromobutane and hence the 2-bromobutane becomes the major product during the bromination. **(1)**
Remark: The explanation must base on the stability of intermediate carbenium ion.

(iv) Methane reacts with chlorine via free radical substitution mechanism. The formation of free radicals (chlorine radicals) needs either **very high temperature** or **ultra violet (UV)** light and hence the reaction cannot take place in dark at room temperature. (**1**)

$$Cl - Cl \xrightarrow{\text{UV light or very high temperature}} Cl^{\bullet} + Cl^{\bullet}$$

Remarks: To get full score the examinee must explain in terms of free radical formation and mention both temperature factor and light factor.

(c) (i) Bromine water test. (**0.25**)

But-2-yne being unsaturated hydrocarbon will give positive test by decolourising reddish-brown colouration of bromine water while butane being saturated will give the negative test. **(0.75)**

(ii) Ammonical silver nitrate test (**0.25**)
1-butyne having terminal triple bond, gives positive test by giving white precipitate of silver 1-butynide while but-2-yne does not because it has no terminal triple bond. (**0.75**)
Remark: Any other suitable test is acceptable. (Like liquid bromine test for (i) or ammonical copper (I) hydroxide for (ii)).

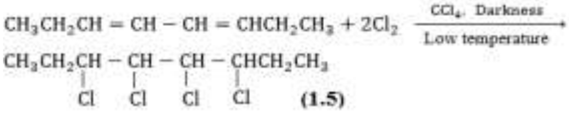
(d) The molecular formula C_8H_{14}, confirm the general molecular formula of C_nH_{2n-2} (**0.5**)
- Thus Q may be either aliphatic diene or aliphatic alkyne with only one $C \equiv C$. (**0.5**)
  Product obtained on the chlorination, suggests that **2 moles** of Cl_2 were added (**0.5**)
- This insists that Q must be either the diene or the alkyne. (**0.5**)

Since Q does not react with ammonical silver nitrate, there is no terminal $C \equiv C$ in Q. (**0.5**)

Products obtained on ozonolysis confirm that Q must be aliphatic diene (alkyne would give carboxylic acids). (**0.5**)

Hence the structural formula of Q is: $CH_3CH_2CH = CH - CH = CHCH_2CH_3$ (**1**)

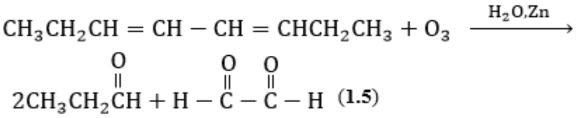
With chlorine:



$$CH_3CH_2CH = CH - CH = CHCH_2CH_3 + 2Cl_2 \xrightarrow[\text{Low temperature}]{CCl_4,\ \text{Darkness}} CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{CH}} - \underset{\displaystyle Cl}{\underset{|}{CH}} - \underset{\displaystyle Cl}{\underset{|}{CH}} - \underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3$$

(1.5)

With chlorine:



$$CH_3CH_2CH = CH - CH = CHCH_2CH_3 + O_3 \xrightarrow{H_2O, Zn}$$

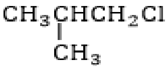
$$2CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}H + H - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - H$$

(**1.5**)

Question 9

(a) (i)

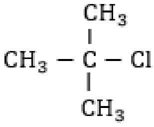
1. $CH_3CH_2CH_2CH_2Cl$ **(0.25)** **Name:** 1-cholorobutane **(0.25)**
2.



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Cl$$

(0.25) **Name:** 1-chloro-2-methylpropane **(0.25)**

3.

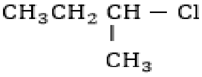


$$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - Cl$$

(0.25)

Name: 2-chloro-2-methylpropane **(0.25)**

4.



$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}} - Cl$$

(0.25)

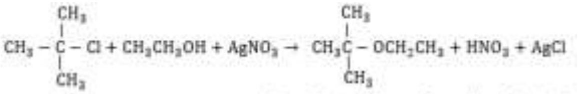
Name: 2-chlorobutane **(0.25)**

(ii) Chemical test: Alcoholic $AgNO_3$ test (**0.25**)

Explanation:

With alcoholic silver nitrate solution, the rate of haloalkane in S_N reaction is determined and differ depending to the class of haloalkane with 3° haloalkane having fastest S_N reaction and 1° haloalkane has the slowest one. Isomers (1) and (2) being primary haloalkane take longer time to form white precipitate of AgCl while isomer (4) being secondary haloalkane forms precipitate after few seconds and isomer (3) being tertiary haloalkane forms precipitate immediately. **(1)**

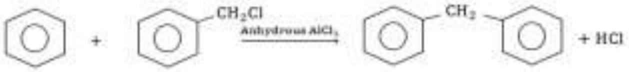
$CH_3CH_2CH_2CH_2Cl$ (or $CH_3 - CH(CH_3)CH_3Cl$) $+ CH_3CH_2OH + AgNO_3 \rightarrow$
$CH_3CH_2CH_2CH_2OCH_2CH_3$
(or $CH_3CH(CH_3)CH_2OCH_2CH_3$) $+HNO_3 + AgCl$
(While precipitate is formed after some minutes) (**0.25**)
$CH_3CH_2CH(CH_3) - Cl + CH_3CH_2OH + AgNO_3 \rightarrow$
$CH_3CH_2CH(CH_3)OCH_2CH_3 + HNO_3 + AgCl$ (Precipitate is formed after few seconds) (**0.25**)



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl + CH_3CH_2OH + AgNO_3 \rightarrow CH_3\overset{CH_3}{\underset{CH_3}{C}}-OCH_2CH_3 + HNO_3 + AgCl$$

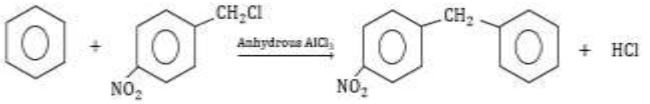
(Precipitate is formed immediately) (**0.25**)

(b) (i)



(1)

(ii)

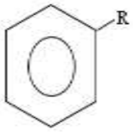


(1)

(c) (i)The molecular formula C_9H_{12}, suggests the general molecular formula of C_nH_{2n-6}

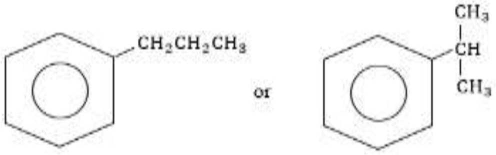
- Thus the two compounds are aromatic hydrocarbons (**0.5**)

Since P gives monocarboxylic acid on oxidation, it must be alkyl benzene of this nature



(0.5)

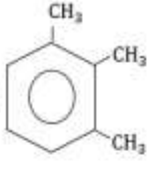
Hence the structure of P must be either:



(0.5)

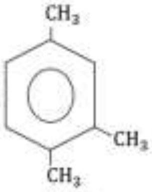
Since Q gives tricarboxylic acids on oxidation, it must be trimethylbenzene with one of the following structure:

(i)



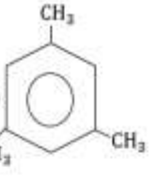
(0.25)

(ii)



(0.25)

(iii)

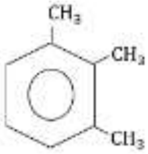


(0.25)

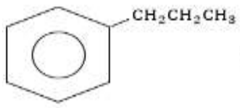
Where:

(i) Gives two products on mononitration. (**0.25**)
(ii) Gives three products on mononitration. (**0.25**)
(iii) Gives only one product on mononitration. (**0.25**)

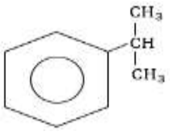
Hence the structure of Q must be



Hence:
Structure of P is

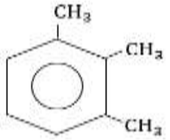


or

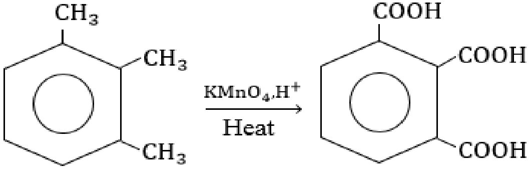


(0.5)

Structure of Q is



(0.5)

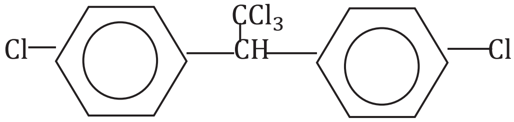


(0.5)

(i) Benzoic acid **(0.5)**

(d)

(i)



(1)

(ii) Is used as **insecticide** to kill disease-carrying insects like those responsible for malaria. **(1)**

(iii)

1. It is **non-biodegradable**. **(1)**
2. It causes the problem of **biomagnification**. **(1)**.

Question 10

(a) (i) High voltage from electric discharge is able to dissociate oxygen molecules from air as per equation;

$$O_3(g) \xrightarrow[\text{High voltage}]{} 2O(g) \ \mathbf{(1)}$$

Then the dissociated oxygen atom combines with undissociated oxygen molecule to form ozone as per equation;

$$O(g) + O_2(g) \longrightarrow O_3(g) \ \mathbf{(1)}$$

(ii) Ozone absorbs harmful radiation while itself is dissociated to oxygen molecules and oxygen atom. The dissociation of ozone by harmful radiation is endothermic and therefore the harmful ultra violet radiation energy is converted to heat energy and hence these radiations are prevented from reaching the Earth's surface. **(2)**

$$O_3(g) \xrightarrow[\text{Harmful UV radiation}]{} O(g) + O_2(g) \qquad \mathbf{(0.5)}$$

Oxygen gas being more stable than ozone cannot be dissociated by these harmful UV radiation (they are not energetic enough to dissociate oxygen gas which is more stable than ozone) and hence oxygen cannot prevent the radiation. **(1.5)**

$$O_2(g) \xrightarrow[\text{Harmful UV radiation}]{} \text{No reaction}$$

(iii)

1. Eye irritation **(0.5)**
2. Aggravation of respiratory conditions like asthma **(0.5)**

3. Increased susceptibility to infection **(0.5)**
4. Compromised lung function **(0.5)**

Remarks:

- Any other relevant harmful effect is acceptable
- Harmful effect of ozone depletion like skin cancer are **not** acceptable

(b) (i) Is a synthetic fertilizer designed to supply only one primary nutrient. **(0.75)** Example: Urea **(0.25)**

(ii) Is a synthetic fertilizer which contains two or all three primary plant nutrients. **(0.75)** Example: diammonium phosphate. **(0.25)**

(c) (i)

1. **Increase in organic content of the soil (0.5)**

   Increasing organic matter in agricultural soil improve the soil structure, creates more air space, increases CEC thus improving minerals and water retention within the soil. **(0.5)**

2. **Reduction in soil erosion (0.5)**

   A higher proportion of organic material in the soil (as result of application of manure) will also prevent soil erosion. **(0.5)**

3. **Healthy ecosystem (0.5)**
   Manure is gentler on microorganisms and earthworms living in the soil, creating a healthy ecosystem that is sustainable and conducive to long term use. **(0.5)**

4. **Steady release of nutrients (0.5)**
   The natural release of elements through manure application means that there is reduced risk of nutrient burn from over fertilization and nutrients are preserved in the soil rather than leaching away with rainwater. **(0.5)**

5. **Environment friendly (0.5)**
   The combined influence of increased organic matter and reduced nutrient leaching means that elements such as nitrogen and phosphorous will end up in plants roots instead of the local water – ways thus avoiding water pollution. **(0.5)**

6. **Cost –effective(0.5)**

   The raw materials needed to make organic fertilizer (manure) can be found easily. **(0.5)**
   Remark: Any three of well **outlined** advantages are enough to award the examinee the **maximum** of 3marks.

(ii)

Molar mass of $Ca(NO_3)_2$ is 164g/mol or 0.164kg/mol **(0.25)**
Mass of nitrogen in one mole of $Ca(NO_3)_2$ is 28g or 0.028kg **(0.25)**
Thus 0.028kg of N is contained in 0.164kg of $Ca(NO_3)_2$ **(0.25)**
And 160kg of N will be contained in $\frac{160\times0.164}{0.028}$ or 937.14kg of $Ca(NO_3)_2$ **(0.5)**
But the fertilizer is 80% $Ca(NO_3)_2$
Then 80kg of $Ca(NO_3)_2$ is contained in 100kg of the fertilizer; **(0.25)**
And 937.14kg of $Ca(NO_3)_2$ will be contained in $\frac{937.14\times100}{80}$**(0.5)** or 1171kg of the fertilizer
Hence 1171kg of the fertilizer is required to meet the requirement. **(0.5)**

Solutions Examination Two
CHEMISTRY 2A

Question 1

(a) (i) Saturated vapour pressure is the vapour pressure of the liquid in equilibrium with excess liquid at **given temperature. (0.5)**

(ii) Raoult's law is the law that relate the partial vapour pressure of a particular component in ideal solution to its mole fraction. **(0.5)**

Remark: The examinee is required to **define** and **not** to state the law.

(iii) Azeotropic point is the boiling point of the azeotropic mixture. (**0.5**)

(iv) Ideal solution is the mixture of substances of similar chemical structures and polarities. **(0.5)**

Remark: Definition in terms of intermolecular forces or Raoult's law is acceptable.

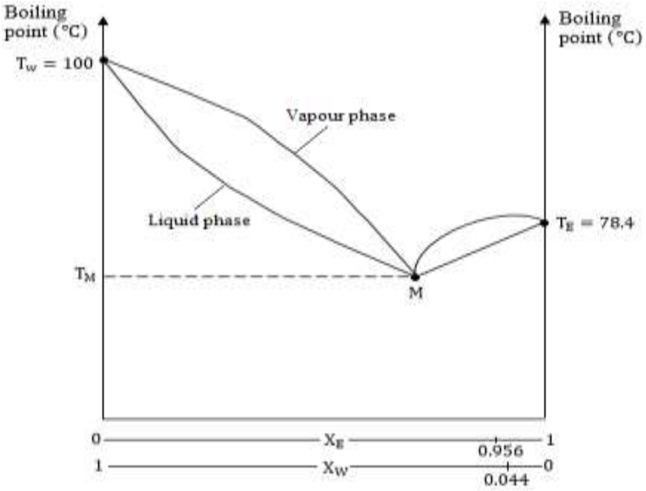
(b) The separation of components stopped due to formation of azeotropic mixture in the distillate. **(1)**

Also the formation of azeotropic mixture in the distillate suggest that the binary mixture of A and B is the non-ideal solution of positive deviation. **(1)**
Distribute:

(i) 1 mark for mentioning **azeotrope** (or **azeotropic mixture**) formation as the barrier for the separation process.

(ii) 1 mark for deducing that solution is **non-ideal solution of positive deviation** (or **minimum boiling azeotrope)**.

(c) (i)



(2)

Where: T_W is the boiling point of pure water
T_E is the boiling point of pure ethanol
T_M is the boiling point of azeotropic mixture (azeotropic point)
M is the azeotropic mixture
X_E is the mole fraction of ethanol
X_W is the mole fraction of water **(1)**

(ii) The solution will boil in such a way that the vapour formed is richer in ethanol until its percentage in the collector rises to 95.6%. Finally on successive distillation and condensation the filtrate in the collector will be azeotropic mixture with 95.6% ethanol and the residue in the distillation flask will be pure water.**(2)**

(iii) By introducing suitable dehydrating agent like calcium oxide (CaO) so as to remove water which is only 4.4%. **(1)**

Remark: Concentrated sulphuric acid as dehydrating agent is **not** acceptable (concentrated H_2SO_4 would react with the alcohol to give alkene).

(d) (i) When non-volatile solute is introduced into the container containing two immiscible solvents mixture, the solute tends to distribute itself in such a way that there is a fixed ratio of concentration of solute in the two solvents, provided that the molecular state of the solute remains the same in the two solvents and temperature is kept constant. **(1)**

(ii) Distribution law is not applicable when:

1. The temperature is not kept constant. (**0.5**)
2. The molecular state of the solute in the two solvents is not the same. (If the solute undergoes either association or dissociation in one of the solvent). (**0.5**)
3. The distribution of solute in the two solvents is not at equilibrium. (**0.5**)
4. The solute concentration in the two solvents is high. (**0.5**)
5. The solvents are miscible. (**0.5**)

Remark: Any **three** limitations are enough to award the examinee the **maximum** score of 1.5marks.

(iii) The law is applied in solvent extraction to remove impurities; in liquid chromatography to separate solutes and also in determination of solubility of substances like solubility of drugs in water and other solvents. **(1.5)**

(d) Because the mixture is completely miscible, Raoult's law is applicable.

Thus $P_{soln} = X_x^L P_x^o + X_y^L P_y^o$ **(1)**

Where:

P_{soln} is the vapour pressure of the solution $= 1.013 \times 10^5 N/m^2$

P_x^o is the vapour pressure of pure X $= 1.15 \times 10^5 N/m^2$

P_y^o is the vapour pressure of pure Y $= 6.04 \times 10^4 N/m^2$

X_x^L and X_y^L are mole fractions for X and Y respectively in liquid phase

But $X_x^L + X_y^L = 1$

From which $X_x^L = 1 - X_y^L$ **(0.5)**

Substituting:

$1.013 \times 10^5 = \left(1 - X_y^L\right)1.15 \times 10^5 + (6.04 \times 10^4)X_y^L$ (**1**)

From which $X_y^L = 0.25$ (**0.5**)

And $X_x^L = 1 - X_y^L = 1 - 0.25 = 0.75$ (**0.5**)

Then partial vapour pressure of each X and Y will be as follows:

$P_x' = X_x^L P_L^o = 0.75 \times 1.15 \times 10^5 = 86145 N/m^2$ (**0.5**)

$P_y' = X_y^L P_L^o = 0.25 \times 6.04 \times 10^4 = 15155 N/m^2$ (**0.5**)

Mole fraction in the vapour phase, $X^V = \frac{P'}{P_{soln}}$ **(0.5)**

$X_x^V = \frac{P_x'}{P_{soln}} = \frac{86145 N/m^2}{15155 N/m^2} = 0.85$ (**0.5**)

Hence the mole fraction of X in vapour phase is 0.85. **(0.5)**

Question 2

(a) (i) Are powers of the concentration of reactants in the rate law. (**0.5**)

It expresses how the change of concentration of particular reactant affect the rate of the given reaction and how the rate of given reaction is sensitive to the change of concentration of reactants whereby greater reaction order of reactant means that the change of reactant concentration has greater effect on the reaction rate and greater reaction order of the reaction means that the reaction is more sensitive to the change of reactant concentration. **(1)**

(ii) Are sequence of steps involved in a chemical reaction. (**0.5**)

It shows the path followed by the reaction course in the forming the products thus enabling to study the pattern drawn by the chemical reaction, to predict the product of chemical reaction and to study the reaction rate. **(1)**

(iii) Is the minimum energy required to activate atoms or molecules to a state in which they can undergo a chemical reaction. **(0.5)**

It expresses the extent to which reactants resist to undergo given chemical reaction whereby greater activation energy means greater resistance the reactants will provide to undergo chemical reaction and hence slower reaction rate. **(1)**

Remark: To get full score, the examinee must give the meaning of the term **and** provide extra relevant information about the term (in (i), (ii) and (iii)).

(b) Given that: $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$ (**0.5**)

From which $K_c = \frac{[NH_3]}{[NH_4^+][OH^-]} = 1 \Big/ \frac{[NH_4^+][OH^-]}{[NH_3]}$ (**0.5**)

But $\frac{[NH_4^+][OH^-]}{[NH_3]} = K_b(NH_3)$ (**0.5**)

Then $K_c = \frac{1}{K_b(NH_3)} = \frac{k_f}{k_r}$ (**0.5**); From which: $k_r = k_f \times K_b(NH_3)$ (**0.5**)

Where;

K_r is the required rate constant of reverse reaction which involves proton transfer from water to NH_3 (**0.5**)

k_f is the rate constant of forward reaction

$= 3.4 \times 10^{10} dm^3 mol^{-1} sec^{-1}$

But because NH_4^+ and NH_3 form conjugate pair;

$k_a(NH_4^+) k_b(NH_3) = k_w = 10^{-14} mol^2 dm^{-6}$ (**0.5**)

And ionisation constant of NH_4^+ in water is actually K_h (hydrolysis constant) of NH_4^+ which is equal to $k_a(NH_4^+)$

That is $k_a(NH_4^+) = 5.6 \times 10^{-10}$ $moldm^{-3}$ (**0.5**)

Thence from $k_a k_b = k_w = 10^{-14} mol^2 dm^{-6}$

$k_b(NH_3) = \frac{10^{-14} mol^2 dm^{-6}}{5.6 \times 10^{-10}\ moldm^{-3}} = 1.7857 \times 10^{-5} moldm^{-3}$ (**0.5**)

The substituting this value of $k_b(NH_3)$ and given value of k_f to $k_r = k_f \times k_b(NH_3)$

$$k_r = 3.4 \times 10^{10} \cancel{dm^3 mol^{-1}} sec^{-1} \times 1.7857 \times 10^{-5} \cancel{moldm^{-3}} = 6.1 \times 10^5 sec^{-1}$$

Hence the rate constant is $6.1 \times 10^5 sec^{-1}$ **(1)**

Remark: To get full score, the examinee must show clearly each step of calculation and give the answer in $\mathbf{sec^{-1}}$**.**

(c) (i) Is the electrode potential which is measured when an electrode is in contact with 1M solution of its ions at 25°C and 1atm (standard conditions). **(0.5)**

(ii) Is the chemical reaction which involves transfer of electrons. **(0.5)**

(iii) Corrosion is the degradation of the metal caused by unwanted oxidation over its surface. **(0.5)**

(iv) Is the redox reaction whereby both reduction and oxidation occurs in the same element. **(0.5)**

(d) (i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ (**1**)
Oxidant is potassium dichromate (**0.5**) Reductant is iron(II) sulphate (**0.5**)

(ii) $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$ (**1**)
Oxidant is potassium iodate (**0.5**) Reductant is potassium iodide (**0.5**)

(iii) $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$ (**1**)
Oxidant is copper (II) sulphate (**0.5**) Reductant is potassium iodide (**0.5**)

(iv) $2Cl_2 + 6OH^- \rightarrow ClO_3^- + 5Cl^- + 3H_2O$ (**1**)
Oxidant is chlorine gas (**0.5**) Reductant is chlorine gas (**0.5**)

(e) To enable formation of $\mathbf{Fe(OH)_2}$, then $\mathbf{Fe(OH)_3}$ and finally to hydrate $\mathbf{Fe_2O_3}$ to form the rust ($\mathbf{Fe_2O_3 \bullet xH_2O}$). **(1)**
That is:
$H_2O \rightleftharpoons H^+ + OH^-$
Then $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
Then $Fe(OH)_2 + O_2 + H_2O \rightarrow Fe(OH)_3$
And finally $Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \bullet XH_2O$ **(1)**

Question 3

(a) (i) Buffer solution cannot maintain its pH value in any amount of acid/base. Buffer solution can only maintain its pH on addition of small amount of acid or base without exceeding its buffer capacity. **(2).**

(ii) Basically common ion effect is the depression of ionization of weak electrolyte which is not necessary accompanied with depression in solubility. Adding strong electrolyte like HCl and NaOH in weak acid or weak base like CH_3COOH and NH_3 merely depress their ionization without affecting their solubility because their dissolution process is not based on ionisation. (Only for salts decrease in ionisation leads to decrease in solubility). **(2)**

(b) Given that:
Volume of $CaCl_2$ = Volume of $Na_2CO_3 = Vdm^3$
Then using $n = MV$;
Number of moles of $CaCl_2 = 0.1V$ mol
Number of moles of $Na_2CO_3 = 0.1V$ mol
Na_2CO_3 reacts with $CaCl_2$ to give $CaCO_3$ according to the following equation:
$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$ (**0.5**)
From which mole ratio is 1:1 and because number of moles of $CaCl_2$ is equal to the number of moles of Na_2CO_3 (0.1V mol); nothing present in excess (**0.5**)
Also from the reaction equation; mole ratio of $CaCl_2$ (or Na_2CO_3) to $CaCO_3$ is 1: 1; thus number of moles of $CaCO_3$ produced was also 0.1V mol. (**0.5**)
Using $[\,] = \frac{n}{V}$;
Number of moles of $CaCO_3$ produced in $1\,dm^3$ of the solution $= \frac{0.1\text{ V mol}}{(V+V)dm^3} = 0.05\ moldm^{-3}$ (**0.5**)
Then using mass concentration in gdm^{-3} = Molar concentration × Molar mass
Mass of solid $CaCO_3$ produced (just before being dissolved in the solution)
$= 0.05 \times 100 = 5\ gdm^{-3}$ (**0.5**)
The produced $CaCO_3$ dissolves only slightly according to the following equation:

$$\begin{array}{ccc} CaCO_3(s) \rightleftharpoons & Ca^{2+}(aq) + & CO_3^{2-}(aq) \\ & x & x \end{array}$$

where x is the molar solubility of $CaCO_3$

Then using $K_{sp} = [Ca^{2+}][CO_3^{2-}] = x^2$ **(0.5)**

From which $x = \sqrt{K_{sp}} = \sqrt{1.69 \times 10^{-8} mol^2dm^{-6}} = 1.3 \times 10^{-4} moldm^{-3}$ **(0.5)**

Then using mass solubility = Molar solubility × Molar mass

Mass solubility of $CaCO_3 = 1.3 \times 10^{-4} \times 100 = 0.013\ gdm^{-3}$ **(0.5)**

And therefore mass of the precipitation in $1dm^{-3}$ of the solution

$= (5 - 0.013)gdm^{-3}$ **(0.5)**

$= 4.987gdm^{-3}$

Hence the mass concentration of $CaCO_3$ precipitate $4.987gdm^{-3}$ **(0.5)**

(c) (i) Water undergo self-ionization according to the following equation:

$2H_2O \rightleftharpoons H_3O^+ + OH^-$ **(0.5)**

Where $[OH^-] = [H_3O^+]$

Then $K_w = [OH^-][H_3O^+] = [H_3O^+]^2$ **(0.5)** $[H_3O^+] = \sqrt{K_w}$ **(0.5)**

And $pH = -\log[H_3O^+] = -\log\sqrt{K_w}$ **(0.5)**

But at 30°C; $K_w = 1.471 \times 10^{-14}$

Substituting $pH = -\log\sqrt{1.471 \times 10^{-14}} = 6.9$

Hence the pH of water at 30°C is 6.9 **(0.5)**

(ii) Since both KOH and HCl are strong base and acid respectively, they give **neutral solution** at the equivalence point. **(0.5)**

And for neutral solution; $[OH^-] = [H_3O^+]$

Then $K_w = [OH^-][H_3O^+] = [H_3O^+]^2$ **(0.5)** $[H_3O^+] = \sqrt{K_w}$

And $pH = -\log[H_3O^+] = -\log\sqrt{K_w}$

Where at 10°C, $K_w = 0.293 \times 10^{-14}$

Substituting $pH = -\log\sqrt{0.293 \times 10^{-14}} = 7.3$

Hence the pH at equivalence point is 7.3. **(0.5)**

(d)(i) HA reacts with NaOH according to the following equation:

$HA + NaOH \rightarrow NaA + H_2O$ **(0.25)**

To make the solution with pH = 6 (acidic solution), the acid HA must be in excess **(0.25)**

But if the weak acid HA and produced NaA forms acidic buffer solution whose pH value is given by the following equation: **(0.25)**

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

Where $[Salt] = [NaA]$

And $[Acid] = [HA]$

Thus $pH = pK_a + \log\frac{[NaA]}{[HA]}$ **(0.5)**

$6 = 6 + \log\frac{[NaA]}{[HA]}$ **(0.25)**

From which $\frac{[NaA]}{[HA]} = \log^{-1}(0) = 1$

Whence $[NaA] = [HA]$ (after the reaction) for the solution to have pH of 6 **(0.5)**

Let volume of HA taken be V_{HA}

And volume of NaOH taken to V_{NaOH}

Using $n = MV$; $n_{HA} = 0.1V_{HA}$ and $n_{NaOH} = 0.1V_{NaOH}$

Then from mole ratio of the reaction equation:

n_{NaA} produced $= 0.1V_{NaOH}$ **(0.25)**

n_{HA} unreacted $= 0.1V_{HA} - 0.1V_{NaOH}$ **(0.25)**

Using $[\ \ ] = \frac{n}{V}$ and

$[HA]$ unreacted $= [NaA]$ produced

$\frac{0.1V_{HA} - 0.1V_{NaOH}}{V_{HA} + V_{NaOH}} = \frac{0.1V_{NaOH}}{V_{HA} + V_{NaOH}}$ (**0.5**)

From which

$0.1V_{HA} = 0.2V_{NaOH}$ or $V_{HA} = 2V_{NaOH}$ (**0.5**)

Hence to prepare the solution with pH of 6, the volume of HA solution mixed must be twice the volume of NaOH mixed. (**0.5**)

(ii) Also from $pH = pK_a + \log\frac{[NaA]}{[HA]}$

If $pH = 5$.

$5 = -\log(1 \times 10^{-6}) + \log\frac{[NaA]}{[HA]}$ (**0.25**)

$-1 = \log\frac{[NaA]}{[HA]}$; $\frac{[NaA]}{[HA]} = 0.1$

Whence after the reaction; $[NaA] = 0.1[HA]$ (**0.5**) for the pH to be 5; n_{HA} mixed $= 0.1V_{HA}$

n_{NaOH} mixed $= 0.1V_{NaOH} = n_{NaA}$ produced (NaOH was limited reactant)

n_{HA} unreacted $= (0.1V_{HA} - 0.1V_{NaOH})$

But $[NaA]$ produced $= 0.1 \times [HA]$ unreacted

Thus $\frac{0.1V_{NaOH}}{V_{HA} + V_{NaOH}} = \left(\frac{0.1V_{HA} - 0.1V_{NaOH}}{V_{HA} + V_{NaOH}}\right) \times 0.1$ (**0.5**)

From which $V_{HA} = 11V_{NaOH}$ (**0.5**)

Hence to prepare the solution with pH of 5, the volume of HA solution mixed must be 11 times the volume of NaOH mixed (**0.5**)

The best buffer solution is the solution with $pH = 6$ because at $pH = 6$, $[salt]([NaA]) = [Acid]([HA])$ making $pH = pK_a$ where the buffer capacity become maximum. (**0.75**)

Question 4

(a) (i)Hydration energy is the measure of strength of electrostatic force of attraction a nucleus of ion exerts to lone pairs of oxygen atom in water molecule. When ionic radius is small, lone pairs will be closer to the nucleus leading to greater attraction and hence hydration energy will be large. **(2)**

(ii) In atomizing given elements, metallic bonds are broken. Sodium having **large metallic radius** accompanied with only **one valence electron,** has very **weak metallic bond** making easier to atomize it than magnesium. **(2)**

(iii) Magnesium being above calcium in the group, has smaller atomic size accompanied with higher ionisation energy thus making its valence electrons to be firmly held by its nuclear attractive force such that heat energy from the flame is not enough to excite them.(**2**)

(iv) Molten NaCl contain Na^+ which has smaller size than K^+ in KCl; and in anhydrous form, smaller ions are lighter and thus have greater mobility. **(2)**

(v) Compounds whose ions are small, have very large lattice energy which in turn means very large hydration energy is required to break the ionic lattice for them to dissolve in water (**2**)

(b)

(i) **Concentration of the ore**

This is done by **froth flotation** by using **pine oil (1)**

(ii) **Roasting of the ore**

The concentrated ore is heated in a limited supply of air and the following reactions occur: **(1)**

1. $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$ (**0.5**)
2. $2CuFeS_2 + 4O_2 \rightarrow Cu_2S + 2FeO + 3SO_2$ (**0.5**)

The roasted product is then mixed with limited supply of air and the following reactions occur: **(1)**

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$ **(0.5)**

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ **(0.5)**

Thus after roasting, the mixture is now consisting of FeO, Cu_2O and unreacted Cu_2S**(0.5)**

(iii) **Removal of iron impurities**

To remove FeO (iron impurities) from the mixture, the mixture obtained after roasting in (ii) is mixed with SiO_2 and heated strongly, the slag of $FeSiO_3$ is formed which is poured out from the mixture. **(2)**

$FeO + SiO_2 \underset{\Delta}{\rightarrow} FeSiO_3$ (slag) (**0.5**)

Cu_2O and Cu_2S do not react (**0.5**)

(iv) **Self-reduction**

Auto-reduction between Cu_2S and Cu_2O to give blister copper. (**1**)

$Cu_2S + 2Cu_2O \rightarrow 6Cu(s) + SO_2$ (**0.5**)

Question 5

(a) (i) Electronic configuration of Mn^{2+} is $[Ar]3d^5$ (**0.75**)

Electronic configuration of V^{3+} is $[Ar]3d^2$ (**0.75**) Electronic configuration of Fe^{3+} is $[Ar]3d^5$ (**0.75**)

(ii) With electronic configuration $[Ar]3d^5$, Mn^{2+} has all of its d-orbitals unpaired with electrons and therefore it has stability of completely unpaired electronic structure unlike Mn^{3+} which has electronic configuration of $[Ar]3d^4$ that has one empty d-orbital and four unpaired d-orbitals. (**1.75**)

(b) (i) As you go across the period from Fe to Ni via Co, electrons are added to penultimate shell thus making the increase in screening effect to counterbalance with the increase in nuclear attractive force while from Na to Al via Mg, electrons are added to outermost shell thus making the increase in nuclear attractive force to be greater than the increase in screening effect. (**2**)

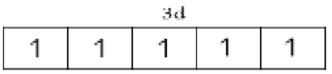
(ii) In Mg, the two valence electrons are filled in 4s-orbitals which has highest energy of all sub energy levels in Mg making it to fit in s-block of the modern periodic table. This is different to Zn whereby although the two valence electrons are found at 4s-orbitals like in Mg, the sub energy level with highest energy in Zn is 3d of penultimate shell making it to fit in d-block and hence they are fund in different groups (**2**)

(iii) With electronic configuration $[Ar]3d^64s^2$, iron has four unpaired electrons in 3d-orbitals and therefore it become paramagnetic while zinc has no any unpaired electron in its electronic configuration, $[Ar]3d^{10}4s^2$. (**2**)

(c) (i) Cl^- being larger in size than F^-, exerts stronger steric hindrance thus making difficult for Fe^{2+} to accommodate six ligands of Cl^- so as to exhibit coordination number of 6 like in $[FeF_6]^{4-}$ and therefore it opt to accommodate four ligands to form the complex with coordination number of 4 in $[FeCl_4]^{2-}$ (**2**)

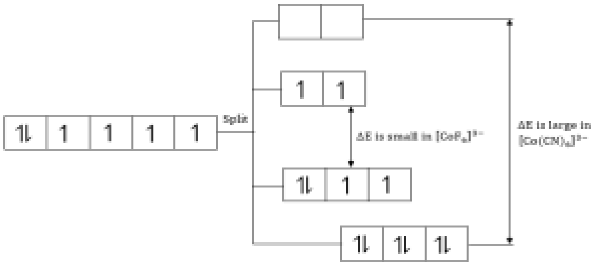
(ii) Presence of at least one unpaired electron in their d-orbitals (or even 4s-orbital for copper) in their electronic structure. (**1**)

(iii) Before introduction of ligands in the complex, the 3d electronic configuration of Co^{3+} is



(0.25)

After introducing ligands (F^- and CN^-), the five degenerated orbitals split into treble and double degenerate whereby CN^- being strong ligand causes large energy gap between the two sets and therefore leading to redistribution of electrons while F^- being weak ligand causes the small energy gap and therefore not leading to the redistribution of electrons. (**1.5**)



(1.5)

Thus after re-distribution of electrons, Co^{3+} in $[Co(CN)_6]^{3-}$ has all of its electrons paired and hence become diamagnetic while in $[CoF_6]^{3-}$ still it has four unpaired electrons making it paramagnetic. (**0.75**)

(iv) **Reason:** Fe^{2+} in $[Fe(CN)_6]^{4-}$ uses outer 4d-orbitals in the complex formation while Co^{3+} in $[CoF_6]^{3-}$ uses inner 3d-orbitals in the complex formation (**0.75**)

Explanation: Both Fe^{2+} and Co^{3+} have 3d electronic configuration of

whereby CN^- being strong ligand cause pairing in 3d-orbitals leaving two empty inner 3d-orbitals for accommodating ligands ()

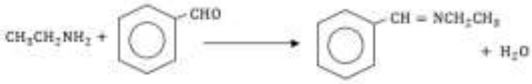
While F^- being weak ligand does not cause the pairing, forcing Co^{3+} to use outer 4d-orbitals (**1.25**)

Hybridisation in $[Fe(CN)_6]^{4-}$ is d^2sp^3 (**0.5**)

Hybridisation in $[CoF_6]^{3-}$ is sp^3d^2 (**0.5**)

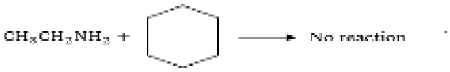
Question 6

(a) (i)



(1)

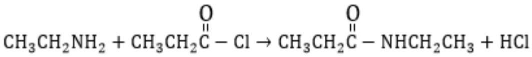
(ii)



(1)

(iii) $CH_3CH_2NH_2 + HNO_2 \xrightarrow{\text{Freezing temperature}} CH_3CH_2OH + N_2 + H_2O$ **(1)**

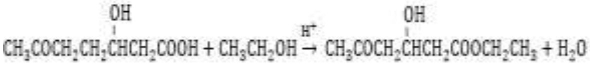
(iv)



$$CH_3CH_2NH_2 + CH_3CH_2\overset{O}{\overset{\|}{C}} - Cl \rightarrow CH_3CH_2\overset{O}{\overset{\|}{C}} - NHCH_2CH_3 + HCl$$

(1)

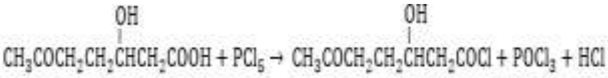
(b) (i)



$$CH_3COCH_2CH_2\overset{OH}{\overset{|}{C}}HCH_2COOH + CH_3CH_2OH \xrightarrow{H^+} CH_3COCH_2\overset{OH}{\overset{|}{C}}HCH_2COOCH_2CH_3 + H_2O$$

(1)

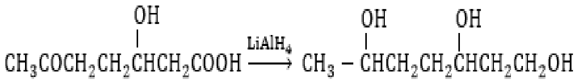
(ii)



$$CH_3COCH_2CH_2\overset{OH}{\overset{|}{C}}HCH_2COOH + PCl_5 \rightarrow CH_3COCH_2CH_2\overset{OH}{\overset{|}{C}}HCH_2COCl + POCl_3 + HCl$$

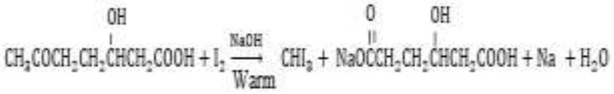
(1)

(iii)



$CH_3COCH_2CH_2\overset{OH}{C}HCH_2COOH \xrightarrow{LiAlH_4} CH_3-\overset{OH}{C}HCH_2CH_2\overset{OH}{C}HCH_2CH_2OH$ **(1)**

(iv)



$CH_3COCH_2CH_2\overset{OH}{C}HCH_2COOH + I_2 \xrightarrow[Warm]{NaOH} CHI_3 + NaO\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{OH}{C}HCH_2COOH + Na + H_2O$ **(1)**

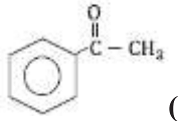
(c)(i)

Composition by element	**C**	**H**	**O**
% composition of each atom	80	6.66	13.33
Mass of each in 100g of the compound	80g	6.66g	13.33g
Number of moles of each, $n = \frac{m}{M_r}$	$\frac{80g}{12g/mol}$ $= 6.67mol$	$\frac{6.66g}{1g/mol}$ $= 6.66mol$	$\frac{13.33g}{16g/mol}$ $= 0.83mol$
Dividing by smallest number of moles to get simpler ratio	$\frac{6.67mol}{0.83\ mol}$ $= 8$	$\frac{6.66mol}{0.83\ mol}$ $= 8$	$\frac{0.83mol}{0.83\ mol}$ $= 8$

(2)

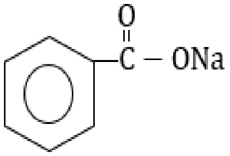
The emprical formula of P is C_8H_8O (**0.75**)
Let the molecular formula be $(C_8H_8O)_n = C_{8n}H_{8n}O_n$
Then $96n + 8n + 16n = M_r = \text{Vapour density} \times 2$ (**0.25**)
$120n = 60 \times 2 = 120; n = 1$ (**0.25**)
Hence the molecular formula of P is C_8H_8O (**0.75**)

(ii) Since the compound does not respond to silver mirror test, it must be ketone with the following structure:



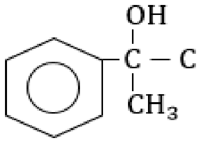
(1)

(d) (i)



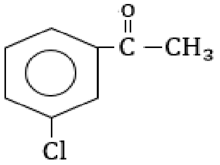
and CHI_3 (**1**)

(ii)



(**1**)

(iii)



(1)

(e)

Uses:

1. As a organic solvent **(1)**
2. In perfume industry **(1)**
3. In manufacture of dyes **(1)**
4. In synthesis of other organic compound **(1)**
5. As disinfectant, germicide and insecticide **(1)**
6. In silvering mirror **(1)**
7. As artificial and natural additives to food **(1)**

Remark: Any **two** relevant uses are enough to award an examinee the **maximum** score of 2marks.

Hazards:

1. They are inflammable **(1)**
2. Chemical burn **(1)**
3. Respiratory and allergic effect **(1)**
4. They are carcinogenic compounds **(1)**

Remark: Any **two** relevant hazards are enough to award an examinee the **maximum** score of 2marks.

Solutions Examination Three
CHEMISTRY 1B

Question 1

(a)(i) Bohr's atomic model. **(0.5)**

(ii) The model viewed an electron as being placed at certain distance from nucleus; this is against Heisenberg uncertainty principle (one of wave mechanical atomic model) which states that, "It is impossible at any moment to predict simultaneously the exact position and velocity of an electron in an atom". **(1.5)**

Remark: To get full score, the examinee must interpret the given assumption of Bohr's atomic model **and** show contradiction between the assumption and Heisenberg uncertainty principle. (Distribute **0.75 mark** for correct interpretation of Bohr's atomic model and **0.75 mark** for the Heisenberg uncertainty principle as it contradict to the interpretation).

(b) In Rutherford's α −scattering experiment, very few α −particles were either deflected or reflected and most of them passed through the gold foil without being deflected or reflected**.(0.5)** This led to the following conclusion:

(i) Since some $\alpha -$ particles were deflected**,** the nucleus is **positively** charged.(**0.5**)

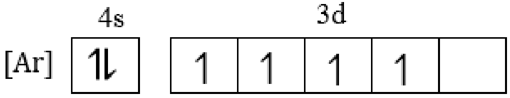
(ii) Since some $\alpha -$ particles were reflected, the nucleus is **heavy**. (**0.5**)

(iii) Since most of $\alpha -$ particles passed through the gold foil with neither deflection nor reflection, nucleus occupies **small volume**. **(0.5)**

Remark: Distribute (**0.5 mark** for stating the relevant observation of Rutherford's α −scattering experiment and **0.5 mark** for **each** explanation on conclusion made as related to the observation of the experiment).

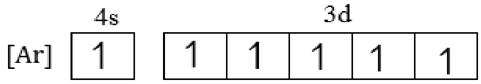
(c) **First example:** Electronic configuration of Cr (Atomic number = 24)

In accordance to Aufbau principle, the electronic configuration of Cr was expected to be;



(0.5)

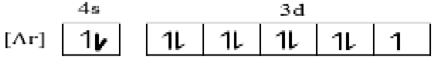
However due to stability of half-filled orbitals electronic configuration, the practical electronic configuration of Cr is;



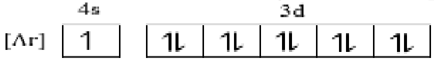
(0.5)

Second example: Electronic configuration of Cu (Atomic number = 29)

In accordance to Aufbau principle, the electronic configuration of Cu was expected to be:



(0.5) However due to stability of completely filled orbitals electronic configuration, the practical electronic configuration is;



(0.5)

Remarks:

(i) To get full score the examinee must show clearly that the electronic configuration violate Aufbau principle due to stability of half-filled and completely filled orbitals. (One example **must** be for half-filled and another for completely filled orbitals).

(ii) Any other relevant example, for example the stability of Fe^{2+} and Fe^{3+} (conversion of Fe^{2+} to Fe^{3+} and that of Fe^{3+} to Fe^{2+}) is **acceptable.**

(d) Using $\Delta E = nhf$ **(0.5)**

But $f = \frac{c}{\lambda}$

Then $\Delta E = \frac{nhc}{\lambda}$

But from Rydberg equation: $\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Thus; $\Delta E = nhcR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ **(0.5)**

Since 1g of hydrogen atoms is equivalent to one mole of hydrogen atoms which by definition of mole, it represents 6.02×10^{23} atoms, $n = 6.02 \times 10^{23}$ **(1)**

Also by giving line of lowest energy in visible spectrum means that $n_1 = 2$ and $n_2 = 3$. **(0.5)**

Thence substituting;

$\Delta E = 6.02 \times 10^{23} \times 6.626 \times 10^{-34} J\cancel{s} \times 3 \times 10^8 m\cancel{s^{-1}} \times 1.097 \times 10^7 \cancel{m^{-1}} \times \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$**(0.5)**

$= 182324J = 182.324kJ$

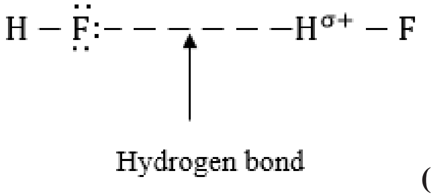
Hence the energy emitted was $182.324kJ$ **(1)**

Question 2

(a)

(i) Is the electrostatic force of attraction between the partially positively charged hydrogen atom in a polar covalent bond and lone pair on a nearby small electronegative atom or ion. **(0.5)**

Example: intermolecular hydrogen bond between molecules of HF.

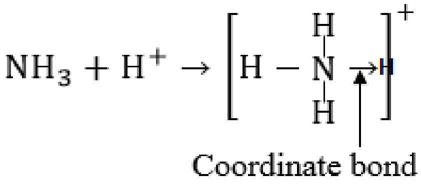


(0.5)

Remark: The definition which suggests that hydrogen bond is the electrostatic force of attraction between partially positively charged hydrogen and **partial negatively charged** atom instead of **lone pair** is **not** acceptable.

(ii) Is the type of covalent bond which is formed when all shared electrons are contributed by just one atom. **(0.5)**

Example: Formation of ammonium ion from NH_3 and H^+.



(0.5)

(iii) Is the type of covalent bond which is formed between non-metal atoms of different electronegativity resulting to the formation of partial charges. **(0.5)**

Example:

The bond which is formed between H and Cl whereby Cl is more electronegative. $H^{\sigma+} - Cl^{\sigma-}$ **(0.5)**

(b)

(i) **Similarity**

They are both chemical bonds which involve very strong electrostatic force of attraction holding ions together in a crystal. **(1)**

Difference

In metallic bond, the electrostatic force of attraction is between metallic positively charged ions and delocalized valence electrons (of metal atoms) and the bond is accounting for the structure and properties of metals which are elements while electrostatic forces of attraction in electrovalent (ionic) bond is between cations and anions (oppositely charged ions) accounting for structure and properties of ionic compounds (not elements like metallic bond). **(1)**

(ii) **Similarity**

They are both **intermolecular forces** accounting for **physical properties** of substances.**(1)**

Difference

Hydrogen bond is stronger than Van der Waals forces and is only responsible for covalent compounds with hydrogen atom bonded to N, O or F while Van der Waal forces is more broad being responsible for all covalent compounds (whether they contain H or not), non-metallic elements and noble gases .**(1)**

Remarks:

(i) To get full score the examinee must give both **basic** similarity and **basic** difference with **1 mark for each.**
(ii) In giving the difference, don't just give the definitions of the two terms; the difference must be based on the proper understanding of the two terms and thus being able to identify it. (**Award zero score** for the difference, if the examinee merely defined the two terms instead of identifying the difference).

(c) (i) CH_3CH_2OH (**0.25**)

Reason:

In CH_3CH_2OH, there is very strong hydrogen bonding existing between its molecules unlike in CH_3CHO where there is no partial positively hydrogen to enable such hydrogen bonding. **(1)**

(ii) NaCl **(0.25)**

NaCl is more ionic in characters than $AlCl_3$ as result of its lower degree of polarisation brought about by smaller polarising power of larger sized Na^+ than Al^{3+} in $AlCl_3$. **(1)**

Question 3

(a)

(i) Separation of gases having different densities by diffusion. **(0.5)**

Remarks: One of the following applications is also **acceptable**.

1. In determination of densities and molar masses of unknown gases by comparing the rates of diffusion with known gases.
2. In separation of isotopes of some of the elements.

(ii) During the preparation of gases by downward displacement of water **(0.5)**
(iii) In determination of molecular formula of gases. **(0.5)**

Remarks: One of the following applications is also **acceptable**.

1. In determination of atomicity of gases.
2. In establishing the relationship between relative molecular mass and vapour density.

(b) (i) $\frac{n^2a}{v^2}$ is the pressure deviation of real pressure from ideal pressure and therefore it corrects the real pressure (P) to be ideal pressure $(P+\frac{n^2a}{v^2})$. (**0.5**)

nb is the volume deviation of real gas from ideal gas and therefore it corrects the real volume (V) to be ideal volume $(V-nb)$. (**0.5**)

(ii) Compressibility factor, $z=\frac{PV}{nRT}$ (**0.25**)

From which; $V=\frac{ZnRT}{P}=\frac{0.5\times1\cancel{\mathrm{mol}}\times0.082\cancel{\mathrm{atm}}\mathrm{dm^3}\cancel{\mathrm{mol^{-1}K^{-1}}}\times273\cancel{\mathrm{K}}}{100\cancel{\mathrm{atm}}}=0.11193\ \mathrm{dm^3}$ (**0.5**)

But the volume of gas molecules is negligible, $b=0$ and the given Van der Waals equation becomes:

$\left(P+\frac{n^2a}{v^2}\right)V=nRT$ (**0.25**)

Then substituting;

$\left(100\mathrm{atm}+\frac{1\mathrm{mol^2}\times a}{0.11193^2\mathrm{dm^6}}\right)\times0.11193\cancel{\mathrm{dm^3}}=1\cancel{\mathrm{mol}}\times0.082\mathrm{atm}\cancel{\mathrm{dm^3mol^{-1}K^{-1}}}\times 273\cancel{\mathrm{K}}$ (**0.5**)

From which $a=1.252\ \mathrm{dm^6atmmol^{-2}}$

Hence Van der Waals constants are;

$a=1.252\ \mathrm{dm^6atmmol^{-2}}$ and $b=0$ (**1**)

(c) (i) From ideal gas equation; $PV=nRT$; where $n=\frac{m}{M_r}$

$PV=\frac{m}{M_r}RT$; From which $m=\frac{PVM_r}{RT}$ (**1**)

$m=\frac{207000\cancel{\mathrm{Nm^{-2}}}\times8.98\times10^{-3}\cancel{\mathrm{m^3}}\times28\mathrm{g}\cancel{\mathrm{mol^{-1}}}}{8.31\cancel{\mathrm{Nmmol^{-1}K^{-1}}}\times293\cancel{\mathrm{K}}}$ $(1\mathrm{Pa}=1\mathrm{Nm^{-2}}, 1\mathrm{J}=1\mathrm{Nm}$ and $1\mathrm{dm^3}=10^{-3}\mathrm{m^3})$ (**1**)

$=21.4\mathrm{g}$ (**0.5**)

Mass of nitrogen gas is 21.4g (**0.5**)

(ii) From ideal gas equation;

$PV=nRT$; $P=\frac{nRT}{V}$; $P\propto T$ (When V and n are constant) (**0.5**)

Thus the increase in temperature will result in an increase in pressure of the tyres. (**0.5**)

(iii) Nitrogen having fewer number of protons while shielding (screening) effect is the same for both; (both N and O have the same number of shells) experiences weaker effective nuclear attractive force. (**1**)

Question 4

(a)

(i) Are properties of the solution which depend on relative amount of solute and solvent and not on the nature of the solute. (**0.5**)

(ii) Is the boiling point elevation of the solvent in the solution which is obtained when one mole of non-volatile solute is dissolved in 1 kg of solvent. (**0.5**)

(iii) Is the pressure required to be applied to the side of higher solute concentration so as to prevent movement of solvent molecules by osmosis. (**0.5**)

(b) Using $\Delta T=iK_b\times\mathrm{Molality}$ (**0.5**)

Where $\Delta T=(104.4-100)°\mathrm{C}=4.4°\mathrm{C}$ (100°C is the boiling point of pure water).

And $K_b=0.512°\mathrm{Ckgmol^{-1}}$ (Given)

Substituting $4.4\ \cancel{°\mathrm{C}}=1.8\times0.512\cancel{°\mathrm{C}}\mathrm{kgmol^{-1}}\times\mathrm{Molality}$ (**0.5**)

$\mathrm{Molality}=4.7743\ \mathrm{mol/kg}$ (**0.5**)

Thus the required molality for the NaCl solution to boil at 104.4°C is 4.7743 mol/kg

But $\%\left(\frac{m}{m}\right)$ of NaCl $= \left(\frac{\text{mass of NaCl}}{\text{mass of solution}}\right) \times 100\%$ (**0.5**)

And mass of NaCl $= n_{NaCl} \times M_{NaCl} = 4.7743\text{mol} \times 58.5\text{g/mol} = 279.29655\text{ g}$ (**0.5**)

The mass of solution mass of NaCl (solute) + mass of H_2O (solvent)

$= (279.29655\text{ g}) + (1000g) = 1279.29655g$ (**0.5**)

Thence $\%\left(\frac{m}{m}\right)$ of NaCl $= \left(\frac{279.29655\text{ g}}{1279.29655\text{g}}\right) \times 100\% = 21.8\ \%$ (**0.5**)

Whence in terms of mas percentage, 21.8% NaCl boils at 104.4°C.

But the given mass percentage is 13.5% which is smaller than the required 21.8%; hence **the solute would be added** to increase the percentage and make the boiling point of solution 104.4°. **(0.5)**

Using mass = Density × Volume

Mass of the given solution $= 1.12\text{g}/\cancel{\text{mL}} \times 100\cancel{\text{mL}} = 112\text{g}$

Out of which; mass of NaCl $= \frac{13.5}{100} \times 112\text{g} = 15.12\text{g}$ (**0.5**).Then let mass of NaCl added be x in grams.

It follows that $21.8 = \left(\frac{15.12+x}{112+x}\right) \times 100$ (**0.5**) From which $x = 11.9$

Hence the mass of NaCl added is 11.9 g (**0.5**)

(c) From Raoult's law of relative lowering in the vapour pressure:

$X_{su} = \frac{\Delta P}{P^{o}_{sv}}$ (**0.5**) but $X_{su} = \frac{n_{su}}{n_{su}+n_{sv}}$

And for very dilute solution; $n_{su} + n_{sv} \approx n_{sv}$

Thence $\frac{n_{su}}{n_{sv}} = \frac{\Delta P}{P^{o}_{sv}}$ (**0.5**)

But $n_{su} = \frac{m_{su}}{M_{su}}$ and $n_{sv} = \frac{m_{sv}}{M_{sv}}$

Then $\frac{m_{su} \times M_{sv}}{M_{su} \times m_{sv}} = \frac{\Delta P}{P^{o}_{sv}}$

From which $M_{su} = \frac{m_{su} \times M_{sv} \times P^{o}_{sv}}{m_{sv} \times \Delta P}$ (**0.5**)

Where:

M_{sv} =molar mass of water (solvent) = 18 g/mol

P^{o}_{sv} = vapour pressure of pure water = $1.992 \times 10^4 \text{Nm}^{-2}$

ΔP =Lowering in vapour pressure $= P^{o}_{sv} - P_{soln} = (1.992 - 1.891) \times 10^4\ \text{Nm}^{-2}$

$= 1.01 \times 10^4 \text{Nm}^{-2}$ (**0.5**)

m_{su} = mass of solute = 10.6 g

m_{sv} = mass of solvent (water) = 90g

Substituting $M_{su} = \frac{10.6\cancel{g} \times 18\text{g/mol} \times 1.992 \times 10^4 \cancel{\text{Nm}^{-2}}}{90\cancel{g} \times 1.01 \times 10^3 \cancel{\text{Nm}^{-2}}}$ (**0.5**)

$= 41.8\text{ g/mol}$

Hence the molecular mass is 41.8 g/mol (**0.5**)

Question 5

(a) (i) CaO **(0.5)**

Remark: Any oxide with oxygen in oxidation state of −2 is **acceptable**.

(ii) Na_2O_2 **(0.5)**

Remarks:

- Any peroxide of alkali metal (except Li) is **acceptable**.
- Peroxide of Sr or Ba is **acceptable**.
- Peroxide of H is **acceptable**.

(iii) Fe_3O_4 **(0.5)**

Remark: Pb_3O_4 is **acceptable**.

(iv) KO_2 **(0.5)**

Remark: Only superoxide of alkali metals **below** sodium in group IA are **acceptable**.

(b)

(i) Sodium peroxide can do both absorbs carbon dioxide and liberates oxygen at the same time and therefore acting as oxygen source in emergency breathing devices. **(1)**

$2Na_2O_2(s) + 2CO_2(g) \longrightarrow 2Na_2CO_3(s) + O_2(g)$ **(0.5)**

(ii) Precipitation method suits to prepare insoluble compounds. Due to their ability of making intermolecular hydrogen bonding with water molecules all bicarbonates are water soluble and hence the method unsuits them. **(1)**

(iii) Upon heating sodium bicarbonate is capable of undergoing thermal decomposition liberating carbon dioxide which acts as leavening agent to make cake porous and palatable. **(1)**

$NaHCO_3 \underset{\Delta}{\rightarrow} Na_2CO_3 + CO_2 + H_2O$ **(0.5)**

(iv) Sodium is so reactive that its reaction with dilute H_2SO_4 cause an explosion thus making unsafe to conduct the experiment in the laboratory. **(1)**

(c)

(i) $B(OH)_3 + HCl \longrightarrow$ No reaction **(0.5)**

(ii) $NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$ **(0.5)**

(iii) $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$ **(0.5)**

(iv) $MgCl_2(s) + H_2O(g) \longrightarrow Mg(OH)Cl(s) + HCl(g)$ **(0.5)**

(v) $AgNO_3 + KOH \longrightarrow Ag_2O + KNO_3 + H_2O$**(0.5)**

(vi) $Na_2CO_3 + H_2CO_3 \longrightarrow NaHCO_3$**(0.5)**

Question 6

(a)

(i) Heat of solution is the **heat change** when **one mole of solute** is added to so much water that further addition **of water produces no further heat change under given conditions of temperature and pressure. (1)**

(ii) Heat of solution is the **heat change** when **one mole of a solute** dissolves in **specified amount of water** to give a solution under **given conditions of temperature and pressure. (1)**

Relation:

When the solution is diluted to infinite dilution, heat of solution becomes equal to heat of dilution. **(1)**

(b)

$$\begin{tikzcd}
Mg(OH)_2(s) \arrow[rr, "\mathbf{\Delta H_{soln}}"] \arrow[dr, "\text{Positive }\mathbf{L.E}"'] & & Mg^{2+}(aq) + 2OH^-(aq)\ \mathbf{(1)} \\
& Mg^{2+}(g) + 2OH^-(g) \arrow[ur, "\mathbf{H.E}"'] &
\end{tikzcd}$$

$\Delta H_{soln} = \text{Positive L.E} + \text{H.E}$ **(0.5)**

Where $\text{L.E} = -2842\text{kJ/mol}$

and $\text{H.E} = \Delta_{hyd}(Mg^{2+}(aq)) + 2\Delta_{hyd}(OH^-(aq))$

$= -1920\text{kJ/mol} + 2 \times -460\text{kJ/mol} = -2840\text{kJ/mol}$ **(0.5)**

Thus $\Delta H_{soln} = 2842\text{kJ/mol} - 2840\text{kJ/mol} = 2\text{kJ/mol}$ **(1)**

(c) Using $\Delta H = MC\Delta T = \rho VC\Delta T$ $(M = \rho V)$ **(0.5)**

$\rho_{water} = 1\text{kgdm}^{-3}, V = 200\text{cm}^3 = 0.2\text{dm}^3$ $C = 4.18\text{kJkg}^{-1}\text{K}^{-1}$

$\Delta T = (31.24 - 25)°C = 6.24°C$

$\Delta H = 1\cancel{\text{kg dm}}^{-3} \times 0.2\cancel{\text{dm}}^3 \times 4.18\text{kJ}\cancel{\text{kg}}^{-1}\cancel{\text{K}}^{-1} \times 6.24\cancel{\text{K}}$ $(\mathbf{0.5})$ $= 5.21664\text{kJ}$

The heat value of ethanol is 5.21664kJ. **(0.5)**

Mass of ethanol burnt = $(56.69 - 56.46)\text{g} = 0.23\text{g}$ **(0.5)**

Number of males of ethanol burnt $= \frac{0.23\text{g}}{46\text{gmol}^{-1}} = 0.005\text{mol}\left(n = \frac{M}{Mr}\right)$ **(0.5)**

From the given equation of ethanol combustion mole ratio of ethanol to CO_2 is 1:2

Thus number of moles of CO_2 produced = (2×0.005) mol =0.01mol **(0.5)**

Used $n = \frac{V}{GMV} = \frac{V}{22.4\text{L/mol}}$ $V = n \times 22.4\text{L/mol}$ **(0.5)**

$V = 0.01\cancel{\text{mol}} \times 22.4\text{L}/\cancel{\text{mol}} = 0.224\text{L}$

Volume of CO_2 produced was 0.224L **(0.5)**

Question 7

(a)

(i) Is the ratio of product of concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients obtained in the course of the chemical reaction. **(0.5)**

(ii) Is the temperature dependent fixed ratio which is obtained as the quotient of the product of equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficient **(0.5)**

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Pressure at $t = 0$ $\quad P_0 \quad 0 \quad 0$

Pressure at equilibrium $P_0 - P \quad P \quad P$ **(0.5)**

(Since pressure is directly proportional to the number of moles, pressure ratio is equal to the mole ratio and therefore pressure can be treated as moles in the equation).

Also from, pressure-mole relationship:

Degree of dissociation, $\alpha = \frac{P}{P_0}$ **(0.5)**

And $\alpha = 20\% = 0.2$ (PCl_5 dissociated to 80%)**(0.5)**

Thus $0.2 = \frac{P}{P_0}$ or $P = 0.2P_0$ **(0.5)**

Total pressure at equilibrium;

$P_0 - P + P + P = 1.5$

Or $P_0 + P = P_0 + 0.2P_0 = 1.2P_0 = 1.5$

From which $P_0 = 1.25$ atm **(0.5)**

And $P = 0.2P_0 = 0.2 \times 1.25 \text{ atm} = 0.25 \text{ atm}$

Hence:

Partial pressure of $PCl_5 = P_0 - P = (1.25 - 0.25)\text{atm}$
$= 1 \text{ atm}$ **(0.5)**

Partial pressure of $PCl_3 = P = 0.25$ atm **(0.5)**

Partial pressure of $Cl_2 = P = 0.25$ atm **(0.5)**

(c) For gases, the most common method of representing equilibrium constant is K_P. So the given value of Equilibrium constant is K_P value.

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

At $t = 0$ $\quad 2 \quad 2 \quad 0$

At equilibrium $\quad 2 - x \quad 2 - 2x \quad 2x$ **(0.5)**

$K_p = 4.3 \times 10^{-3}$

$K_p = \frac{(P_{NO_2})^2}{(P_{N_2})(P_{O_2})^2}$ **(0.5)** $= \frac{(X_{NO_2}P_T)^2}{(X_{N_2}P_T)(X_{O_2}P_T)^2} = \frac{(X_{NO_2})^2}{(X_{N_2})(X_{O_2})^2 P_T}$ **(0.5)**

Using $X = \frac{n}{n_T}$; where $n_T = 2 - x + 2 - 2x + 2x = 4 - x$

Then $K_p = \frac{\left(\frac{2x}{4-x}\right)^2}{\left(\frac{2-x}{4-x}\right)\left(\frac{2-2x}{4-x}\right)^2 \times 1} = 4.3 \times 10^{-3}$ **(0.5)**

$\frac{4x^2(4-x)}{(2-x)(2-2x)^2} = 4.3 \times 10^{-3}$

$\frac{16x^2 - 4x^3}{8 - 20x + 16x^2 - 4x^3} = 4.3 \times 10^{-3}$

From which; $3.982x^3 - 15.9312x^2 - 0.086x + 0.0344 = 0$ **(1)**

Solving the above equation, gives the practical value of x which is 0.044. **(1)**

Hence the composition of each is as follows:

Number of moles of $N_2 = 2 - x = 1.956$ mol **(0.5)**

Number of moles of $O_2 = 2 - 2x = 1.912$ mol **(0.5)**

Number of moles of $NO_2 = 2x = 0.088$ mol **(0.5)**

Question 8

(a) (i) Is the organic compound which consists of carbon and hydrogen only. Its bonds are all $C - H$ bonds in the carbon chain. **(0.75)**

An example of hydrocarbon is **alkane (0.25)**

Remarks:

- The examinee was required to **'explain'** and **not** simply to define.
- Alkene or alkyne or arene as an example is **acceptable**.
- Specific compound like heptane as an example is **not** acceptable. This also applies for (ii) and (iii) of this part of the question. (The word '**family**' in the question restrict to give only functional group (homologous series) as an example and not the unique compound).

(ii) Is the hydrocarbon with carbon-carbon single bond as functional group. It contains maximum number of hydrogens the carbon may contain with each carbon being sp^3 hybridised. **(0.75)**

An example: Alkane **(0.25)**

(iii) Is the hydrocarbon with carbon-carbon multiple bond as functional group. With at least two carbons either in sp^2 hybridisation or sp hybridisation they may accommodate more hydrogens. **(0.75)**

An example: Alkene **(0.25)**

Remark: Alkyne or arene as an example is **acceptable**.

(b) (i) 2 – methylbutane **(0.5)** (ii) But-1-en-3-yne **(0.5)** (iii) Propene **(0.5)** (iv) 4-methyleneocta-2,6-diene **(0.5)**

(c) (i) Alkanes with **different length of carbon chains** have different strength of Van-der-Waals intermolecular forces and therefore they have **different boiling points** and hence making the fractional distillation possible. **(2)**

(ii) $C_8H_{18} \longrightarrow C_2H_4 + C_6H_{14}$ **(0.5)**

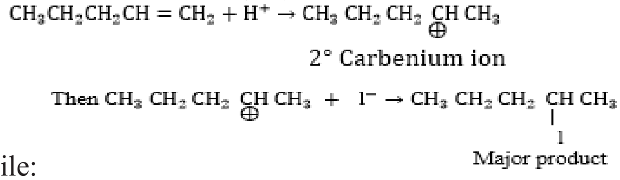
$C_8H_{18} \longrightarrow 2C_2H_4 + C_4H_{10}$ **(0.5)**

$C_8H_{18} \longrightarrow 3C_2H_4 + C_2H_6$ **(0.5)**

Remarks:

- Any **two** of above equations are **acceptable** with maximum score of **1mark**.
- Equation that form hydrogen; i.e. $C_8H_{18} \longrightarrow 4C_2H_4 + H_2$ is **not** acceptable.

(d) (i) In the formation of 2-iodopentane, the intermediate carbenium ion is secondary which is more stable than primary intermediate carbenium ion formed during the formation of 1-iodopentane and hence 2-iodopentane becomes the major product in accordance to the Markonikoff's rule **(0.5)**



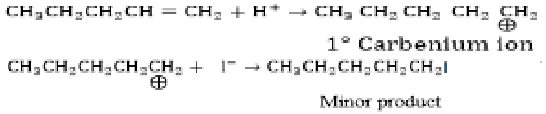
$CH_3CH_2CH_2CH=CH_2 + H^+ \rightarrow CH_3\,CH_2\,CH_2\,\underset{\oplus}{CH}\,CH_3$

2° Carbenium ion

Then $CH_3\,CH_2\,CH_2\,\underset{\oplus}{CH}\,CH_3 + I^- \rightarrow CH_3\,CH_2\,CH_2\,\underset{\underset{I}{|}}{CH}\,CH_3$

Major product **(0.5)**

While:



$CH_3CH_2CH_2CH=CH_2 + H^+ \rightarrow CH_3\,CH_2\,CH_2\,CH_2\,\underset{\oplus}{CH_2}$

1° Carbenium ion

$CH_3CH_2CH_2CH_2\underset{\oplus}{CH_2} + I^- \rightarrow CH_3CH_2CH_2CH_2CH_2I$

Minor product **(0.5)**

(ii) Due to presence of terminal$C \equiv C$, but-1-yne contain acidic hydrogen which may be replaced by metal like copper while but-2-yne has no the replaceable acidic hydrogen). **(0.5)**

$CH_3CH_2C \equiv CH + CuCl \rightarrow CH_3CH_2C \equiv CCu + HCl$

Brick red precipitate **(0.5)**

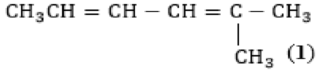
While $CH_3C \equiv CCH_3 + CuCl \rightarrow$ No reaction

(iii) Trans-but-2-ene has uniform structure and therefore there is a cancellation of dipole moments making it pure non-polar in contrast to cis-but-2-ene making the cis-isomer to have permanent dipole-dipole forces in additional to the London dispersion forces they both have. **(0.5)**

(d) (i) Is the organic reaction where the carbon-carbon multiple bonds in unsaturated organic compound (alkene, alkyne or benzene) are broken by ozone (O_3). **(1)**

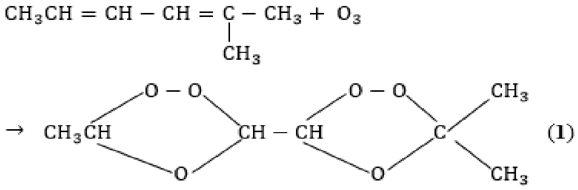
(ii) The molecular formula C_7H_{12}, suggests the general molecular formula of C_nH_{n-2}. Thus the given hydrocarbon may be aliphatic diene or aliphatic alkyne with only one $C \equiv C$. **(1)**

Products obtained on ozonolysis, confirm that the hydrocarbon is diene with the following structure:



$CH_3CH=CH-CH=\underset{\underset{CH_3}{|}}{C}-CH_3$ (1)

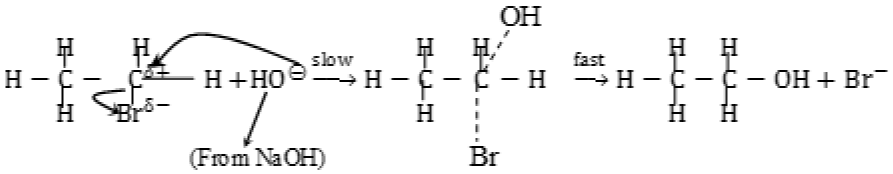
Ozonolysis of the compound gives ozonide as per equation;



(1)

Question 9

(a) (i)



(2.5)

Remarks:

- If words ‘slow’ and ‘fast’ are not included in the mechanism is **allowable**.
- S_N1 mechanism is **not** acceptable (award **zero** score if the transition state involves positively charged carbon).

(ii) Reagents: Dilute nitric acid and aqueous silver nitrate. **(0.75)**
Result: Cream (or light yellow) precipitate. **(0.75)**

(b) Multi-step **(0.5)**

Explanation:
In propane, secondary hydrogen is more reactive in free radical substitution reaction than primary hydrogen thus its direct bromination gives 2-bromopropane as major product and not 1-bromopropane. **(1)**
Conversion:

$$CH_3CH_2CH_3 \xrightarrow{Br_2,U.V} CH_3CH(Br)CH_3 \xrightarrow{\text{Conc } KOH, C_2H_5OH, \Delta} CH_3CH = CH_2 \xrightarrow{HBr, CH_3OOCH_3} CH_3CH_2CH_2Br \textbf{(1)}$$

(c)

(i) $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$ **(0.5)**
(ii) **Concentrated** sulphuric acid **(0.5)**
(iii) NO_2^+ **(0.5)**
(iv) Electrophilic substitution reaction **(0.5)**

(d)
(i) In the production of poly(phenylethene)/polystyrene. **(0.5)**
(ii) **Reactive specie:** $CH_3CH_2^+$; **(0.5)**
Formation: $\underbrace{CH_2 = CH_2 + HCl}_{\text{Forms } CH_3CH_2Cl} + AlCl_3 \longrightarrow CH_3CH_2^+ + AlCl_4^-$ **(0.5)**
(iii) Elimination reaction. **(0.5)**
Remark: Dehydrogenation is also **acceptable**.

(e) (i) Presence of **$\pi -$ bonds,** makes benzene **nucleophile** that is why it react with electrophile. Also because these **$\pi -$ bonds are stabilized** by **delocalization in mesomerism,** benzene tends to undergo **substitution reaction** rather than addition reaction. **(1.5)**
Remark: The explanation must answer the following questions: (i) Why it is ‘**electrophilic**’? (ii) Why it is ‘**substitution**’?

(ii) Acylation of benzene ring is **electrophilic substitution reaction.** Amino group in aniline **activate** the benzene ring reactivity towards **electrophile** through positive mesomerism while chlorine in chlorobenzene **deactivate it** by negative inductive effect.**(1.5)**

(iii) Silver nitrate is **covalent;** so a **single lone pair** in nitrogen of nitro group being **more nucleophilic** than **two lone pairs** in oxygen will be donated to positively charged carbon resulting to the formation of nitroalkane while potassium nitrate being **ionic** the electrons will be **donated** by **negatively charged** oxygen resulting to the formation of alkyl nitrites. **(1.5)**

Question 10

(a) (i) Mainly is absorbed as $\mathbf{H_2PO_4^-}$ **(0.5)** (at low pH) and as $\mathbf{HPO_4^{2-}}$**(0.5)** (at high pH).

(ii) At pH < 6, iron and aluminium form insoluble compound with phosphorous and therefore phosphorous become unavailable for plants. **(1)**

At pH> 7.5, starts forming insoluble compounds with calcium and therefore phosphorous become unavailable for plants. **(1)**

At pH range of 6 to 7.5 phosphorous become available for plants. **(1)**

(iii)

1. It promotes root growth **(0.5)**
2. It strengthens the resistance of plant to diseases**(0.5)**
3. It is needed by Rhizobia bacteria in order to fix nitrogen from the air**(0.5)**
4. It is an essential component of DNA and RNA**(0.5)**

(iv)

1. Super phosphate **(0.5)**
2. Triple phosphate **(0.5)**
3. Ammonium phosphate **(0.5)**

Remark: Any **two** correct names with maximum score of **1mark**.

(b)

(i) Are very small organic and inorganic particles present in the soil which are responsible for potential fertility of the soil.**(0.5)** These may be: layer silicate clays, iron and aluminium oxide clays, allophane and associated amorphous clays or humus**. (0.5)**

Remark: The question asked 'what' and not simply to define. So the examinee must add to the meaning some relevant information to get full score.

(ii) To hold mineral nutrients as it forms a sol on soil surface. **(0.5)**

(iii)

1. Surface area **(0.5)**
2. Electric (surface) charge **(0.5)**
3. Ion exchange (adsorption of cation) **(0.5)**
4. Swelling and shrinkage**(0.5)**
5. Dispersion and flocculation**(0.5)**

(c) Number of moles of NaOH used in the reaction

$= \frac{12}{1000} \times 0.1\text{mol} = 1.2 \times 10^{-3}\text{mol}$ **(0.5)**

NaOH reacts with HCl according to the following equation:

$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + H_2O$

From which mole ratio of NaOH to HCl is 1:1; **(0.5)**

Thus number of moles of HCl used in the neutralization was also 1.2×10^{-3}mol**(0.5)**

But total number of moles of HCl initially present in 10g of soil was $\frac{20}{100} \times 0.1\text{mol} = 2 \times 10^{-3}$mol**(0.5)**

Thus, $2 \times 10^{-3} - 1.2 \times 10^{-3}$ mol or 8×10^{-4}mol of HCl was used to produce 8×10^{-4}mol of H^+ (1 mole of HCl produce 1mole of H^+, so number of moles of H^+= Number of moles of HCl) which were used to exchange exchangeable base cations in the soil (in cation exchange reaction) **(1)**

But 8×10^{-4}mol of $H^{+} = 8 \times 10^{-4}$eq or 0.8meq **(0.5)**
And number of equivalents (or milliequivalents) of H^{+} used in the cation exchange reaction = number of exchangeable base cations. **(0.5)**
It follows that: Number of exchangeable base cations in 10g of oven dry soil is also 0.8meq **(0.5)**
And number of exchangeable base cations in 100g of oven dry soil is $\frac{0.8 \times 100}{10}$ or 8meq**(0.5)**
Using; percentage base saturation = $\frac{\text{number of exchangeable base cations}}{\text{CEC of the soil}} \times 100\%$**(0.5)**
$= \frac{8}{25} \times 100\% \quad (\mathbf{0.5}) = 32\%$
Hence the percentage base saturation of the soil is 32%**(1)**

Solutions Examination Four
CHEMISTRY 2B

Question 1

(a) (i) Is the method of removing (extracting) a solute from a certain solvent by introducing the second solvent**(**extractive solvent**)** which is immiscible to the first one and then allowing the solute to distribute itself in the two solvents. **(1)**

(ii)

First condition: The solute must be more soluble in extractive solvent than in the first solvent. That is, to ensure that greater amount of solute goes to extractive solvent, the partition coefficient between extractive solvent and first solvent, K_d should be large. **(1)**
Second condition: The volume of extractive solvent should be divided into small portions (partitions) rather than using the whole large volume at once. That is, greater amount of solute is extracted by having larger number of portions of volume of extractive solvent. **(1)**

(b)

(i) Are liquids which do not mix at all so that they tend to form separating layer when they are mixed. These are liquids like water and benzene whose intermolecular forces differ much. **(1)**

(ii)

1. **Vapour pressure (0.25)**

Vapour pressure of the immiscible liquid mixture is the arithmetic summation of vapour pressure of individual pure components. **(0.75)**
Remarks:

- **Accept**: in immiscible liquid system each liquid exerts vapour pressure independently.
- **Accept**: vapour pressure of immiscible liquid mixture is greater than either of individual pure component.

2. **Intermolecular forces (0.25)**

Intermolecular forces in pure liquids is different to intermolecular forces in the solution. **(0.75)**
Remark: Liquids which form immiscible mixture have different intermolecular forces.

(iii)

1. The liquid must be immiscible with water and the solution should boil to a temperature close to 100˚C. **(0.5)**
2. The vapour pressure of liquid (at temperature close to 100˚C) should be greater than that of water. **(0.5)**
3. The molar mass of the liquid should be large compared to that of water. **(0.5)**

Remark: Any **two** conditions are acceptable with maximum of **1mark**.

(c) Using $\frac{m_o}{m_w} = \frac{P_o \times M_o}{P_w M_w}$ **(1)**

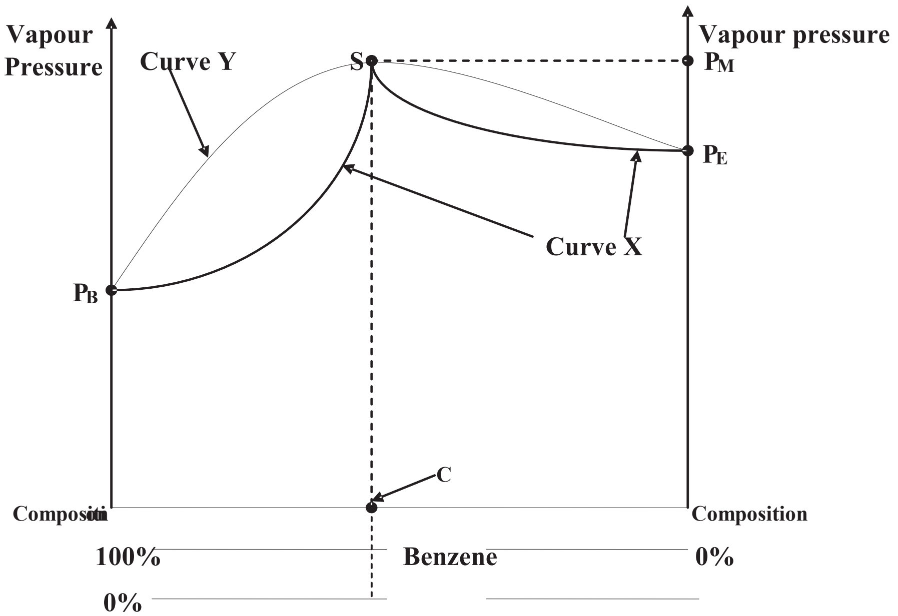
But $\frac{m_o}{m_w} = 0.48$, $(\mathbf{0.5})$ $P_o = 5.3\text{kPa}, P_w = 95\text{kPa}$ and $M_w = 18\text{g/mol}$
Then $0.48 = \frac{5.3\text{kPa} \times M_o}{95\text{kPa} \times 18\text{g/mol}}$ **(1)**
From which $M_o = 155\text{g/mol}$ **(0.5)**
Molar mass of the organic acid is 155g/mol **(1)**

(d)

(i) Curve x represent vapour phase of the solution **(0.5)**
Curve y represent liquid phase of the solution **(0.5)**

(ii) **Q** is the vapour formed after distillation (boiling) of liquid **P** at given temperature and **R** is the liquid formed after condensation of vapour **Q**. **(1)**

(i) **A sketched graph to illustrate the vapour pressure – composition relationship for benzene ethanol system**



Where:

P_B and P_E are vapour pressures of pure benzene and ethanol respectively
S is the azeotrope (azeotropic mixture)
Curve Y represent liquid phase of the solution.
Curve X represent vapour phase of the solution
C is he azeotropic composition
P_M is the vapour pressure of azeotropic mixture (maximum vapour pressure of the solution) **(3)**

Remark: Distribute 2marks for **drawing** and 1mark for **labelling** making a **total** of **3marks**.

(e) Since the solution is very dilute (mole fraction of benzene is 0.09), the given solution is ideal and hence Raoult's law is applicable. **(0.5)**

Partial vapour pressure of benzene, P_B
$= X_B P_B^o = 0.09 \times 75.2\text{mmHg} = 6.768\text{mmHg}$ **(0.5)**
Partial vapour pressure of ethanol, $P_E = X_E P_E^o$
But $X_E = 1 - X_B = 1 - 0.09 = 0.91$ $(\mathbf{0.5})$
If follows that, $P_E = 0.91 \times 43.6\text{mmHg} = 39.676\text{mmHg}$ **(0.5)**
Using $P_{soln} = P_B + P_E$ (Dalton's law of partial pressure) **(0.5)**
$P_{soln} = (6.768 + 39.676)\text{mmHg} = 46.444\text{mmHg}$

(i) Hence total vapour pressure of the mixture is 46.444mmHg **(0.5)**

(ii) $X_B = \frac{P_B}{P_{soln}}(\mathbf{0.5}) = \frac{6.768}{46.444} = 0.146$

Hence the mole fraction of benzene in the vapour phase is 0.146 **(0.5)**

Question 2

(a)

(i) Disagree **(0.5)**

Explanation

Change in concentration has no effect on reaction rate of **zeroth order** chemical reaction.**(1)**

(ii) Disagree **(0.5)**

Explanation

The value of rate constant can also be affected by adding/removing **catalyst**. **(1)**

(iii) Agree **(0.5)**

Explanation

High pressure means high collision frequency and hence high reaction rate. **(1)**

(iv) Disagree **(0.5)**

Even exothermic reaction may have high **activation energy** leading to slow reaction. **(1)**

(b) Initially, the reaction rate is low because both reactants are negatively charged making to repel each other and hence high activation energy for the reaction. **(1)**

Thereafter, the reaction rate increases because Mn^{2+} ions which act as autocatalyst provides an alternative route with lower activation energy. **(1)**

Finally, near the end of the reaction, the reaction rate decreases because the concentration (amount) of reactants has been decreased. **(1)**

(c)

(i) **Salt** which is **strong electrolyte (0.5)** like potassium nitrate (KNO_3) **(0.5)**

Remarks:

- The question asked '**state what**…'; so the two components must appear in the answer.
- The following examples are also **acceptable**: potassium chloride, sodium nitrate, sodium chloride, ammonium nitrate, ammonium chloride.
- If more than one example is given, **all** must be correct.

(ii) Salt bridge allows flow of ions while the wire allows flow of electrons and not the required flow of ions. **(2)**

(d)

(i) Number of moles of $KMnO_4 = \frac{20.25}{1000} \times 0.02\text{mol} = 4.05 \times 10^{-4}\text{mol}$ (**0.5**)

$KMnO_4$ reacts with H_2O_2 according to the following equation:

$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$ **(1)**

From which mole ratio of MnO_4^- to H_2O_2 reacted $= \frac{5}{2} \times 4.05 \times 10^{-4}$ mol (**0.5**)

$= 1.0125 \times 10^{-3}$ mol in $25cm^3$ of its solution

Then $[H_2O_2] = \frac{n}{V} = \frac{1.0125\times10^{-3}}{25\times10^{-3}}M = 0.0405M$ (**07.5**)

Using dilution principle: $M_cV_c = M_dV_d$ (**0.75**)

Then substituting $M_c \times 50 = 0.0405 \times 1000$; $M_c = 0.81M$.

Hence original concentration of H_2O_2 was 0.81 $moldm^{-3}$ **(0.5)**

(ii) $NaMnO_4$ is hygroscopic. **(1)**

The titre volume would be larger than the obtained one. **(1)**

(iii) Concentrated H_2SO_4 is good oxidizing agent; so it would oxidize H_2O_2 as $KmnO_4$ does. **(1)**

The titre volume would therefore be less than the obtained one. **(1)**

Question 3

(a) Acid is any hydrogen containing specie which is capable of donating one or more hydrogen proton to a base. **(0.5)**

Base is any specie which is capable of accepting one or more hydrogen proton from an acid. **(0.5)**

Advantages of Bronsted-Lowry theory

1. It expands the list of potential acids and bases to include positive and negative ions as well as species with lone pair. **(0.5)**
2. It explains the role of water in acid-base reaction where it accepts H^+ from acid to form H_3O^+.**(0.5)**
3. It expands to include solvent other than water and reactions which occur in the gas or solid phase. (**0.5**)
4. It explains the difference in relative strength of a pair of acid and a pair of base. **(0.5)**

(b)

(i) The concentration of solid ($Mg(OH)_2(s)$) is constant (unchanged). **(1)**

Remark: Don't accept: the solid does not have concentration.

(ii) From; $K_{sp} = [Mg^{2+}(aq)][OH^-(aq)]^2$

Units of K_{sp} = Units of $[Mg^{2+}(aq)] \times (\text{Units of } [OH^-(aq)])^2$ **(1)**
Units of $K_{sp} = moldm^{-3} \times (moldm^{-3})^2 = mol^3dm^{-9}$ **(1)**

(c) When [HCl] and whence $[H^+]$ is large, the $[H^+]$ from self ionisation of water can be ignored. However when [HCl] and thus $[H^+]$ is very small, $[H^+]$ from self-ionisation of water cannot be ignored. **(2)**

Calculation of pH of 10^{-9}MHCl:

$$\begin{array}{ccccc} HCl & \rightarrow & H^+ & + & Cl^- \\ 10^{-9}M & & 10^{-9}M & & \end{array}$$

If x moles of H_2O are ionised to its respective ions in $1dm^3$ of the solution;

$$\begin{array}{ccccc} H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & x + 10^{-9} & & x \end{array}$$ **(0.5)**

Then $Kw = [H^+][OH^-] = 10^{-14} = (x + 10^{-9})x$ **(1)**
From which: $x^2 + 10^{-9}x - 10^{-14} = 0; x = 9.95 \times 10^{-8}$ **(1)**
Thus $[H^+] = (9.95 \times 10^{-8} + 10^{-9})M$
$= 1.005 \times 10^{-7}M$ (**0.5**)
And $pH = -\log[H^+] = -\log(1.005 \times 10^{-7})$ **(0.5)**
$= 6.9978$
Hence pH of the solution is 6.9978 (**0.5**)

(d) After adding 10mL of strong base, the solution was still acidic suggesting that the acid was excess. **(0.5)**

The unreacted weak acid and produced salt forms **acidic buffer solution (0.5)** whose pH is given by the following equation:

$\mathrm{pH} = \mathrm{pKa} + \log\frac{[\mathrm{Salt}]}{[\mathrm{Acid}]}$; $(\mathbf{0.5})$ $\mathrm{pH} = \mathrm{pKa} + \log\frac{\text{Number of moles of salt}}{\text{Number of moles of acid}}$

Where $\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log 10^{-5} = 5$ **(0.5)**

If the base is monoacid, MOH, and the acid is monobasic, HA, then the reaction equation will be:

$\mathrm{HA+MOH} \longrightarrow \mathrm{MA} + \mathrm{H_2O}$ (mole ratio is 1:1 for all scenarios) **(0.5)**

Number of moles of base in 10mL of its solution

= Number of moles of produced salt

$=\frac{10}{100} \times \mathrm{M_b}$ ($\mathrm{M_b}$ is unknown concentration of base) $= 0.01\mathrm{M_b}$**(1)**

Volume of base used to neutralize the acid in the buffer solution

$= (22.22 - 10)\mathrm{mL} = 12.22\mathrm{mL}$**(0.5)**

Number of moles of acid in the buffer = Number of moles of base used to neutralize it

$=\frac{12.22}{1000} \times \mathrm{M_b} = 0.01222\mathrm{M_b}$**(1)**

Then from $\mathrm{pH} = \mathrm{pKa} + \log\frac{\text{Number of moles of salt}}{\text{Number of moles of acid}}$ **(0.5)**

$5 = \mathrm{pKa} + \log\frac{0.01\mathrm{M_b}}{0.01222\mathrm{M_b}}$; From which $\mathrm{pKa} = 5.087$**(1)**

$\mathrm{Ka} = \log^{-1}(-\mathrm{pKa}) = \log^{-1}(-5.087)(\mathbf{0.5}) = 8.18 \times 10^{-6}$

Dissociation constant for the acid is 8.18×10^{-6}**(1)**

Question 4

(a)

(i) Electronegativity is the ability of an atom of an element to attract covalent bonded (or shared) electrons towards itself. **(0.5)**

Remark: The definition **must contain** the keywords '**covalent bonded**' (or **'shared'**). (Electronegativity is for covalent bonded atom and **not** for isolated atom).

Oxidation number is the number of electrons gained or lost by an atom in combining with another atom by assumption that the bond formed between the atoms is ionic. **(0.5)**

Remark: The phrase, "by assumption that the bond formed between atoms is ionic" or the equivalent idea **must** be contained in the definition.

(ii) Larger electronegativity difference, more ionic character in the molecule. **(0.75)**

(iii) More electronegative atom has negative oxidation number while less electronegative atom has positive oxidation number. **(0.75)**

(iv) Noble gases do not form (covalent) bonds and hence the term electronegativity is not defined for noble gases. **(1)**

(v)

1. Oxidation number gives the charge an atom or group of atoms can have while valence number gives the number of bonds that a specie can form. **(0.75)**
2. Oxidation number of an atom of the same element may have different value depending on the nature of the atom it combine with while valence number is usually fixed. **(0.75)**
3. Oxidation number may be whole number or fraction while valence number must be whole number. **(0.75)**
4. Oxidation number may be zero while valence number can never be zero except for noble gases. **(0.75)**

Remark: Any **two** differences are acceptable with maximum of **1.5marks**.

(b)

(i) The gas that turns red litmus paper blue (basic gas) is ammonia. **(0.5)**

- Since the gas (ammonia) was evolved after adding sodium hydroxide, there is ammonium ion in A. **(0.5)**

Silver nitrate test presence of halide ion in the compound (A). **(0.5)**

- The formation of cream precipitate suggests presence of bromide ion. **(0.5)**

Hence:

- The cation is ammonium ion **(0.5)**
- The anion is bromide ion **(0.5)**
- The name of salt A is ammonium bromide **(0.5)**

Remarks:

- Ammonia instead of ammonium is **not** acceptable.
- Bromine instead of bromide is **not** acceptable.

(ii)

TEST	OBSERVATION
Add excess dilute ammonia to the precipitate**(0.5)**	The precipitate does not dissolve (is insoluble)**(0.5)**
Add excess concentrated ammonia to the precipitate.**(0.5)**	The precipitate dissolves to give clear (colourless) solution.**(0.5)**

Remark: The following alternative test is acceptable:
Test: Add concentrated sulphuric acid. Observation: Reddish-brown (of bromine). (Here the examinee must give its corresponding chemical equation to get full score of 2marks).

(iii) $NH_4Br(s) + NaOH(aq) \longrightarrow NH_3(g) + NaBr(aq) + H_2O(l)$ **(0.5)**

(c) (i)

1. Have smallest size of atoms and their ions in their groups **(0.5)**
2. Have highest electronegativity in their groups(**0.5**)
3. Have highest ionisation energy in their groups(**0.5**)
4. Have no d-orbitals (**0.5**)

Remarks: Any **three** reasons are acceptable with maximum score of **1.5marks**.

(ii)

1. In most cases, lithium has greatest physical properties than alkali metals. (**0.5**)
2. Lithium reacts with oxygen to give normal oxide only while other alkali metals can give different types of oxides, from normal oxides, peroxides to superoxides. (**0.5**)
3. Lithium can combine with nitrogen to give lithium nitride while other alkali metals cannot. (**0.5**)
4. Compounds of lithium are less thermally stable than compounds of other alkali metals (**0.5**)
5. Compounds of lithium are more covalent in characters while those of other alkali metals are strongly ionic. (**0.5**)
6. Lithium chloride forms hydrated crystals ($LiCl.2H_2O$) in aqueous solution while other alkali metals forms anhydrous chloride (**0.5**)

Remarks: Any **five** differences are acceptable with maximum score of **2.5marks**.

(iii) A: Lithium being on the top of group IA has greatest polarizing power as result of its smallest cationic radius thus distorting peroxide ion (O_2^{2-}) into normal oxide ion (O^{2-}). **(1.5)**

Remark: The explanation must base on effect of **polarizing power** in the peroxide ion.

B: Lithium being on the top of group IA, has smallest cationic radius thus making lattice energy between Li^+ and N^{3-} to be large enough to compensate very high dissociation energy of $N \equiv N$ to N(g) and net electron affinity involved in forming N^{3-}(g) from N(g) which is highly endothermic process. (**1.5**)

Remark: The explanation must base on effect of **lattice energy** in stability of the nitride.

(iv)

1. They both form hydrated chloride ($LiCl.2H_2O$ and $MgCl_2.6H_2O$) (**0.5**)
2. They both combine with oxygen gas to form normal oxides only (Li_2O and MgO) **(0.5)**
3. They both react with nitrogen to form nitride which reacts with water to liberate ammonia. (**0.5**)
4. Hydroxides and carbonates of both lithium and magnesium decompose on heating. (**0.5**)
5. Nitrates of both lithium and magnesium decompose in similar way in heating whereby they both gives oxides accompanied with evolvement of brown fumes of NO_2 (**0.5**)
6. Solid bicarbonates of both lithium and magnesium do not exist at room temperature. (**0.5**)

Remarks: Any **four** diagonal relationships are acceptable with maximum score of **2marks**.

Question 5

(a)

(i) This is because:

- Transition elements have **stronger metallic bond** due to their small metallic radii.**(0.75)**
- Transition elements can form very **strong d-d covalent bond** between their atoms because they have unpaired d-orbitals in the penultimate shell. **(0.75)**

(ii) In transition elements, the increase in screening effect is enough to counterbalance with the increase in nuclear attractive forces because as their atomic numbers increase, electrons are added to the penultimate shell. **(1.5)**

(iii) Due to their small atomic radii, transition elements can hold small elements like carbon, nitrogen and hydrogen in their interstices of their metallic lattice. **(1.5)**

(iv) This is because:

- They have **variable oxidation state** so that they can form unstable intermediate products with the reactants **(0.75)**
- They have **large surface areas** to adsorb the reactants on their surfaces and activate them in the process **(0.75)**

(b) Firstly; Fe^{2+}, is oxidised to $Fe^{3+}$by $S_2O_8^{2-}$ and therefore promoting the formation of SO_4^{2-} as per the following equation: **(1)**

$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$ **(1)**

Then $Fe^{3+}$is reduced by $I^-$and therefore promoting the formation of I_2 while the catalyst, Fe^{2+}, is regenerated. **(1)**

$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$ **(1)**

(c)

(i) Protein **(0.5)**

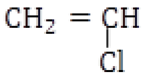
Remark: Any other relevant example like starch, cellulose, silk, wool or natural rubber is **acceptable**.

(ii) Bakelite plastic **(0.5)**

Remark: Any other relevant example like melamine is **acceptable**.

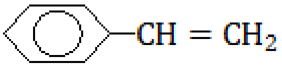
(iii) Vulcanised rubber (or any other relevant example) **(0.5)**
(iv) Nylon (or terylene) **(0.5)**
(d)

(i)



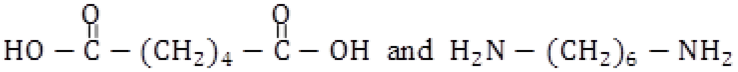
$CH_2 = \underset{Cl}{\underset{|}{CH}}$ **(1)**

(ii)



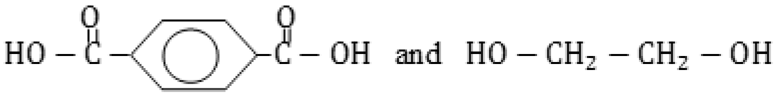
(1)

(iii)

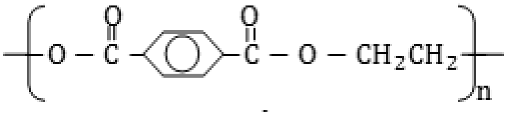


$HO - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - OH$ and $H_2N - (CH_2)_6 - NH_2$ **(1)**

(iv)



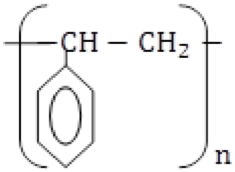
(e) (i)



(0.5)

Type: Condensation polymerisation **(0.5)**

(ii)



(0.5)

Type: Addition polymerisation **(0.5)**

(iii) Polymers in clothes terylene contain an ester group (polymers in clothing are polyester) which is hydrolyzed by alkali while poly(phenylethene) is an addition polymer contain uncreative non-polar $C - C$ which is saturated. **(2)**

Question 6

(a)

(i) Potassium permanganate test: Methyl methanoate decolourises purple colouration of potassium permanganate while methyl ethanoate does not. **(1)**

(ii) Nitrous acid test: With nitrous acid, N-methylethanamine gives yellow oil liquid while N,N-dimethylethanamine gives clear solution. **(1)**

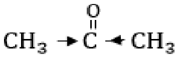
(b)

(i) The $-NH_2$ group in phenylamine increases electron density in benzene ring by positive mesomerism thus activating electrophilic substitution reaction of benzene like nitration while the $-CHO$ group in benzene carbaldehyde decrease the electron density by negative mesomerism deactivating the benzene ring toward electrophile (nitro group). (**1**)

(ii) With the structure, $CH_3-CO-CH_3$, propanone has terminal methyl group bonded to the carbonyl group while the propan-1-ol which has structure, $CH_3CH_2CH_2OH$, has terminal methyl group bonded to carbon with OH to enable iodoform reaction for it. (**1**)

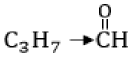
(iii) This is because:

1. Carbon in carbonyl group of propanone experience stronger positive inductive effect from two alkyl groups in two directions making it less positively polarized and hence less reactive toward the nucleophile unlike propanal which experience positive inductive effect from one direction only. (**0.75**)



$CH_3 \rightarrow \overset{O}{\overset{\|}{C}} \leftarrow CH_3$

Propanone



$C_3H_7 \rightarrow \overset{O}{\overset{\|}{C}}H$

Propanal

2. The two alkyl groups surrounding the carbonyl group in propanone exert stronger steric hindrance than one alkyl group in propanal making easier for nucleophile to add to propanone than to propanal. (**0.75**)

(c)

The general molecular formula of ester is either $C_nH_{2n}O_2$ for aliphatic esters or $C_nH_{2n-8}O_2$ for aromatic ester; where n must be positive whole number. **(0.5)**

For aliphatic ester, $C_nH_{2n}O_2$

$12n + 2n + 32 = 150$; from which $n = 8.43$ which is not whole number. Thus compound P cannot be aliphatic ester.

For aromatic ester, $C_nH_{2n-8}O_2$

$12n + 2n - 8 + 32 = 150$ or $n = 9$

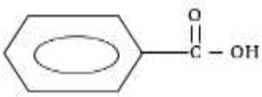
Which is positive whole number. **(1)**

(Remark: This **1mark** is for correct recognition of value of n regardless to whether you started with aliphatic ester or aromatic).

Thus P is aromatic ester with 9 carbons. And by substituting $n = 9$ in the general molecular formula, $C_nH_{2n-8}O_2$, its molecular formula becomes $C_9H_{10}O_2$ **(0.5)**

Since R was produced from the reaction between monobasic acid and ethanol; Q must be aromatic carboxylic acid with 7 carbons of molecular formula $C_7H_6O_2$ **(0.5)**

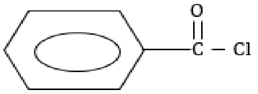
Since there is only **one isomer** of aromatic carboxylic acid with 7 carbons, the correct structure of Q is



(Structure of Q) (0.5)

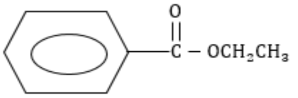
The compound which gives carboxylic acid (Q) upon hydrolysis (with diluteH_2SO_4) is **acid chloride. (0.5)**

- Thus P is the aromatic acid chloride with the following structure



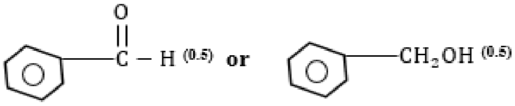
(Structure of P) **(0.5)**

Esterification of Q with ethanol gives the following ester which is R



(Structure of R) **(0.5)**

Reduction of P (acid chloride) may give either **aldehyde** or **alcohol (0.5)** depending on the extent of reduction. Thus structure of S may be one of the following:



(Structure of S)

(d) (i) Molecular formula $C_5H_{10}O$ confirm general molecular formula of $C_nH_{2n}O$. Thus C is either aldehyde, ketone or unsaturated alcohol with $C = C$. **(0.5)**

Formation of crystalline product with 2,4-dinitrophenylhydrazine confirms that there is carbonyl group in C. **(0.5)**

- Thus C cannot be alcohol, it must be either aldehyde or ketone. **(0.5)**

Since C gives positive iodoform test, there is a terminal methyl group which is directly bonded to carbonyl group in C.**(0.5)** And because, the only aldehyde which gives positive iodoform test is ethanal which has only two carbons, C cannot be aldehyde, it must be methyl ketone.**(0.5)**
A compound that gives ketone on oxidation is secondary alcohol. Thus B must be secondary alcohol. **(0.5)** Carbonyl compound which gives secondary alcohol with Griginard reagent (methyl magnesium bromide) are aldehydes with more than one carbon. Thus A is the aldehyde with two carbons or more. **(0.5)**
Product formed after reaction between methyl magnesium bromide followed by hydrolysis, indicates that there are four carbons in A.**(0.5)**

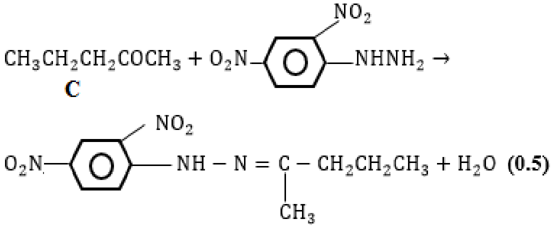
- Thus A must be aldehyde with four carbons and B must be secondary alcohol with five carbons.**(0.5)**

Since A is unbranched:
Structure formula of A is $CH_3CH_2CH_2\overset{\overset{O}{||}}{C} - H$ **(0.5)**
Structure formula of B is $CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HCH_3$ **(0.5)**
Structure formula of C is $CH_3CH_2CH_2\overset{\overset{O}{||}}{C} - CH_3$ **(0.5)**
Equations for reactions:

$$\underset{\textbf{A}}{CH_3CH_2CH_2\overset{\overset{O}{||}}{C} - H} \xrightarrow{\text{(i)}CH_3MgBr\text{ (ii) }H_2O} CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HCH_3 + Mg(OH)Br$$ **(0.5)**

$$CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HCH_3 + H_2CrO_4 \rightarrow CH_3CH_2CH_2\overset{\overset{O}{||}}{C}CH_3$$

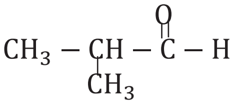
B **(0.5)**



(0.5)

$$CH_3CH_2CH_2COCH_3 + I_2 + NaOH \rightarrow CHI_3 + CH_3CH_2CH_2COONa + NaI + H_2O$$ **(0.5)**

(ii) The isomer is



$$CH_3 - \underset{\displaystyle CH_3}{CH} - \overset{\displaystyle O}{\overset{\|}{C}} - H$$ **(0.5)**

Solutions Examination Five

CHEMISTRY 1C

Question 1

(a)

(i) Nuclide is a **nucleus** of a particular atom characterized by a defined **atomic number** and **mass number.(0.5)**

(ii) Isotones are **atoms** of different **elements** with different atomic numbers but the **same neutron number.(0.5)**

Remarks:

- The definition which starts with phrase; '**are elements'** instead of atoms is **not** acceptable. **(**Isotones are atoms, not elements)**.**
- The definition which just state; "Are atoms with the same neutron number" is **not** acceptable.
- The definition which does not mention '**different elements'** but mention 'with different atomic number' (Or the definition which does not mention 'with different atomic number' but mention 'different elements') is **acceptable**. (Atoms of different element automatically have different atomic number. And if atoms have different atomic numbers, they must come from different elements).

(iii) Isotopes are **atoms** of the **same element** with the same atomic number but **differ in their mass number.(0.5)**

Remarks:

- The definition which starts with phrase; '**are elements'** instead of atoms is **not** acceptable. **(**Isotopes are atoms, not elements)**.**
- The definition which just state; "Are atoms with different mass number" is **not** acceptable.
- The skipping of phrase; **'same element'** if the phrase '**with the same atomic number'** is included and vice versa is **acceptable**. (Atoms of the same element automatically have the same atomic number and if atoms have the same atomic number, they automatically come from the same element).

(a)

$\text{Number of protons} = \text{the number in the subscript} = 7\ (\mathbf{0.5})$

$\text{Number of electrons} = \text{Number of protons} = 7\ (\mathbf{0.5})$

$\text{Number of neutrons} = \text{Mass number (in the superscript)} - \text{Number of protons}$

$$= 15 - 7 = 8\ (\mathbf{0.5})$$

(b) Electronic configuration of calcium is as follows: $1s^2 2s^2 2P_x^2 2P_y^2 2P_z^2 3s^2 3P_x^2 3P_y^2 3P_z^2 4s^2$ **(0.75)**

(i) Total number of electrons in n = 3 of $3s^2 3P_x^2 3P_y^2 3P_z^2$ is $2 + 2 + 2 + 2$ or 8 electrons.
Hence 8 electrons have quantum number of $n = 3$ **(0.75)**

(ii) $m_l = 0$ represents s and P_y orbitals in $1s^2 2s^2 2P_y^2 3s^2 3P_y^2 4s^2$ with total of $2 + 2 + 2 + 2 + 2 + 2$ or 12 electrons.
Hence 12 electrons have quantum number of $m_l = 0$ **(0.75)**

(iii) $l = 1$ represents P orbitals in $2P_x^2 2P_y^2 2P_z^2 3P_x^2 3P_y^2 3P_z^2$ with total of $2 + 2 + 2 + 2 + 2 + 2$ or 12 electrons.
Hence 12 electrons have quantum number of $l = 1$ **(0.75)**

(c)

First information:
If two electrons occupy the same orbital, the electrons must have the opposite spin. This because, if two electrons are in the same orbital, have the same first three quantum numbers (n, l and m_l); so they must spin in opposite direction in order to have different fourth quantum numbers (m_s) **(1)**
Remark: Distribute **0.25 mark** is for mentioning 'electrons in the same orbital have the opposite spin' and **0.75 mark** for explaining it.
Second information:
Maximum number of electrons in an orbital is two. This because, there are only two directions of spinning and therefore only two values for m_s. Having more than two electrons in an orbital would make more than one electron to have the same value of m_s and hence all four quantum numbers would be the same. **(1)**
Remarks:

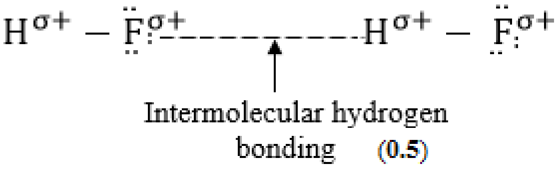
- Distribute **0.25 mark** is for mentioning 'maximum number of electrons in an orbital is two' and **0.75 mark** for explaining it.
- **Ignore** the order of information (second information may be the first one and vice-versa).

(d)

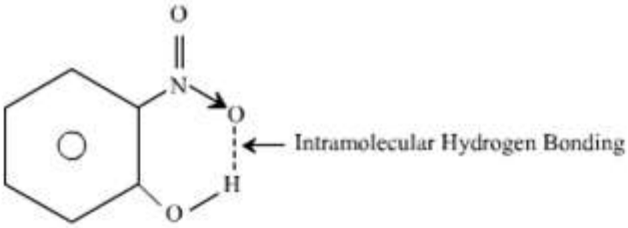
From Bohr theory;
$\Delta E = nhf = \frac{nhc}{\lambda}$ **(0.5)**
Where $n = 6.02 \times 10^{23} mol^{-1}$ if the energy is in J/mol
Substituting
$145.684 \times 10^3 \cancel{Jmol^{-1}} = \frac{6.02\times10^{23}\cancel{mol^{-1}}\times6.63\times10^{-34}\cancel{Js}\times3\times10^{8}m\cancel{s^{-1}}}{\lambda}$ **(0.5)**
From which $\lambda = 8.219 \times 10^{-7} m$ **(0.5)**
But $1A^0 = 10^{-10} m$
So $8.219 \times 10^{-7} m = \frac{8.219\times10^{-7}}{10^{-10}} A^0 = 8219A^0$
Hence the wavelength of radiation is $8219A^0$ **(0.5)**
Remark: To get full score, the examinee must show each step clearly including **manipulation of units** and the final correct answer must be in angstrom (A^0). (**Deduct 0.5 mark** if the units manipulation is not shown and also **deduct 0.5 mark** if the correct answer is not in angstrom (A^0)).

Question 2

(a)(i) Is the interaction between partial positively charged hydrogen atom in one molecule and **lone pair** of nearly small sized electronegative atom of another molecule. (**1**)



(i) Is the interaction between partial positively charged hydrogen atom and **lone pair** of nearby small sized electronegative atom within the same molecule. (**1**)



(0.5)

Remarks:

- Any idea which suggests that the hydrogen bonding is the '**force**' (or bonds) is **not** acceptable. (**'ing'** in bonding restrict our meaning to start with **'interaction'.** Bonding is interaction, not **force; force** is for bond, not for bonding**).**
- An idea which suggests that the hydrogen bonding is an interaction between partial positively charged hydrogen and partial **negatively charged** of strong electronegative atom is **not** acceptable.

(b) $H_2O(104.5°) < CCl_4(109.5°) < CO_3^{2-}(120°) < HCN(180°)$ **(2)**

Remark:

To get the indicated marks the examinee must arrange all entities at right position (**Award zero score** if at least one entity is kept at wrong position).

(c) The given molecules have different bond angles despite the fact that they have the same electron pair geometry because they have different number of lone pairs in each of their central atom. Since lone pair exert stronger repulsion than bonded electron pair, the size of bond angle decreases as number of lone pair increases whereby CH_4 having no lone pair has largest bond angle $(109.5°)$ followed by NH_3 $(107°)$ which has one lone pair in N while O in H_2O having two lone pairs has smallest bond angle. $(104.5°)$ **(2)**

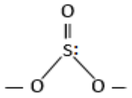
Remark:

To get full score, the examinee must give an explanation which have the following elements:

- The reason of difference of the bond angles. (**Award 1 mark** for this).
- Correct trend on bond angles of the given molecules. (**Award 1 mark** for this).

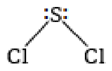
(d)

(i) Consider the structure of SO_3^{2-} below:



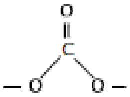
With three sigma bonds and one lone pair, type of hybridisation in sulphur is sp^3 hybridisation.**(1)**

(ii) Consider the structure of SCl_2 below:



With two sigma bonds and two lone pairs, type of hybridisation in sulphur is sp^3 hybridisation. **(1)**

(iii) Consider the structure of CO_3^{2-} below:



With three sigma bonds and zero lone pair, type of hybridisation in carbon is sp^2 hybridisation.**(1)**

Remark: To get maximum marks, the examinee must show briefly how to arrive to the answer. (For each part of the question, **deduct 0.5 mark** from maximum marks if the work is not shown but the answer is correct).

Question 3

(a)

(i) Is the temperature at and above which a gas cannot be liquefied, no matter how much pressure is applied.**(0.5)**

(ii) Is the volume occupied by one mole of a gas at critical temperature and pressure.(**0.5**)

(iii) Is the pressure required to liquefy a gas at its critical temperature (**0.5**)

(b) From ideal as equation; $R = \frac{PV}{nT}$

It follows that: $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$ **(0.5)**

If $P_1 = P_2 = P$ and $V_1 = V_2 = V$ (P and V are constants)

Then $\frac{PV}{n_1T_1} = \frac{PV}{n_2T_2}$ or $n_1T_1 = n_2T_2$ **(0.5)**

Substituting $n_1 \times 300 = n_2 \times 360$ **(0.5)**

From which; $\frac{n_2}{n_1} = \frac{5}{6}$ **(1)**

Where n_1 is the number of moles of air before heating and n_2 is the number of moles of air after heating.

Then the percentage of air remained $= \frac{5}{6} \times 100\%$

$= 83.33\%$

And hence percentage of air expelled

$= (100 - 83.33)\% = 16.67\%$ **(1.5)**

(c)

(i) 'a' is determined by the strength of the **intermolecular forces** of attraction between molecules of real gases **(0.5)**

'b' is determined by the amount of actual **volume** of a molecule of real gas **(0.5)**

Remarks:

- The use of 'pressure' instead of 'intermolecular forces' is not allowed.
- The use of 'size' instead of 'volume' that is 'size of molecule' (molecular size) instead of volume of a molecule (molecular volume) is **acceptable**.

(ii) H_2S has higher value of 'a' **(0.25)**

Explanation:

H_2S molecules experience stronger intermolecular forces of attraction. Since having greater molar mass, H_2S has stronger Van der Waals dispersion forces and being polar, it has dipole-dipole forces in addition to the dispersion forces unlike lighter non-polar H_2.**(1)**

H_2S has higher value of 'b' **(0.25)**

Explanation:

Having greater molar mass, H_2S molecule has greater size and therefore greater volume than H_2 **(1)**

Remark: To get full sore on explanation, the examinee must explain both **molecular weight (size)** and **polarity** of H_2S as compared to H_2 in relation to their intermolecular forces strength (in case of value of a). In case of value of b, only explanation relating molecular size to molecular volume are required.

(iii) 'a' is correlated to boiling point. The greater value of 'a' means stronger intermolecular forces of attraction and hence higher boiling point. **(0.75)**

Remark: The examinee is **not** expected to **explain** how intermolecular forces strength affect boiling point (the question just asked 'how' and not to 'explain').

Question 4

(a)

(i) Molarity **(0.5)**

Explanation:
Molarity depends on the volume which is temperature dependent unlike molality which depends on mass and the mass is not affected by temperature. **(1)**

(ii) Measurement of freezing point depression or boiling point elevation involves changing the temperature of the solution, the action which would change the molarity of the solution. Since molality is temperature independent, it becomes more appropriate to be used in their respective mathematical equations than molarity. **(1)**

(iii) Due to **dissociation** of the electrolyte, the observed number of solute particles becomes larger than the expected one leading to the greater freezing point depression and hence the observed freezing point becomes lower. **(1)**

(iv) Diluted solution. **(0.5)**

Explanation:
In accordance to Ostwald's dilution law, the degree of dissociation (ionisation) is greater in the more diluted solution and therefore the discrepancy becomes greater. **(1)**

(b)

(i) Osmotic pressure is the pressure required to be applied to the side of higher solute concentration so as to prevent movement of solvent molecules by osmosis. **(0.5)**
Reverse osmosis is the non-spontaneous flow of solvent through semi-permeable membrane from a solution of higher solute concentration to one of lower solute concentration. **(0.5)**

(ii) 1 mole of particles $= 6.02 \times 10^{23}$ particles **(0.25)**

But mass of 1 particle $= 10^{-9}\text{g}$
Thus molar mass of particles $= 10^{-9}\text{g}/$~~particle~~ $\times 6.02 \times 10^{23}$ ~~particles~~/mol **(0.5)**
$= 6.02 \times 10^{14}\text{g/mol}$**(0.25)**
Then using;

$$\text{Molarity} = \frac{\text{Mass concentration in g/L}}{\text{Molar mass}}$$

Molarity of solid particles $= \frac{60\ \text{g/L}}{6.02\times10^{23}\text{g/mol}}$
$= 9.9668 \times 10^{-14}\cancel{\text{mol}}/\text{L}$ **(1)**
Then from;
$\pi v = nRT; \pi = \left(\frac{n}{v}\right)RT$ or $\pi = [\quad]RT$**(0.5)**

Substituting;

$\pi = 9.9668 \times 10^{-14}\cancel{\text{mol}}/\cancel{\text{L}} \times 0.082\text{atm}\cancel{\text{Lmol}}^{-1}\cancel{\text{K}}^{-1} \times 298\cancel{\text{K}}$ **(1)**

$= 2.44 \times 10^{-12}\text{atm}$

Hence the osmotic pressure of the suspension is

$2.44 \times 10^{-12}\text{atm}$ **(0.5)**

Remark: To get full score the examinee must show each step clearly including manipulation of units. (Deduct **not more than 1 mark** for poor manipulation of units).

Question 5

(a)

(i) $Zn(OH)_2 \xrightarrow[\Delta]{} ZnO + H_2O$

(ii) $K_2CO_3(s) \xrightarrow[\Delta]{}$ No reaction

(iii) $ZnSO_4 \xrightarrow[\Delta]{} ZnO + SO_3$

(iv) $2Mg(NO_3)_2 \xrightarrow[\Delta]{} 2CuO + 4NO_2 + O_2$

(b)

(i) Due to less electropositivity of boron, its hydroxide is acidic (not basic) so it is more appropriate to name it as boric acid to reflect it acid behaviour rather than boron hydroxide which reflect base behaviour. **(1)**

(ii) For sulphate of a metal to be prepared by displacement method, the metal should not only be able to displace hydrogen but also the resulting sulphate must be soluble. Calcium sulphate is **insoluble** and therefore its formation prevents further reaction.**(1)**

$$Ca(s) \; + H_2SO_4(\text{dil}) \rightarrow \text{No reaction}$$

(iii) In $BeCl_2$ there are two empty orbitals, p_y and p_z which enable the molecules of $BeCl_2$ to associate to infinite thus forming a polymer while $AlCl_3$ having only one p_z empty orbital only ends to the dimer.**(1)**

(iv) Nitrates have low lattice energy due to large size of NO_3^- accompanied with only single charge while the hydration energy is very large due to possibility of NO_3^- to make hydrogen bonds with water molecules and hence they become water-soluble.**(1)**

(c)

1. **Use:** In agricultural fertilizers. **(0.5)**

   Explanation: Nitrogen is among nutrients required by plants in large proportion and thus it said to be primary nutrient. Nitrates are commonly used nitrogenous fertilizers, for example: calcium nitrate, sodium nitrate and potassium nitrate. **(1)**
   Feature: They have high solubility and high biodegradability. **(0.5)**

2. **Use:** In making explosives. **(0.5)**

   Explanation: Metal nitrates are used in explosives like in fireworks and gunpowder; for example potassium nitrate in gunpowder. **(1)**
   Feature: They are very good oxidising (combusting) agent. **(0.5)**

Question 6

(a)

(i) Is the enthalpy change when molar quantities represented by the equation react under given conditions of temperature and pressure, the substance being on their normal physical state for those conditions **(1)**

(ii) Is the heat evolved when a dilute solution containing sufficient mass of acid to provide one mole of H^+ ions reacts with dilute solution containing sufficient alkali to provide one mole of OH^- so as to give one mole of water under standard conditions of temperature and pressure. **(1)**

Remark: The definition begin with 'heat **change**' or 'heat **absorbed (**or **required)** is **not** acceptable.

(iii) Is the heat required to convert an element in its normal state into one mole of its corresponding gaseous atoms under given conditions of temperature and pressure. **(1)**

Remark: The definition begin with 'heat **change**' or 'heat **released (**or **evolved)** is **not** acceptable.

(iv) Is the heat evolved when one mole of an element or compound is completely burnt in oxygen under standard conditions of temperature and pressure (25°C and 1 atm). **(1)**

Remark: The definition begin with 'heat **change**' or 'heat **absorbed (**or **required)** is **not** acceptable.

(b) (i) Equation for combustion of C_2H_6

$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$ **(1)**

Using:

$$\Delta H_r^{\emptyset} = \sum \Delta H_f^{\emptyset}(\text{Products}) - \sum \Delta H_f^{\emptyset}(\text{Reactants})$$

$= 2\Delta H_f^{\emptyset}(CO_2) + 3\Delta H_f^{\emptyset}(H_2O) - \frac{7}{2}\Delta H_f^{\emptyset}(O_2) - \Delta H_f^{\emptyset}(C_2H_6)$ **(1)**

But $\Delta H_f^{\emptyset}(O_2) = 0, \Delta H_f^{\emptyset}(CO_2) = \Delta H_c^{\emptyset}(\text{carbon}) = -393 \text{ kJ/mol}$

$\Delta H_f^{\emptyset}(H_2O) = H_c^{\emptyset}(\text{Hydrogen}) = -285.6 \text{ kJ/mol}$

$\Delta H_r = \Delta H_c^{\emptyset}(C_2H_6) = -1560\text{kJ/mol}$

Then; $-1560 = (2 \times -393) + (3 \times -285.6) - -\Delta H_f^{\emptyset}(C_2H_6)$ **(0.5)**

From which $\Delta H_f^{\emptyset}(C_2H_6) = -82.8\text{kJ/mol}$ **(0.5)**

Remark: The examinee must include the superscript of standard, $\emptyset$ in each symbol of heat of reactions as **standard** values were given and the question asked to calculate **standard** heat of formation. (**Deduct 0.5mark** only **once** if the superscript was not used).

(ii) Using; $\Delta H_r = \sum \text{B.E(Reactants)} - \sum \text{B.E(Products)}$**(0.5)**

Then from the equation of combustion in (i);

$\Delta H_r = \Delta H_c(C_2H_6)$

$= (C - C) + 6(C - H) + \frac{7}{2}(O = O) - 4(C = O) - 6(O - H)$ **(0.5)**

$= 347 + (6 \times 412) + \left(\frac{7}{2} \times 498\right) - (4 \times 805) - (6 \times 464)$

From which $\Delta H_c(C_2H_6) = -1442 \text{ kJ/mol}$ **(0.5)**

The bigger source of error is that, the calculations in (ii) does not take into account the enthalpy of vapourisation of water. Extra energy would be released from condensation of water giving a more exothermic value which is closer to -1560 kJ/mol **(1.5)**

Remark: In the final part the question the examinee is required to give a reason and explain the reason for deviation as the question asked to explain (**explain** the why). (**Deduct 0.75 mark** if reason was given without further explanation).

Question 7

(a)

(i) Is the condition which occurs in reversible reaction when the rate of forward reaction is equal to the rate of reverse reaction. **(0.5)**

For example; the equilibrium formed in the reaction between nitrogen gas and hydrogen gas to form ammonia gas.
$2N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ **(0.5)**

(ii) Is the system whose physical state does not change whereby the same substance exists in two different physical states simultaneously. **(0.5)**

For example, the equilibrium between liquid and gaseous state in evaporation of water;
$H_2O(l) \rightleftharpoons H_2O(g)$ **(0.5)**

(b) By adding hydrogen gas **(0.5)**

Explanation:
Decreasing volume of the container has no effect on the position of chemical equilibrium. This is because the decrease in volume will increase the total pressure of the system and since the reaction is not accompanied with change in number of gas molecules, the change in pressure has no effect on the position of equilibrium and thus no effect on the yield of HI too. However according to Le-Chatelier's principle, the increase in concentration of hydrogen gas shift the position of equilibrium to HI side and therefore increasing the yield of HI. **(2.5)**

(c)

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
At equilibrium	0.28atm		1.1atm

$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(1.1\text{atm})^2}{(0.28\text{atm})} = 4.32\text{atm}$ **(1)**

If the volume is doubled from V_1 to V_2 such that $V_2 = 2V_1$

By Boyle's law; $P_1V_1 = P_2V_2$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{P_1V_1}{2V_1} = \frac{P_1}{2}$$

For N_2O_4; $P_2 = \frac{0.28\text{atm}}{2} = 0.14\text{atm}$ **(0.5)**

For NO_2; $P_2 = \frac{1.1\text{atm}}{2} = 0.55\text{atm}$ **(0.5)**

The decrease in pressure will shift equilibrium position to the NO_2 side.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$	
At new equilibrium	$0.14 - x$		$0.55 + 2x$	**(1)**

Then;

$4.32 = \frac{(0.55+2x)^2}{0.14-x}$ **(0.5)**

From which;

$4x^2 + 6.52x - 0.3023 = 0;\ x = 0.045$

Hence at new equilibrium:

Partial pressure of N_2O_4

$= 0.14 - 0.045 = (0.14 - 0.045)\text{atm} = 0.095\text{atm}$ **(0.75)**

Partial pressure of NO_2

$= 0.55 + 2x = (0.55 + 2 \times 0.045)\text{atm} = 0.64\text{atm}$ **(0.75)**

Question 8

(a)(i) Is the effect which occurs when the large sized groups within a molecule prevents chemical reactions that are observed in related molecules with smaller groups. **(0.5)**

(ii) Peroxide effect is the change in regioselectivity of the addition of HBr to unsymmetrical alkene in presence of organic peroxide leading to Anti-Markonikoff's addition reaction. **(0.5)**

(iii) Is the type of isomerization reaction in which a compound exist in two readily interconvertible different structures with different functional groups leading to dynamic equilibrium. **(0.5)**

(iv) Are organic compounds with the same molecular formula and function group but differ in their parent chain.**(0.5)**

(b)

(i) $CH_3CH_2CH_3 + 2Cl_2 \xrightarrow{UV} CH_3CH_2CH_2Cl + CH_3CHClCH_3 + 2HCl$ **(1)**

(ii) $CH_2 = CH_2 + H_2SO_4(\text{dilute}) \longrightarrow CH_3CH_2OH$(**1**)

(iii) $CH \equiv CH + Cl_2|H_2O \longrightarrow CHCl_2 - CHO + HCl$(**1**)

(c)

(i) Is the chemical reaction between haloalkane and sodium under presence of heated dry ether to give alkane. **(0.5)**

(ii) With water in ether solution, sodium would react explosively to give NaOH which would react with haloalkane to give alcohol and alkene thus yielding mixture of organic products and hence the yield of alkane would be decreased. **(1.25)**

$2CH_3CH_2Br + 2Na \xrightarrow[\Delta]{\text{Dry ether}} CH_3CH_2CH_2CH_3 + 2NaBr$ **(0.5)**

$CH_3CH_2CH_2Br + 2Na \xrightarrow[\Delta]{\text{Dry ether}} CH_3CH_2CH_2CH_3CH_3CH_3 + 2NaBr$ **(0.5)**

(iii) The method was not correct because it gives mixture of products (butane and hexane apart from pentane) whose separation is difficult and thus decreasing the yield of pentane. **(1)**

(iv) **No: (0.25)**

Methane has only one carbon while Wurtz reaction doubles (increases) number of carbon atoms in the organic molecule. So the lowest member of alkane which can be prepared by the method is ethane which has two carbons. **(1)**

(d) Four possible isomers of $C_3H_6Cl_2$ are:

1. 
$CH_3 - \underset{\displaystyle Cl}{\underset{|}{C}}H - CH_2Cl$ **(0.25)**
2. $ClCH_2CH_2CH_2Cl$ **(0.25)**
3. $CH_3CH_2CHCl_2$ **(0.25)**
4. $CH_3CCl_2CH_3$ **(0.25)**

Further chlorination of (1) gives the following isomeric products:

(a) $CH_3CHClCHCl_2$ **(0.25)**

(b) $CH_3CCl_2CH_2Cl$ **(0.25)**

(c) $ClCH_2CHClCH_2Cl$ **(0.25)**

Thus (1) gives three compounds and therefore it can be A and B.
Further chlorination of (2) gives the following products:

(a) $ClCH_2CH_2CHCl_2$ **(0.25)**
(b) $ClCH_2CHClCH_2Cl$ (**025**)

Thus (2) gives two compounds and therefore it must be D
Further chlorination of (3) gives the following

(a) $CH_3CH_2CCl_3$ (**0.25**)
(b) $CH_3CHClCHCl_2$ (**0.25**)
(c) $ClCH_2CH_2CHCl_2$ (**0.25**)

Thus (3) gives three compounds and therefore it can be A or B
Further chlorination of (4) gives the following product:
$CH_3CCl_2CH_2Cl$ (**0.25**)
Thus (4) gives one product only and hence it must be C **(0.25)**

(i)
Structure of C is $CH_3CCl_2CH_3$ **(0.25)**
Structure of D is $ClCH_2CH_2Cl$ **(0.25)**

(ii)
Since trichloropropane from C ($CH_3CCl_2CH_2Cl$) is identical to that of (b) from (1) the structure of A is (1) and whence (3) is structure of B.**(0.25)**
That is:
Structure of A is $CH_3CHClCH_2Cl$ **(0.25)**
The structure of B is $CH_3CH_2CHCl_2$ **(0.25)**

Question 9

(a)(i) In benzene $\pi -$ bonds are uniformly delocalized through mesomerism. Thus every carbon-carbon bond has sigma bond and partially pi bond making each bond to behave as partially carbon-carbon double bond with intermediate characters between those of single and double bond (**1.5**)

(ii) Griginard reagent is so reactive that would react with water in ether solution to give alkane rather than yielding the reagent as final product or being efficiently utilized in the intended reaction. (**1.5**)

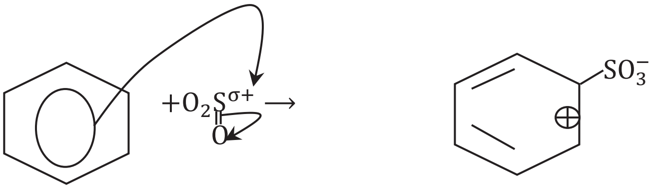
$$\underset{\text{Griginard reagent}}{RMgX} + H_2O \rightarrow \underset{\text{Alkane}}{RH} + Mg(OH)X \quad (\mathbf{0.5})$$

(iii) Atomic radii of given halogens in alky halides decrease in the following order: $I > Br > Cl > F$. Larger atomic size leads to larger $C - X$ bond length which in turn makes the bond weaker, easier to break and hence the ability to be substituted by OH in nucleophilic substitution reaction will be in the same order. **(1.5)**

(iv) Firstly the intermediate tertiary (3°) carbenium ion, $(CH_3)_3C^+$ formed by $(CH_3)_3CBr$ is more stable than the primary (1°) carbenium ion, $CH_3CH_2^+$ formed by CH_3CH_2Br. (**1**)

Secondly the three alkyl groups surrounding carbon with Br in $(CH_3)_3CBr$ exert stronger steric hindrance than one alkyl group in CH_3CH_2Br**(1)**
The two factors make $(CH_3)_3CBr$ to undergo S_N1 mechanism while CH_3CH_2Br undergoes S_N1.

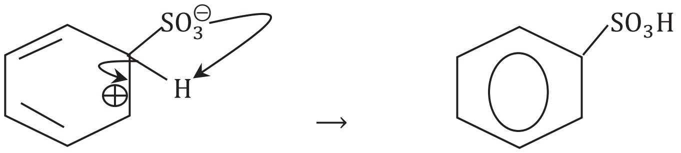
(a) Step 1: Formation of intermediate carbenium ion



Carbenium ion

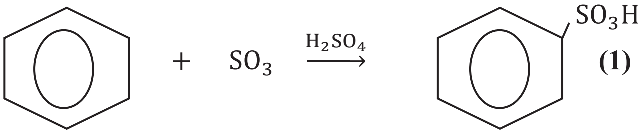
(1.5)

Step 2: Formation of product



(1.5)

Hence the overall reaction equation is;



(1)

(c) Alkyl groups in both of given compounds being activator are ortho-para directors that is why in both cases meta products have lowest percentage. (**1.5**)

However CH_3- group being smaller in size, exerts weaker steric hindrance making methylbenzene to form greater percentage of ortho product than para product (as there are two ortho carbon in every one para carbon in the monosubstituted benzene) in contrast to $(CH_3)_3C-$ group which exerts stronger steric hindrance making 1,1,1-trimethyltoluene to form greater percentage of para product than ortho product. (**2.5**)

Question 10

(a)

(i) **Method:** Chemical oxidation and reduction (Redox) method **(1)**

Equation: $2NaCN + 5Cl_2 + 8NaOH \rightarrow 10NaCl + 4H_2O + 2CO_2 + N_2$ **(1)**

(ii) **Method:** Chemical precipitation method **(1)**

Equation: $Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$ **(1)**

(iii) **Method:** Chemical precipitation method **(1)**

Equation: $Pb^{3+}(aq) + 2OH^-(aq) \rightarrow Pb(OH)_2(s)$ **(1)**

(iv) **Method:** Acid – base neutralization method (1)

Equation: $2HNO_3 + Ca(OH)_2 \longrightarrow Ca(NO_3)_2 + 2H_2O$ **(1)**

(v) **Method:** Hydrolysis method **(1)**

Equation: $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$ **(1)**

(b)

(i) Is the basic soil with high salt concentration.

(ii) Is the maximum quantity of total cations, of any class, that a soil is capable of holding at a given pH value, available for exchange with soil solution.

(c) Let the needed mass of sulphate of ammonia fertilizer be x and the needed mass of single superphosphate fertilizer be y

The mass of N $= \frac{21x}{100} = 120\text{kg}$ $(\mathbf{0.5})$

From which $x = 571\text{kg}$ $(\mathbf{0.5})$

And mass of P $= \frac{18y}{100} = 60\text{kg}$ $(\mathbf{0.5})$

From which $y = 333\text{kg}$ $(\mathbf{0.5})$

Hence:

The mass of sulphate of ammonia fertilizer is 571kg **(1)**

The mass of superphosphate fertilizer is 333kg **(1)**

Solutions Examination Six
CHEMISTRY 2C

Question 1

(a)

(i) Partial vapour pressure of a particular constituent (component) in a solution which contains two or more volatile miscible liquids is the product of its mole fraction and its vapour pressure of the pure liquid at given temperature. **(1)**

(ii) Negative deviation **(1)**

(iii) Ion-ion interactions **(1)**

(iv) Real vapour pressure of non-ideal solution with negative deviation is smaller than that predicted by Raoult's law. **(2)**

(b)

(i) Vapour tension is the pressure exerted by volatile component of a substance formed over its surface at given temperature. **(0.5)**

Remark: The omission of phrase; 'at given temperature' is **not** allowed. **(**Vapour tension (pressure) is the temperature dependent and therefore at their values are always given at specified temperature).

(ii) Saturated vapour pressure is the vapour pressure of the liquid in equilibrium with excess liquid at given temperature. **(0.5)**

Remark: Like in (i), again the omission of the phrase; 'at given temperature' is not allowed.

(iii) Azeotrope is the **constant boiling point mixture** whose **vapour** and **liquid composition** remain **unchanged** on distillation. **(0.5)**

Remark: The shorter definition: *Is the mixture which boils at constant temperature or is the mixture whose vapour and liquid composition remain unchanged on distillation* is allowed. (If the mixture boils at constant temperature automatically implies that the liquid and vapour composition remain unchanged on distillation and vice versa).

(c) Increase in temperature **increases concentration** and **speed** of vapour particles leading to **more frequent collisions** between vapour particles and walls of the container and hence greater vapour pressure. **(1.5)**

Remark: To get full score, the examinee must do the following:

(i) Mention both 'concentration' and 'speed' factors. (**Deduct 0.5 mark** for missing of either factor).

(ii) Correlate clearly the 'speed' and 'concentration' factors and vapour pressure of liquid (How increase in concentration and speed, increases vapour pressure).

(d)

(i) Is the temperature at which vapour pressure of the liquid is equal to the atmospheric (external) pressure. **(0.5)**

(ii) Increasing external pressure, increases the boiling point. **(0.5)**

(iii) Using $n = \frac{m}{M_r}$;

$n_{acetone} = \frac{116g}{58\ g/mol} = 2\ mol$ **(0.5)**

$n_{water} = \frac{72g}{18\ g/mol} = 4\ mol$ **(0.5)**

Then $X_{acetone} = \frac{n_{acetone}}{n_{acetone}+n_{water}} = \frac{2}{2+4} = \frac{1}{3}$ **(0.5)**

And $X_{water} = 1 - X_{acetone} = 1 - \frac{1}{3} = \frac{2}{3}$ **(0.5)**

From Raoult's law and Dalton's law of vapour pressure;

$P_{soln} = X_{acetone}P^0_{acetone} + X_{water}P^0_{water}$ **(0.5)**

Substituting $P_{soln} = \frac{1}{3}P^0_{acetone} + \frac{2}{3}P^0_{water}$

But the liquid boils when;

Vapour pressure = Atmospheric pressure = 1atm **(0.5)**

The finding by trial and error, the temperature at which $P_{soln} = 1$ atm

At 60°C : $P_{soln} = \left(\frac{1}{3} \times 1.14\right) + \left(\frac{2}{3} \times 0.198\right) = 0.512\text{ atm } < 1\text{ atm}$

At 70°C : $P_{soln} = \left(\frac{1}{3} \times 1.58\right) + \left(\frac{2}{3} \times 0.312\right) = 0.735\text{ atm } < 1\text{ atm}$

At 80°C : $P_{soln} = \left(\frac{1}{3} \times 2.12\right) + \left(\frac{2}{3} \times 0.456\right) = 1.01\text{ atm } \approx 1\text{ atm}$ **(0.5)**

Hence the boiling point of the solution is 80°C **(0.5)**

(e)

(i) Solvent extraction is the method of removing (extracting) a solute from a certain solvent by introducing the second solvent**(extractive solvent)** which is immiscible to the first one and then allowing the solute to distribute itself in the two solvents. The layer of extractive solvent is then removed with significant amount of the solute and on successive extractions which are done by introducing fresh extractive solvent again and again, the solute is finally completely removed from the first solvent (or very small amount remain in the first solvent). **(2)**

(ii) **Similarity:** They both separate components of the mixture based on the boiling point.**(1)**

Difference: Steam distillation separates thermally unstable component of the mixture which is immiscible to water while fractional distillation separates thermally stable components of miscible liquid mixture. **(1)**

Steam distillation is therefore takes place at temperature below the boiling point of components while fractional distillation takes place at boiling point of components. **(1)**

(ii) Using $\frac{M_N}{M_W} = \frac{P_N M_N}{P_W M_W}$ $(\mathbf{0.5})$

Where N and W stand for nitrobenzene and water respectively

By Dalton's law of partial pressure;

$P_N + P_W = \text{atmospheric pressure} = 1.013 \times 10^5 P_a$ $(\mathbf{0.5})$

Then $P_N = 1.013 \times 10^5 \text{Pa} - P_W = (1.013 \times 10^5 - 9.749 \times 10^4)P_a$
$= 3810\text{Pa}$ $(\mathbf{1})$

Also $M_W = 18\text{gmol}^{-1}$and $M_N = 127\text{gmol}^{-1}$

$$\text{Then } \frac{M_N}{M_w} = \frac{3810\text{Pa} \times 127\text{gmol}^{-1}}{9.749 \times 10^4\text{Pa} \times 18\text{gmol}^{-1}} = 0.2757 \ (\mathbf{1})$$

$$\%\left(\frac{m}{m}\right)\text{Nitrobenzene} = \left(\frac{0.2757}{1 + 0.2757}\right) \times 100\% = 21.6\%$$

The percentage of nitrobenzene is 21.6% **(1)**

Question 2

(a)

(i) Is the reaction of particular step in the reaction mechanism. **(0.5)**

Remark: Any definition which shows that the examinee is understanding elementary reaction as component of reaction mechanism is allowed.

(ii) Is the product of a particular step of reaction mechanism **(0.5)**

Remark: The definition: *Is 'the product of elementary reaction"* is acceptable.

(iii) Is the total number of reactant molecules which take part in a particular elementary reaction **(0.5)**

Remark: The examinee is not allowed to keep *'chemical reaction'* in place of *'particular elementary reaction.'*

(iv) Is the catalyst of a certain reaction which is automatically produced as the product of the same reaction. **(0.5)**

Remark: Any definition which shows that a student is understanding autocatalyst as the reagent which increases the rate of a particular reaction and it's the product of the same reaction is allowed.

(b)

(i) True **(0.5)**

Increase in temperature tends to increase both collision frequency and collision energy between reacting particles. It is therefore increases the value of rate constant and whence number of reacting particles which attain activation energy increases making the reaction rate higher. **(1.5)**

(ii) False (**0.5**)

Most of reactions are positively catalysed thus leading to increase in the rate of reaction by giving alternative route of reaction which has lower activation energy (**1**)

(iii) False (**0.5**)

The rate of zero order chemical reaction is independent to concentration. (**0.5**)

(c) E_a is the activation energy which express minimum energy required for the reaction to proceed at any absolute temperature, T **(0.5)**

A is the Arrhenius constant which express the total number of **proper oriented** collisions that occur in a reaction

$e^{-\frac{E_a}{RT}}$ is the Boltzmann's constant which gives a fraction of number of **proper oriented** collisions which have attained activation energy. **(0.5)**

$k\left(\text{or } Ae^{-\frac{E_a}{RT}}\right)$ is the rate constant which gives number of collisions which attain activation energy per second. (**0.75**)

Remarks:

(i) The terms with significant meaning in the equation are only: E_a, A, $e^{-\frac{E_a}{RT}}$ and $Ae^{-\frac{E_a}{RT}}$.

(ii) Meanings of T,R and e should be ignored (T is just variable in the equation with no specific meaning in the Arrhenius equation. It is not a '**term**' in the equation while R and e are simple constants with no specific meaning in the equation. Also they are not '**terms**' in the equation).

(iii) "Effective collisions per second" for the meaning of $Ae^{-\frac{E_a}{RT}}(k)$ is acceptable.

(d)

(i)

1. Disappearance of purple colouration of $KMnO_4$(by noting the rate of the change of the colour intensity). **(1)**
2. Formation of carbon dioxide gas (by measuring the rate of increases of volume of the gas) **(1)**

   Remark: The examinee must give properties which are measurable with respect to time.

(ii)

1. Formation of white precipitate of AgCl (By noting the rate of intensity of the colour formation). **(1)**
2. Disappearance of green colouration of $CuCl_2$ (by noting the rate of the change of the colour intensity). **(1)**

   Remark: The examinee must give properties which are measurable with respect to time.

(e)

(i) Reaction mechanism:

$OH + O_2 \rightarrow OOH + O$ ………… (i) **(1)**

$O + NO \rightarrow NO_2$ ……………….. (ii) **(1)**

$OOH + CO \rightarrow CO_2 + OH$ …….. (iii) **(1)**

Adding (i), (ii) and (iii) and then cancelling like terms which appears in both reactants and products side

$\cancel{OH} + O_2 + \cancel{O} + NO + \cancel{OOH} + CO \rightarrow \cancel{OOH} + \cancel{O} + NO_2 + CO_2 + \cancel{OH}$ **(1)**

From which the overall reaction is

$$NO + CO + O_2 \rightarrow NO_2 + CO_2$$

Remark: To get full score:

1. The suggested mechanism must include OH (the catalyst)

   Don't accept the mechanism without OH even if summation of its steps gives the correct overall reaction equation. **Award zero score** if the mechanism did not satisfy this condition.

2. The catalyst, OH, must appear in the first step of the mechanism

   Don't accept the mechanism without OH in the first step even if summation of its steps gives the correct overall reaction equation. **Award zero score** if the mechanism did not satisfy this condition.

3. The OH (catalyst) must be regenerated (formed as product) in the final step

   Don't accept the mechanism which did not show the regeneration of catalyst in the final step. **Award zero score** if the mechanism did not satisfy this condition.

(ii) Intermediates are OOH and O **(1)**

Remark: There are **only two** intermediates as mentioned. (**Award zero score** if neither OOH nor O is mentioned and 0.5 mark for each correct intermediate mentioned).

(iii) OH is catalyst because initially participated in converting oxygen molecule into more reactive oxygen atom (in equation (i)) and finally it was regenerated (in equation (iii)) **(2)**

Remark: The answer must associate reference (must be specific) to the suggested mechanism. (**Don't allow** general explanation like, "OH is catalyst because it took part in the chemical reaction but at the end of reaction remains unchanged").

Question 3

(a)

(i) Base is any specie that can donate a pair of non-bonding electrons. (**0.5**)

Remark: The examinee must provide the meaning in terms 'electron interchange' and not otherwise.

(ii) Presence of one lone pair in nitrogen of ammonia. (**0.5**)

Remark: 'non-bonded electron pair' instead of 'lone pair' is acceptable.

(iii) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$[OH^-]$ at equilibrium $= \alpha c$

But from Ostwald dilution law; $\alpha = \sqrt{\frac{K_b}{c}}$

Then $[OH^-] = C\sqrt{\frac{K_b}{C}} = \sqrt{CK_b}$ (**0.5**)

And $pOH = -\log[OH^-]$ (**0.5**)

$= -\log\sqrt{cK_b}$

Substituting; $pOH = -\log\sqrt{0.1 \times 1.8 \times 10^{-5}} = 2.87$

Then $pH = 14 - pOH$ (**0.5**)

$= 14 - 2.87 = 11.13$

Hence the pH of $0.1M$ $NH_3(aq)$ is 11.13 (**0.5**)

Remark: The application of Ostwald's dilution law $\left(\alpha = \sqrt{\frac{K_a}{c}}\right)$ in solving this question is not acceptable. (The equation, $\alpha = \sqrt{\frac{K_a}{c}}$ (Ostwald's dilution law) holds only when K_a is very small; that is when $K_a < 10^{-3}$. So it is wrong to apply when $K_a > 10^{-3}$ like in this question where $K_a = 0.01$ (10^{-2}).

(b)

(i) Being strong acid, HCl (aq) ionises completely to give H^+ such that: $[HCl] = [H^+]$

Thus $[H^+] = 0.01M$ (**0.5**)

And $pH = -\log[H^+] = -\log 0.01 = 2$ (**0.5**)

(ii) Since K_a is very large, H_2SO_4 ionises completely to give $H^+(aq)$ and from stoichiometry of equation of Stage I: $[H_2SO_4] = [H_3O^+] = 0.1M$

Thus the hydrogen ion concentration is 0.1M (**0.5**)

(iii)

	$HSO_4^-(aq)$	$+ H_2O \rightleftharpoons$	$H_3O^+(aq)$	$+ SO_4^{2-}(aq)$	
[ ] Of each Equilibrium	$0.1 - x$		x	x	(**0.5**)

Then $K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} 0.01$ (**0.5**)

Substituting $\frac{x^2}{(0.1-x)} = 0.01$

From which $x^2 + 0.01x - 0.001 = 0$ (**0.5**)
Solving above equation gives practical value of; $x = 0.0316$
Hence for 0.1M $NaHSO_4$, $[H^+] = 0.0316M$ (**0.5**)
Total $[H^+] = [H^+]$ of first stage + $[H^+]$ of second stage
$= 0.1M + 0.0316M = 0.1316M$ (**0.5**)

(ii) $[H^+]$ of $0.105M < 0.1316M$ because reaction II suppress reaction I by common ion effect. (**1**)

Remark: Any explanation which shows the understanding of decrease in ionisation of reaction I (the shift of position of equilibrium to the left) due to presence of H_3O^+ in the reaction II is allowed.

(c) Molar mass of $CH_3CH_2CHClCOOH = 122.5g/mol$

Number of moles of $CH_3CH_2CHClCOOH = \frac{10g}{122.5g/mol} = 0.08163$ mol (**0.5**)
Neglecting volume of $CH_3CH_2CHClCOOH$ such that:
Volume of water = Volume of solution
But volume of water $= \frac{\text{Mass of water}}{\text{Density of water}} = \frac{250g}{1g/cm^{-3}} = 250\ cm^3$ (**0.5**)
Then $[CH_3CH_2CHClCOOH] = \frac{0.08163\ mol}{0.25\ dm^3} = 0.32652M$ (**0.5**)
By Ostwald's dilution law:

$$\alpha = \sqrt{\frac{K_a}{c}}$$

Degree of dissociation of $CH_3CH_2CHClCOOH = \sqrt{\frac{1.4\times10^{-3}}{0.32652}} = 0.06548$
Using $\alpha = \frac{i-1}{N-1}$ (**0.5**)
As the acid ionises according to the following equation:
$CH_3CH_2CHClCOOH \rightleftharpoons CH_3CH_2CHClCOO^- + H^+; N = 2$ (**0.5**)
Substituting $N = 2$ to $\alpha = \frac{i-1}{N-1}$ gives
$i = \alpha + 1 = 0.06548 + 1 = 1.06548$ (**0.5**)
Then using;
$\Delta T = iK_fm = \frac{1.06548\times1.86\times0.08163}{0.25}$ °C (**0.5**)
$= 0.65°C$
Hence the freezing point depression is 0.65°C (**0.5**)
Remark: The answer in kelvin, that is 0.65K (ΔT in °C = ΔT in K) is acceptable (**Award zero score** for the answer if 0.65 was added to 273 to get 273.65K).

(d) Number of moles of NaOH added $= \frac{36.12}{1000} \times 0.1$ mol $= 3.612 \times 10^{-3}$ mol (**0.5**)

The monobasic acid, say HA, reacts with NaOH according to the following equation:
$HA + NaOH \rightarrow NaA + H_2O$ (**0.5**)
Thus number of moles of NaA formed was also 3.612×10^{-3} mol (**0.5**)
Number of moles of HCl added $= \frac{18.06}{1000} \times 0.1$ or 1.806×10^{-3}mol (**0.5**)
HCl reacts with NaA according to the following equation:
$NaA + HCl \rightarrow NaCl + HA$ (**0.5**)
From which mole ratio of NaA to HCl is 1:1.
So NaA present in excess and

$(3.612 - 1.806) \times 10^{-3}$ or 1.806×10^{-3}mol of it remain unreacted. (**0.5**)

Also as mole ratio of the limited reactant, HCl, to HA is 1:1, number of moles of HA formed was also 1.806×10^{-3}mol (**0.5**)

Hence at the end of the reaction between NaA and HCl there was 1.806×10^{-3}mol of each HA and NaA (**1**)

The two (HA and NaA) will make acidic buffer solution because HA is weak acid and NaA is strong salt containing conjugate base (A^-) of the acid (**1**)

Then for this acidic buffer solution;

$\mathrm{pH} = \mathrm{pK_a} + \log\frac{\text{Number of moles of NaA}}{\text{Number of moles of HA}}$ (**0.5**)

Substituting $4.92 = \mathrm{pK_a} + \log\frac{1.806\times10^{-3}}{1.806\times10^{-3}}$ (**1**)

$4.92 = \mathrm{pK_a} = -\log \mathrm{K_a}$

Thus $\mathrm{K_a} = \log^{-1} -4.92$ (**0.5**)$= 1.2 \times 10^{-5}$

Hence the dissociation constant for unknown acid is 1.2×10^{-5} (**0.5**)

Question 4

(a)

(i) Representative elements are elements which found in s and p-block of modern periodic table. (**0.5**)

Remark: The definition: *Are elements which are found in the major groups;* is acceptable.

(ii) IA, IIA, IIIA, IVA, VA, VIA, VIIA, and VIIIA (**2**)

Remark: Group numbers in roman numerals without letters (e.g. I instead of IA) is not acceptable.

(b)

(i) Phosphorous (**0.5**)

Reason:

With electronic configuration of $[\mathrm{Ne}]3s^2 3P_x^1 P_y^1 P_z^1$, phosphorous has more stable electronic configuration of completely half-filled electronic structure. (**1**)

Remark: The examinee must give the reason based on stability of electronic configuration with the electronic configuration of P included. The electronic configuration must show completely half-filled electronic structure in P (as given in ideal answer or by using boxes and arrows). **Deduct 0.25 mark** if the electronic configuration $[\mathrm{Ne}]3s^2 3p^3$ was given and **0.5 mark** if no electronic configuration was given.

(ii) Chlorine (**0.5**)

Reason:

The size of fluorine is so small that there is large repulsion between inner and outer electrons making difficult to add an electron to it unlike to chlorine whose atomic size is somehow large. (**1.5**)

Remark: The reason must base on repulsion as affected by atomic size.

(c) Lithium is found on the top of group IA elements. Being on the top of the group, lithium has smallest atomic and ionic radius, highest electronegativity and highest ionisation energy. These facts, make properties of lithium to show large deviation from its fellow members in the group. (**2.5**)

For example:

(i) Lithium reacts with oxygen to give normal oxide only while other group IA elements may also give peroxides and superoxides in addition to normal oxides.

(ii) Lithium can combine with nitrogen to give lithium nitride while other group IA elements cannot. **(1)**

(iii) Compounds of lithium are less thermally stable compared to compounds of other group IA elements. **(1)**

(iv) Lithium chloride forms hydrated crystals ($LiCl \bullet 2H_2O$) in aqueous solution while other group IA elements forms anhydrous chloride (**1**)

Distribute:

(i) 2.5 mark for clear and relevant introduction. The introduction must include main (general) differences between lithium and other group members and not specific anomalous chemical properties of lithium.

(ii) **3 (1+1+1) marks** for giving at least **any** three examples of anomalous properties of lithium. **Award 1 mark** for each correct example given.

(d)

(i) In typical elements, atomic radius decreases as you go across the period because in that direction the increase in nuclear attractive force outweighs the increase in screening effect as the electrons are added to the outermost shell unlike in transition elements where electrons are added to penultimate shell making the atomic radius to remain almost constant as the increase in screening effect is enough to counter-balance with the increase in nuclear attractive force. **(1.5)**

Remark: The examinee must explain trend of atomic radii in both transition elements and typical elements. **Deduct 0.5 mark** if the explanation are based only in one side.

(ii) With greater number of protons, potassium ion has stronger nuclear attractive force per electron and hence smaller size for it. **(0.5)**

(e)

(i) **Chemical nature of electrodes**

The anode is impure copper and the cathode is pure copper. (**1**)

(ii) **Chemical nature of electrolyte**

The electrolyte used is a solution of copper (II) sulphate solution acidified with dilute sulphuric acid. (**1**)

(iii) **Redox reactions involved**

At the cathode: Copper (II) ions get discharged (reduced) to deposit copper metal. (**1**)
$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ (**0.5**)
At the anode: Copper get oxidised and goes (dissolves) into solution as Cu^{2+} ions. (**1**)
$Cu(s) \rightarrow Cu^{2+} + 2e$ (**0.5**)
Thus there is a transfer of copper from anode to the cathode and whence cathode gets bigger as more copper is deposited meanwhile the anode gradually disappears leaving impurity. (**2**)

Question 5

(a)

(i) Depolymerisation is the process whereby a polymer is broken into its monomer components. (**0.5**)

(ii) Biopolymers are polymers which consist of biomolecules. (**0.5**)

(iii) Oligomer is a polymer whose molecules consist of relatively few repeating units. (**0.5**)

(iv) Polyester is the condensation polymer whose monomers are linked together by ester group. (**0.5**)

(b)

(i) Polyvinyl chloride (PVC) (**0.5**)

(ii) Dacron (**0.5**)

(iii) Dacron (**0.5**)

(iv) Nylon-6,6

(c) **Meaning of vulcanization of rubber**

of rubber is the chemical process which involves treating rubber with Sulphur and heat. These Sulphur atoms link polymer chain together through covalent bonding. So vulcanization of rubber involves introduction of Sulphur cross-links between chains of rubber polymer. (**2**)

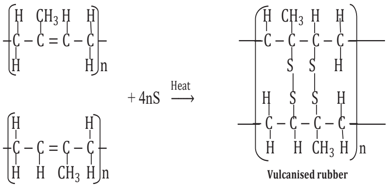
Importance of vulcanization of rubber

Introduction Sulphur cross-links through rubber vulcanization prevents rubber chains from moving independently relative to each other. This makes vulcanized rubber to have very strong physical properties and therefore more suitable for practical use than raw-rubber (unvulcanised rubber) . (**2**)

So as result of introducing these Sulphur cross-links, Vulcanization of rubber improve its elasticity, toughness, strength, durability and enables it to be used over wide range of temperature (**1.5**)

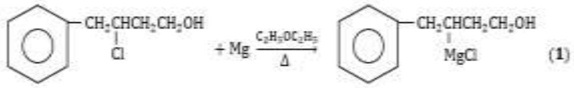
Process of vulcanization of rubber

Vulcanization of rubber is done by mixing sulphur with the raw rubber and then the mixture is heated carefully resulting to formation of bridges. **(1.5)**

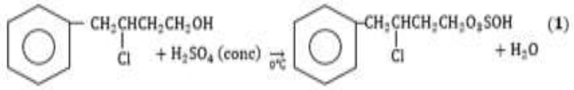


(2)

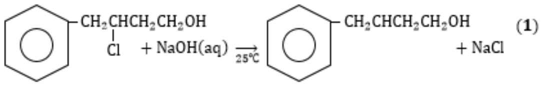
(d) (i)



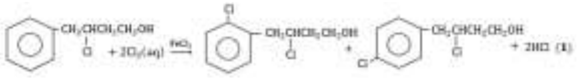
(ii)



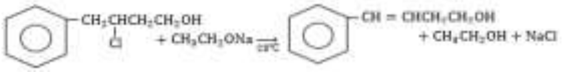
(iii)



(iv)

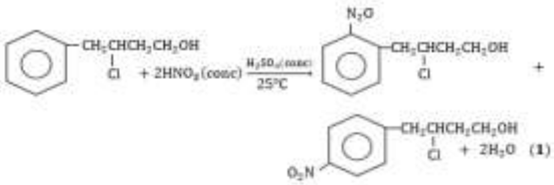


(v)



(vi)

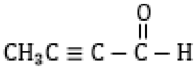
(vii)



Question 6

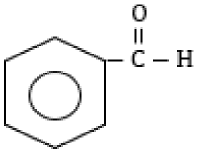
(a)

(i) Structural formula of A is:



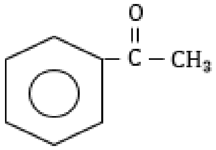
$CH_3C \equiv C-\overset{\overset{\large O}{||}}{C}-H$ **(1)**

(ii) Structural formula of B is:



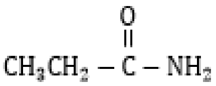
(1)

(iii) Structural formula of C is:



(1)

(iv) Structural formula of D is:



$CH_3CH_2-\overset{\overset{\large O}{||}}{C}-NH_2$ **(1)**

(b)

(i) The acidic strength of benzoic acid is increased by negative inductive effect exerted by sp^2 hybridised carbon in benzene ring which are more electronegative than sp^3 hybridised carbon in ethanoic acid.**(1.5)**

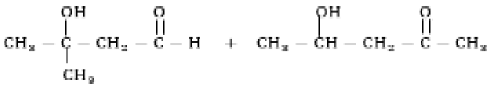
(ii) α – hydrogen in carbonyl compound is acidic and thus reacts with alkaline solution to give carbanion (nucleophile) which will react with another molecule of carbonyl compound to give condensational product via nucleophilic addition reaction**.**

(iii) Unlike trimethylamine, in dimethylamine there is positively polarised hydrogen bonded to nitrogen making possible for the dimethylamine to exhibit intermolecular hydrogen bonding which is stronger intermolecular forces than Van-der-Waals dispersion forces present in trimethylamine and hence higher boiling point for dimethylamine **(1.5)**

(iv) Lone pair in aniline is stabilized by its involvement in mesomerism and therefore making difficult for it to be donated to Lewis acid hence the aniline becomes weaker base leading to the larger pK_b value. **(1.5)**

(c)

(i)



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-H \; + \; CH_3-\overset{\displaystyle OH}{CH}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

(2)

(ii) No reaction **(1)**

(iii) Benzoic acid **(1)**

(d)

(i) Carbylamine test: With chloroform under presence of potassium hydroxide solution, aniline gives offensive smell while phenol does not. (**1.5**)

(ii) Ferric chloride test: With iron (III) chloride, phenol gives violet-purple compound while benzoic acid gives buff-coloured compound. (**1.5**)

(iii) Potassium permanganate test: Ethanedioic acid decolourises purple colouration of acidified potassium permanganate heated to temperature of about 70°C while succinic acid does not. (**1.5**)

(iv) Carbylamine test: With chloroform under presence of potassium hydroxide solution, ethanamine gives offensive smell while N-methylmethanamine does not. (**1.5**)

Solutions Examination Seven
CHEMISTRY 1D

Question 1

(a)

(i) Atom is the smallest individual particle of an element that can be take part in the chemical reaction. **(0.5)**

(ii) Element is the substance which cannot, by any known chemical process, be split up into two or more simpler substances. **(0.5)**

(b) An element is made of one type of atoms. Thus atom is the smallest amount of an element. **(1.5)**

(c) With given isotopes, there are following possibilities of forming triatomic molecule:

(i) Three atoms of ^{m}X **(0.75)**
(ii) Three atoms of ^{n}X **(0.75)**
(iii) One atom of ^{m}X and two atoms of ^{n}X **(0.75)**
(iv) One atom of ^{n}X and two atoms of ^{m}X **(0.75)**

Hence four peaks will be shown in the mass spectrum. **(0.5)**

(d)

(i) Atomic spectrum consists of separate frequency lines with very little or no grouping at all while continuous spectrum consists of all possible lines of all frequencies over a wide range of frequencies with no clear cut between the lies.**(0.75)**

(ii) Minimum energy to cause excitation of electron in the hydrogen atom is obtained when the electron transist from n = 1 to n = 2. **(0.5)**

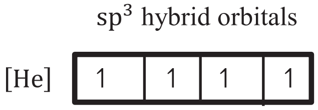
This energy has maximum wavelength possible for causing the excitation. **(0.5)**
Then from Rydberg equation:
$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ **(0.5)**
Substituting $\frac{1}{\lambda} = 1.1 \times 10^7\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$ **(0.5)**
From which $\lambda = 1.21 \times 10^{-7}$m
Thus the maximum possible wavelength to cause the excitation of the electron in the hydrogen atom is 1.21×10^{-7}m **(0.5)**
But the given wavelength of 1.22×10^{-6}m is greater than maximum possible wavelength for the excitation to occur and hence **no excitation** will occur because the given wavelength has too small energy to cause the excitation. **(0.75)**

Question 2

(a) Electronic configuration of carbon is;

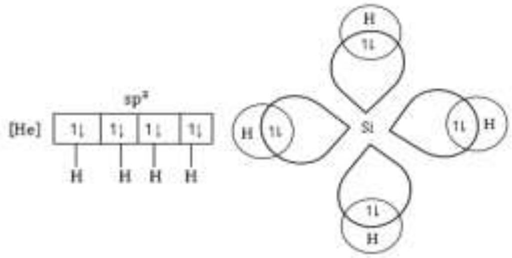
(0.5)

So unhybridised carbon has only two unpaired orbitals. To form four covalent bonds with hydrogen, carbon must form four molecular orbitals through sp^3 hybridisation. **(1)**



(0.5)

After hybridisation, each sp^3 hybrid orbital of carbon undergoes head to head overlap with hydrogen atom to form four covalent sigma bonds. **(1)**
That is in methane, CH_4:



(1)

Where dotted arrow represents electrons from hydrogen atom in the four molecular orbitals while full line arrows are electrons contributed by carbon.
Remark: To get full score, the examinee must:

(i) Show electronic **distribution** in carbon.
(ii) Deduce from the electronic configuration, the necessity for carbon to undergo sp^3 hybridisation in order to form methane.
(iii) Describe clearly the formation of four identical C-H bonds in methane after the hybridisation.
(b) With two hydrogen atoms and therefore two polar bonds; if H_2O would be linear, then there would be no net dipole, and the molecule would be therefore non-polar. **(1)**

Since it's polar, the two lone pairs must be on adjacent sides of tetrahedral electron geometry, leaving the two bonds on adjacent sides. This results in a net dipole with the negative end near to oxygen atom and the positive end near to hydrogen atoms. **(1.5)**
Remark: To get full score, the examinee must:

(i) Explain the linear- non polar relationship.
(ii) Justify the polarity of water by using 'lone pairs' factor as the way of confirming non-linear structure of water.
(c)
(i) 104.5° **(0.25)**
(ii) Water molecule has two lone pairs which exert stronger repulsion than bonded electron pairs and therefore the bond angle becomes less than expected tetrahedral angle of 109.5° **(1)**
(iii) The δ^+ charge comes from the **electronegativity difference** between covalent bonded oxygen and hydrogen atoms. **(0.5)**

The oxygen being more electronegative than hydrogen has greater attraction to covalent bonded (shared) electron making hydrogen slightly deprived in electron and hence the partial positive charge. **(0.5)**

(iv) **Prediction:** Slightly greater than 104.5° **(0.25)**

Explanation: In presence of HF molecule, lone pairs of H_2O interact with H^{δ^+} of HF through hydrogen bonding and therefore they act like bonded electron pair which exert weaker repulsion (than unbonded electron (lone) pairs. **(1)**
Remarks:

1. In the prediction: **"**slightly **different** to 104.5°**"** in place of "slightly **greater** to 104.5°" is **not** allowed.

2. "The angle is slightly greater than the bond angle in pure water" is allowed.
3. To get full marks on the explanation, the examinee must explain in terms of hydrogen bonding.

Question 3

(a) HCl and $\mathrm{NH_3}$ **(0.5)**

Explanation

HCl and $\mathrm{NH_3}$ being polar, they are highly soluble in water; so they will dissolve in it to make a solution and hence they would not come out the other end. **(1.5)**

Remark: If the solubility of $\mathrm{NH_3}$ is explained in terms of hydrogen bonding is acceptable but the solubility of HCl **must** be explained in terms of polarity.

(b) Carbon monoxide gas reacts with oxygen gas according to the following equation:

$2\mathrm{CO(g)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{CO_2(g)}$

Since the CO was in excess, after reaction the gaseous mixture consisted of unreacted CO and produced $\mathrm{CO_2}$. **(0.5)**

Then from Grahm's law of diffusion:

$\frac{t_{mixture}}{t_{Br_2}} = \sqrt{\frac{M_{mixture}}{M_{Br_2}}}$ **(0.5)**

But $t_{mixture} = \frac{1}{2}t_{Br_2}$

Then $\frac{\frac{1}{2}t_{Br_2}}{t_{Br_2}} = \sqrt{\frac{M_{mixture}}{M_{Br_2}}} = \sqrt{\frac{M_{mixture}}{160}}$ **(0.5)**

From which $M_{mixture} = \left(\frac{1}{2}\right)^2 \times 160\mathrm{g/mol} = 40\mathrm{g/mol}$

Hence the average molar mass of the mixture is $40\mathrm{g/mol}$ **(0.5)**

Then let the percentage by volume of CO be x and thus the percentage of $\mathrm{CO_2}$ will be $100 - \mathrm{x}$;

Where molar mass of CO and $\mathrm{CO_2}$ are $28\mathrm{g/mol}$ and $44\mathrm{g/mol}$ respectively.

So $\frac{28}{100}\mathrm{x} + \frac{(100-\mathrm{x})44}{100} = 40$ **(0.5)**

From which $\mathrm{x} = 0.25$ and $100 - \mathrm{x} = 75$ **(0.5)**

Hence:

The percentage of CO is 25% **(0.5)**

The percentage of $\mathrm{CO_2}$ is 75% **(0.5)**

From ideal gas equation: $\mathrm{PV} = \mathrm{nRT}$ **(0.5)**

(c) But $\mathrm{n} = \frac{\mathrm{m}}{\mathrm{M_r}}$**(0.5)** where m is the mass of the gas in grams

Then $\mathrm{PV} = \left(\frac{\mathrm{m}}{\mathrm{M_r}}\right)\mathrm{RT}$ **(0.5)**

Or $\frac{\mathrm{PM_r}}{\mathrm{RT}} = \frac{\mathrm{m}}{\mathrm{v}}$ **(0.5)**

But $\frac{\mathrm{m}}{\mathrm{v}} =$ Density of the gas in $\mathrm{gdm^{-3}}, \rho$ **(0.5)**

Hence $\rho = \frac{\mathrm{PM_r}}{\mathrm{RT}}$ **(0.5)**

Density of the mixture (ρ) is given by $\rho = \frac{\mathrm{PM_r}}{\mathrm{RT}}$

Where $\mathrm{M_r}$ is the average molar mass of the gaseous mixture and;

$\mathrm{P} = \frac{98.65}{101.325}\ \mathrm{atm} = 0.9736\ \mathrm{atm}$

But $M_r = \frac{P_1M_1+P_2M_2+P_3M_3}{P_1+P_2+P_3}$ **(0.5)**

Where $P_1 = 21\%$ $M_1 = 32g/mol$ $P_2 = 1\%$

$M_2 = 40g/mol$ $P_3 = 78\%$ $M_3 = 28g/mol$

$M_r = \frac{(21\times32)+(1\times40)+(78\times28)}{21+1+78} = 28.96\ g/mol$ **(0.5)**

The substituting $\rho = \frac{0.9736\times28.96}{0.082\times293} = 1.17g/dm^3$

Hence the density is $1.17g/dm^3$**(0.5)**

Question 4

(a)

(i) Is the depression of freezing point of the solvent in the solution which is obtained when one mole of non-volatile solute is dissolved in 1 kg of solvent (**0.5**)

(ii) Are properties of solution which depend on relative amount of solute and solvent and not in the nature of the solute. (**0.5**)

(iii) Is the ratio of the number of moles of solute to the total number of all components in the solution. (**0.5**)

(b) Not satisfactory **(0.5)**

Explanation:

Osmotic pressure as one of colligative properties is only applicable when the solution is ideal which demands the solution to be dilute and not concentrated. **(1)**

(c) Using $\Delta T = K_f m$ (**0.25**)

But $m = \frac{n_{su}}{m_{sv}\text{ in kg}}$ and $n_{su} = \frac{m_{su}}{M_{su}}$

It follows that: $\Delta T = \frac{K_f\times m_{su}}{M_{su}\times m_{sv}\text{ in kg}}$

From which $K_f = \frac{\Delta T\times M_{su}\times m_{sv}\text{ in kg}}{m_{su}}$ (**0.75**)

Where $\Delta T = (5.481 - 4.971)℃ = 0.51℃$

m_{sv} in kg $= \frac{25}{1000}kg = 0.025\ kg$ and $M_{su} = 104\ g/mol$

Substituting; $K_f = \frac{0.51\times104\times0.025}{0.321}$ (**1**)

$= 4.13℃kgmol^{-1}$

The freezing point depression constant is $4.13℃kgmol^{-1}$ (**1**)

Using $\Delta T = \frac{K_f\times m_{su}}{M_{su}\times m_{sv}\text{ in kg}}$ (**0.5**)

From which;

$M_{su} = \frac{K_f\times m_{su}}{\Delta T\times m_{sv}\text{ in kg}}$ (**0.5**)

Substituting:

$M_{su} = \frac{4.13\times0.305}{(5.481-5.226)\times25\times10^{-3}} = 197.6\ g/mol$ (**1**)

The relative molecular mass of benzoic acid in benzene solution is approximately 198. (**0.5**)

The molecular formula of benzoic acid is $C_7H_6O_2$ from which the expected relative molecular mass is

$(7\times12) + (6\times1) + (2\times16) = 122$ (**0.5**)

However the observed relative molecular mass (198) is greater than the expected one (122) suggesting that to certain degree benzoic acid exist as a dimer as result of partial association between molecules of benzoic acid brought about by strong hydrogen bonding between them. (**1**)

Question 5

(a) **Definition:** Is the **process** by which a substance absorb water from the surrounding and eventually **forms a solution. (0.75)**

Explanation: If the hydrated salt contain **small sized** and **high charged cation** such that it can **attract (hold) lone pair** off oxygen in water, the salt will then undergo deliquescence. (**0.75**)
Remark: Award zero score if the definition begin with; 'is the substance'. (Deliquescence is not the substance; it is the process. **Deliquescent** substance undergoes deliquescence).

(b)

1. In making fertilizers used in agriculture (**0.5**)

   Example: Potassium sulphate (**0.5**) is used as potassic fertilizer.

2. In making dyes .(**0.5**)
   Example: Copper (II) sulphate is used in the manufacture of certain green pigments. (**0.5**)
3. In medicine (**0.5**)

   Example: Iron (II) sulphate is used to treat anemia. (**0.5**)

(c)

(i) Larger sized HCO_3^- has higher polarisability than CO_3^{2-} and therefore $NaHCO_3$ has higher degree of polarisation and hence on heating $NaHCO_3$ decomposes to give **effervescence of colourless gas** which **turns lime water milky** while Na_2CO_3 does not.

$$2NaHCO_3 \underset{\Delta}{\rightarrow} Na_2CO_3 + CO_2 + H_2O \textbf{ (0.5)}$$

$$Na_2CO_3 \underset{\Delta}{\rightarrow} \text{No reaction}$$

(ii) Brown ring test is the test that employs Iron(II) sulphate to test presence of nitrate by giving brown compound ($[Fe(H_2O)_5NO]SO_4$) which appears as a brown ring. **(0.5)**

- In the testing experiment, the iron(II) sulphate is added to the solution of nitrate, e.g. sodium nitrate mixed with sulphuric acid where the following series of chemical reactions occur: **(0.5)**

Firstly the mixture of the nitrate and sulphuric acid gives nitric acid.
$NaNO_3(aq) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HNO_3(aq)$ **(0.5)**
Produced nitric acid is then reduced to nitrogen monoxide by some of the iron(II) sulphate while the sulphate get oxidised to iron(III) sulphate.

$$6FeSO_4(aq) + 2HNO_3(aq) + 3H_2SO_4(aq) \longrightarrow 3Fe_2(SO_4)_3(aq) + 4H_2O(l) + 2NO(g)(\mathbf{0.5})$$

Finally, the nitrogen monoxide (produced in the above equation) reacts (ligand substitution reaction) with more iron(II) sulphate to give the brown ring of $[Fe(H_2O)_5NO]SO_4$.
$[Fe(H_2O)_6]SO_4(aq) + NO(g) \longrightarrow [Fe(H_2O)_5NO]SO_4(aq) + H_2O$ **(0.5)**
Or ionically; $[Fe(H_2O)_6]^{2+}(aq) + NO(g) \longrightarrow [Fe(H_2O)_5NO]^{2+}(aq) + H_2O(l)$

Question 6

(a)

(i) Is the heat change when the molar quantities represented by equation react **under** conditions of temperature and pressure, the substance being in their normal physical states. **(0.5)**

Remark: 'standard conditions' instead of '**given** conditions' is not allowed.

(ii) Is the chemical reaction in which heat is evolved to the surroundings. **(0.5)**

Remark: 'heat is **radiated'** instead of 'heat is **evolved**' or **liberated** or **given out** or **released** is not allowed.

(iii) Is the chemical reaction in which heat is absorbed from the surroundings. **(0.5)**

Remark: The definition: *is the chemical reaction which does not occur without the absorption of heat,* is not acceptable. (Every reaction is accompanied with absorption of heat in the reactants side but not every reaction is endothermic. Absorption of heat is commonly necessary to initiate reaction).

(b)

(i) Endothermic (**0.25**)

Explanation

The temperature decreased from $22.7°\mathrm{C}$ to $19.4°\mathrm{C}$ suggesting that heat was absorbed from the surroundings (solution) and hence the process is endothermic. (**0.75**)

(ii) $\text{Total heat absorbed} = \text{Heat absorbed by contents} + \text{Heat absorbed by vessel}$

But because plastic beaker does not allow the passage heat;
$\text{Heat absorbed by vessel} = 0$ (**0.5**) (specific heat capacity of plastic beaker is negligible).
$\text{Total heat absorbed}, \Delta H = \text{Heat absorbed by contents}$
But Heat absorbed by contents $= m_c C_c \Delta T$ (**0.5**)
Where $m_c = (1.5 + 36)g = 36.5\ g$ (**0.5**)
$C_c = 4.184\ Jg^{-1}C^{-1}$ (Specific heat capacity of solution is equal to that of water) (**0.25**)
$\Delta T = (22.7 - 19.4)°C = 3.3°C$ (**0.25**)
Substituting $\Delta H = 36.5 \times 4.184 \times 3.3J = 503.9628J$ (**0.5**)
But Heat of solution,
$\Delta H_{soln} = \frac{\text{Heat change}}{\text{Number of moles of solute } (NH_4NO_3)}$ (**0.5**)
Then using $n = \frac{m}{M_r}$; Where $M_r\ (NH_4NO_3) = 80\ g/mol$
Number of moles of $NH_4NO_3 = \frac{1.5g}{80\ g/mol} = 0.01875\ mol$ (**0.5**)
It follows that:
$\Delta H_{soln} = \frac{503.9628J}{0.01875mol} = 26878J/mol$ (**0.5**)
$= 26.878\ kJ/mol$
Hence the heat of solution is $+26.878\ kJ/mol$ (**0.5**)

(c)

(i) Heat change for reaction is **equal in magnitude** but **opposite in sign** to heat change for the reverse reaction. **(1)**

(ii) $C(graphite) + O_2(g) \rightarrow CO_2(g)\ \Delta H_C(graphite) = -393.5kJ/mol$ **(0.25)**

$C(diamond) + O_2(g) \rightarrow CO_2(g)\ \Delta H_C(diamond) = -395.4kJ/mol$ **(0.25)**

$C_{(diamond)} \rightarrow C_{(graphite)}$

$\Delta H_r = \Delta H_f(\text{graphite}) - \Delta H_f(\text{diamond})$ **(0.5)**

Using; $\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$ and the fact that $\Delta H_f(O_2) = 0$

From equation of combustion of graphite;

$-393.5 = \Delta H_f(CO_2) - \Delta H_f(\text{graphite})$…….(i) **(0.5)**

And from equation of combustion of diamond

$-395.4 = \Delta H_f(CO_2) - \Delta H_f(\text{diamond})$….(ii) **(0.5)**

Taking (ii) – (i) gives;

$-1.9 = \Delta H_f(\text{graphite}) - \Delta H_f(\text{diamond})$ **(0.5)**

Hence the heat of transition from diamond to graphite is -1.9 kJ/mol **(0.5)**

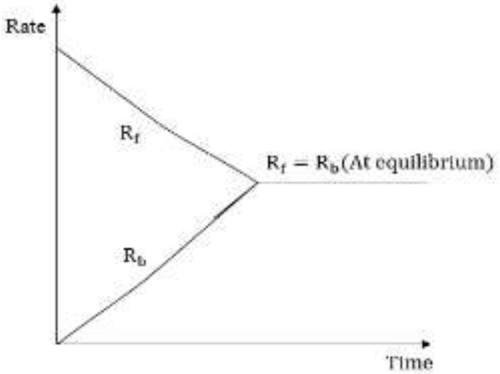
Question 7

(a)

(i) Chemical equilibrium involves balance of the rate of the two reactions which are **proceeding at the same time** in **opposite directions.** So it involves the **constant interchange of particles in motion,** moving in opposite direction of forward and reverse reaction and hence the equilibrium is said to be dynamic. (**2**)

(ii) Consider the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Initially the rate of forming HI (forward reaction) is maximum while that of dissociation of HI to form H_2 and I_2 (backward reaction) is zero because at the beginning, only H_2 and I_2 are present. As the reaction proceed concentration of H_2 and I_2 start to decrease and thus lowering the rate of forward reaction while HI is formed leading to backward reaction. Thus as the reaction proceed, the rate of forming HI is continuously decreasing while that of dissociation of HI is continuously increasing until they become equal where it said that the equilibrium has been attained as illustrated in the following graph:



Where:

R_f is the rate of formation of HI (forward reaction rate)

R_b is the rate of dissociation of HI (backward reaction)

(b) From ideal gas equation; $P = \frac{nRT}{V}$

Then initial pressure exerted by H_2O (P_{H_2O}) will be:

$P_{H_2O} = \frac{0.1 \times 0.082 \times (880+273)}{1}$ atm $= 9.4546$ atm (**1**)

Since pressure exerted by gas varies directly proportional to the number of moles of the gas; Pressure ratio = Mole ratio (**0.5**)

Thus pressure can be treated as number of moles as follows:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

Pressure at $t = 0$ 9.4546 0 0

Pressure at equilibrium $9.4546 - x$ x x (**1**)

$K_P = \frac{P_{CO}P_{H_2}}{P_{H_2O}} = \frac{x^2}{9.4546-x} = 14.1$ (**1**)

$x^2 + 14.1x - 133.30986 = 0$

Solving above equation gives the practical value of x which is 6.4782

Hence:

$P_{H_2O} = 9.4546 - x = 2.9764$ atm (**0.5**)

$P_{CO} = x = 6.4782$ atm (**0.5**)

$P_{H_2} = x = 6.4782$ atm (**0.5**)

Question 8

(a)

(i) Nucleophile is the **electron-rich species** with tendency to **donate** an electron **pair** to electron-poor specie to form new covalent bond. **(0.5)**

Remark: Award zero score if an examinee did not mention a word '**pair**' in the phrase '**an electron pair**'

(ii) Enantiomers are **stereoisomers** that are **mirror images** of each other. **(0.5)**

(iii) Electronic effect is the effect which occurs in a compound as result of movement of electrons. **(0.5)**

Remark: Don't allow: **Partial** movement or **total** movement instead of just 'movement'. But **allow** if the two words appears altogether in the definition simultaneously.

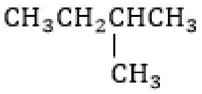
(iv) Isomers are compounds with the same molecular formula but differ in their structures or spatial arrangement in space. **(0.5)**

Remarks:

1. The definition: *Are compounds with the same molecular formula but differ in their properties*, is acceptable.
2. The definition: *Are compounds with the same molecular formula but differ in their structures*, is **not** acceptable (stereoisomers have the same structure).

(b)

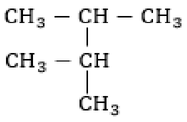
(i) Structure:



$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3$ **(0.5)**

Correct name: 2-methylbutane (**0.5**)

(ii) Structure:

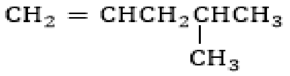


$$\begin{array}{l} CH_3 - CH - CH_3 \\ \qquad\quad | \\ CH_3 - CH \\ \qquad\quad | \\ \qquad\ \ CH_3 \end{array}$$

(0.5)

Correct name: 2,3-dimethylbutane (**0.5**)

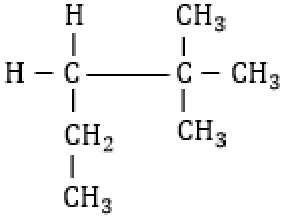
(iii) Structure:



$CH_2 = CHCH_2\underset{\overset{|}{CH_3}}{C}HCH_3$ (**0.5**)

Correct name: The given name is correct which is 4-methylpent-1-ene (**0.5**)

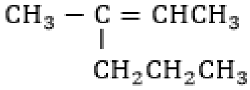
(iv) Structure:



(**0.5**)

Correct name: 2,2-dimethylpentane (**0.5**)

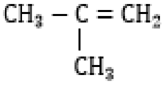
(v) Structure:



$CH_3 - \underset{\overset{|}{CH_2CH_2CH_3}}{C} = CHCH_3$ (**0.5**)

Correct name: 3-methylhex-2-ene (**0.5.**)

(c) Structural formula of P is:



$CH_3 - \underset{\overset{|}{CH_3}}{C} = CH_2$

Structural formula of Q is: $CH_3C \equiv CH$ (**1**)

(d) The large molecular mass of brominated compound which is greater than twice the atomic mass of Br with greatest contribution from the bromine suggests that the hydrocarbon, Q, was unsaturated and not alkane which would give monobrominated product via the substitution reaction by one mole of Br_2. (**1**)

Since only one mole of Br_2 was added, the hydrocarbon Q, must be alkene, with only one $C = C$; it cannot be alkyne which need 2 moles of Br_2. (**0.5**)
Then from general equation of combustion of hydrocarbon, C_xH_y;
$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$ (**0.5**)
But for alkene with only one $C = C$;
$y = 2x$ (**0.5**)
It follows that: $C_xH_{2x} + \frac{3}{2}xO_2 \rightarrow xCO_2 + xH_2O$ (**0.5**)
But it is given that 10 cm^3 of hydrocarbon (C_xH_{2x}) reacts with 45 cm^3 of oxygen.
And according to Avogadro’s law;
Mole ratio = Volume ratio
Thence $45 = \frac{3}{2}x \times 10$ (**0.5**)
From which $x = 3$ and $2x = 6$ (**0.5**)
Hence he molecular formula of Q is C_3H_6 (**1**)
There is only one possible structure for alkene with 3 carbons which is $CH_3CH = CH_2$(**1**)

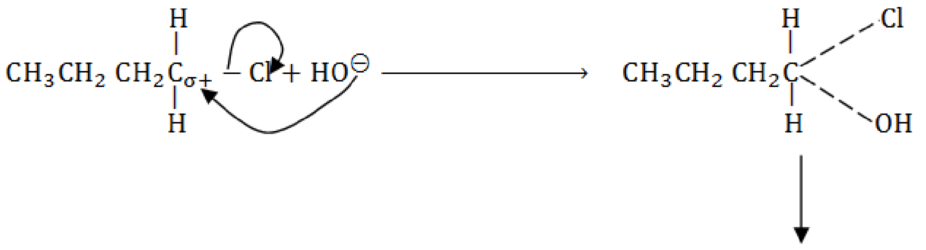
Question 9

(a)

(i) The reaction is nucleophilic substitution reaction. **(0.5)**

The substitution by nucleophile is possible because the carbon with halogen is positively polarised as result of high electronegativity of halogen compared to carbon. **(1.5)**

(ii) **Mechanism:**



$CH_3CH_2\,CH_2OH + Cl^-$ (2)

Difference: 1- chlorobutane undergoes S_N2 mechanism as shown above while 2-chloro-2-methylpropane will undergo S_N1 mechanism. **(1)**

(iii) **Conditions:**

1. The solution should be dilute **(0.5)**
2. Presence of water as reaction solvent medium (aqueous medium) **(0.5)**
3. Low temperature **(0.5)**

(b)

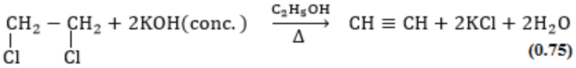
(i) Firstly:

$CH_3CH_2OH + H_2SO_4(conc.) \xrightarrow[170°C]{} CH_2 = CH_2 + H_2O$ **(0.75)**

Then:

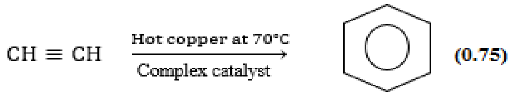
$$CH_2 = CH_2 + Cl_2 \xrightarrow[\text{Low temperature}]{CCl_4,\text{Darkness}} \underset{\underset{Cl}{|}}{CH_2} - \underset{\underset{Cl}{|}}{CH_2}$$ **(0.75)**

Then:



$$\underset{\underset{Cl}{|}}{CH_2} - \underset{\underset{Cl}{|}}{CH_2} + 2KOH(conc.) \xrightarrow[\Delta]{C_2H_5OH} CH \equiv CH + 2KCl + 2H_2O$$ **(0.75)**

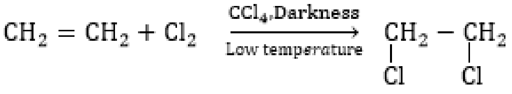
Finally:



(ii) Firstly:

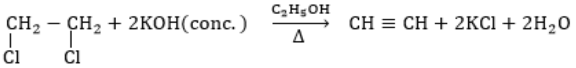
$CH_3CH_2OH + H_2SO_4(conc.) \xrightarrow[170°C]{} CH_2 = CH_2 + H_2O$ **(0.6)**

Then:



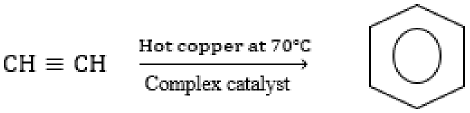
$$CH_2 = CH_2 + Cl_2 \xrightarrow[\text{Low temperature}]{CCl_4,\text{Darkness}} \underset{\underset{Cl}{|}}{CH_2} - \underset{\underset{Cl}{|}}{CH_2}$$ **(0.6)**

Then:



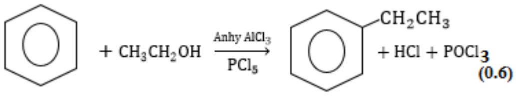
$$\underset{\underset{Cl}{|}}{CH_2} - \underset{\underset{Cl}{|}}{CH_2} + 2KOH(conc.) \xrightarrow[\Delta]{C_2H_5OH} CH \equiv CH + 2KCl + 2H_2O$$ **(0.6)**

Then:



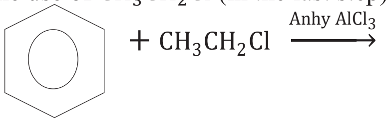
(0.6)

Finally:



Remark: The use of CH_3CH_2Cl (in the last step) is not acceptable.

That is:



(is not acceptable).

(The question asked to used alcohol (CH_3CH_2OH) as the only source of carbon. That is why in the above answer, there is a mixture of CH_3CH_2OH (the only allowed source of carbon) and PCl_5 so as to produce the intended CH_3CH_2Cl).

(c) Halogens are exceptional in manner that they violate deactivating rule as outlined below:

First rule violated: Deactivators exert negative mesomerism to benzene ring.
Commonly deactivators deactivate benzene ring through negative mesomerism. Halogens exert (weak) positive mesomerism and they deactivate the benzene ring through negative inductive effect. **(1.5)**
Second rule violated: Deactivators are meta directors.
Commonly an electrophile attack to meta carbon if the substituent in benzene ring is deactivator. Halogens are only deactivators which direct incoming electrophile to ortho and para carbon (not to meta carbon). **(1.5)**

Question 10

(a)
(i) Can be broken by biology organisms. **(1)**
(ii)

1. Making compost **(1)**
2. Reducing demand on peat **(1)**
3. Less land needed for landfill **(1)**
4. Producing heat (to kill weed seeds) **(1)**

Remark: Any two advantages with maximum score of 2 marks.

(iii)
(b)
(i)

1. To make electricity (generated via steam turbines)**(1)**
2. To provide heat for community **(1)**
3. To dry waste **(1)**

Remark: Any two uses with maximum score of 2 marks).

(ii) A high temperature is needed to prevent formation of toxic dioxin.**(1)**
(c)
(i) Is the warming up of the Earth's surface. It occurs when ultraviolet radiations from the sun are released from the Earth's surface as infrared radiations and thereafter those infrared radiations are absorbed. **(1.5)**

(ii) Large (considerable) amounts of greenhouse gases are released by burning fossil fuels. **(1)**

(iii) No infrared active vibrations because there is no change on dipole moment in the vibration as the nitrogen molecule is non-polar and symmetrical. **(1.5)**

(iv) CFC-12 has: **greater number of bonds** and **highly polarized polar bonds.** **(1)**

(v) $CF_2Cl_2 \xrightarrow{uv} CF_2Cl^\bullet + Cl^\bullet$ **(0.5)**

Mechanism:

Step 1: $Cl^\bullet(g) + O_3(g) \xrightarrow{UV} ClO^\bullet(g) + O_2(g)$. (i) **(0.5)**
Once step 1 has occurred twice, as per equation:
$Cl^\bullet(g) + O_3(g) \rightarrow ClO^\bullet(g) + O_2(g)$.. (ii) **(0.5)**
The two $ClO^\bullet$ radicals produced can react further in step 2
Step 2: $ClO^\bullet + ClO^\bullet \rightarrow ClOOCl$ ……….. (iii) **(0.5)**
Step 3: $ClOOCl \xrightarrow{UV} ClOO^\bullet + Cl^\bullet$ ..… (iv) **(0.5)**
Step 4: $ClOO^\bullet \xrightarrow{UV} Cl^\bullet + O_2$ ………... (v) **(0.5)**

Overall reaction equation:

The net reaction equation is obtained by taking (i) + (ii) + (iii) + (iv) + (v) and cancelling species that appear as both reactants and products as follows: $\cancel{Cl^\bullet} + O_3 + \cancel{Cl^\bullet} + O_3 + \cancel{ClO^\bullet} + \cancel{ClO^\bullet} + \cancel{ClOOCl} + \cancel{ClOO^\bullet} \longrightarrow \cancel{ClO^\bullet} + O_2 + \cancel{ClO^\bullet} + O_2 + \cancel{ClOOCl} + \cancel{ClOO^\bullet} + \cancel{Cl^\bullet} + \cancel{Cl^\bullet} + O_2$ **(0.5)**

Therefore, the balanced overall reaction equation is; $2O_3\ (g) \rightarrow 3O_2(g)$ **(0.5)**

Solutions Examination Eight
CHEMISTRY 2D

Question 1

(a)

(i) Saturated vapour pressure is the vapour pressure of the liquid in equilibrium with excess liquid at **given temperature. (0.5)**

(ii) Raoult's law is the law that relate the partial vapour pressure of a particular component in ideal solution to its mole fraction. **(0.5)**

Remark: Award zero score if an examinee stated the law. (It was asked to '**define**' the law and not to '**state**' the law).

(iii) Azeotropic point is the boiling point of the azeotropic mixture (**0.5**)

Remark: The definition: *Is the temperature at which the azeotrope boils*, is acceptable.

(iv) Ideal solution is the mixture of substances of similar chemical structures and polarities. **(0.5)**

Remark: The definition in terms of Raoult's law or intermolecular forces is acceptable.

(b) Negative deviation **(0.25)**

Explanation:
'Warm solution' suggest that its formation process was exothermic implying that the energy was released in forming A---------B intermolecular forces in the solution is greater than that absorbed in breaking A-----A and B------B intermolecular forces in pure components which in turn means that intermolecular forces in the solution are stronger than those in pure components and hence negative deviation for the solution. **(1.75)**

(c)

(i) Given that $P = -150X + 600$

Then $495 = -150X + 600$ **(0.25)**
From which $X = 0.7 = X_M$ **(0.25)**
But $X_N = 1 - X_M = 1 - 0.7 = 0.3$ **(0.5)**
Hence mole fraction of N is 0.3

(ii) Since the graph has negative slope, M is less volatile component. **(0.5)**

And when $X = 1$, there is only pure M in the container **(0.5)**
So by substituting $X = 1$ in $P = -150X + 600$ gives;
$P = -(150 \times 1) + 600$ **(0.5)**
$= 450\text{mmHg}$
Hence the vapour pressure of pure component which is less volatile is 450mmHg **(0.5)**

(iii) When $X = 0$, there is pure N which is more volatile. **(0.5)**

The substituting $P = (-150 \times 0) + 600$ **(0.5)**
$= 600\ \text{mmHg}$
Hence the vapour pressure of the more volatile component is 600mmHg. **(0.5)**

(iv) The solution is said to boil if the vapour pressure of the solution is equal to the atmospheric pressure. **(0.5)**

When $X_M = 0.1$; $X = 0.01$ and

Substituting $P = (-150 \times 0.01) + 600$ **(0.5)**
$= 485\text{mmHg}$
Hence the amount of atmospheric pressure needed is 485mmHg. **(0.5)**

(d) NaCl is non-volatile solute; introducing it in water, lowers the vapour pressure of water and hence the boiling point is increased. **(1)**

On another hand, methanol is less polar liquid than water; introducing it in water weakens intermolecular forces between water molecules, increasing its vapour pressure and hence boiling point is decreased. **(1)**

(e)
(i) Let:

C_1 be [x] in solvent A
C_2 be [x]in solvent B
α be degree of dissociation of x
n be number of molecules of x associated
Then:

A. $K = \frac{\sqrt[n]{C_1}}{C_2}$ $(\mathbf{0.5})$
B. $K = \frac{C_1(1-\alpha)}{\sqrt[n]{C_2}}$ $(\mathbf{0.5})$
C. $K = \frac{C_1}{C_2(1-\alpha)}$ $(\mathbf{0.5})$

(ii) Using; $\mathbf{W_r} = \mathbf{W_o}\left(\frac{\mathbf{V_b}}{\mathbf{V_b+K_dV_a}}\right)^{\mathbf{n}}$ **(0.5)**

Where:
$\mathbf{W_r}$ is the mass of solute which remain in residue solution after **n** extractions.
$\mathbf{W_o}$ is the original mass of the solute before extraction
$\mathbf{V_b}$ is the volume of residue solution
$\mathbf{V_a}$ is the volume of an extraction solvent used in each extraction (experiment)
n is the number extractions.
$\mathbf{K_d}$ is the partition coefficient
First case:
$\mathbf{W_o} = 50\text{g}, \mathbf{V_b} = 1000\text{cm}^3, \mathbf{V_a} = 1000\text{cm}^3, \mathbf{K_d} = 3$ and $\mathbf{n} = 1$
Then $W_r = 50\left(\frac{1000}{1000+(1000\times3)}\right)^1$ $(\mathbf{0.5})$
$= 12.5\text{g}$
The mass remained by using single extraction is 12.5g **(1)**
Second case:
$\mathbf{W_o} = 50\text{g}, \mathbf{V_b} = 1000\text{cm}^3, \mathbf{V_a} = 500\text{cm}^3, \mathbf{K_d} = 3$ and $\mathbf{n} = 2$
Then $W_r = 50\left(\frac{1000}{1000+(500\times3)}\right)^2$ $(\mathbf{0.5})$
$= 8\text{g}$
The mass remained by using two extraction is 8g **(1)**
Comparison:
Smaller amount of acid is left by using two extractions than one extraction. **(0.75)**
Recommendation:
To get best result of extracting the acid from water, the volume of ether should be divided in smaller portions as possible rather than using the whole volume at once. **(0.75)**

(iii) The acid dissociates in water and thus the molecular state of acid (solute) is not strictly the same in the two solvents. So in this case, the partition law used to derive the given partition coefficient is not strictly valid**. (1.5)**

Question 2

(a)

(i) Greater collision frequency means greater rate of chemical reaction. (**0.5**)

Collision frequency can be changed by doing one of the following:

1. Changing pressure: Increasing pressure, increases collision frequency. (**0.5**)
2. Changing concentration: Increasing concentration of reactants, increases collision frequency. (**0.5**)
3. Changing temperature: Increasing temperature, increases collision frequency. (**0.5**)
4. Changing surface area: Increasing surface area of reactants, increases collision frequency (**0.5**)

(ii) Greater collision energy means greater rate of chemical reaction. (**0.5**)

Collision energy may be changed by changing the temperature whereby increasing temperature, increases collision energy. (**0.75**)

(iii) Greater activation energy means lower rate of reactions. (**0.5**)

Activation energy can be changed by adding or removing catalyst where in most cases addition of catalyst lowers the activation energy. (**0.75**)

(b)

(i) Order of reaction are powers (or exponents) of concentration of reactants in the rate law. (**0.5**)

(ii) For nth order of reaction, unit of rate constant is given by $(\mathrm{L}^{-1}\ \mathrm{mol})^{1-\mathrm{n}}\mathrm{S}^{-1}$ (**0.5**)

But the given rate constant has unit of $\mathrm{Lmol}^{-1}\mathrm{S}^{-1}$
Thus by equating: $(\mathrm{L}^{-1}\ \mathrm{mol})^{1-\mathrm{n}}\mathrm{S}^{-1} = \mathrm{Lmol}^{-1}\mathrm{S}^{-1}$
Then $(\mathrm{Lmol}^{-1})^{\mathrm{n}-1} = (\mathrm{Lmol}^{-1})^{1}$ (**0.5**)
From which $\mathrm{n} - 1 = 1$ or $\mathrm{n} = 2$
Hence the order of reaction is 2 (**0.5**)

(c)

Collision energy factor (0.5)
When temperature is increased kinetic energy of reacting particles is increased. This makes more reacting particles to attain activation energy and therefore the collisions between the particles become more energetic resulting to the formation of activated complex. **(1)**

Collision frequency factor (0.5)
When temperature is increased, speed of reacting particles is increased thus making the particles to collide more frequently and hence the possibility of reaction between the reacting particles become higher. **(1)**

(d)

(i) Reducing agent (**0.5**)
(ii) Reducing agent (**0.5**)
(iii) Reducing agent (**0.5**)
(iv) Oxidizing agent (**0.5**)

(e)

(i) Equation for disproportionation of copper (I) ions:

$2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$(**0.5**);
Its corresponding cell diagram is;
$Cu^+(aq)|\ Cu^{2+}(aq)\ \|\ Cu^+(aq)|Cu(s)$ **(0.5)**
From which; $E^{\emptyset}_{cell} = E^{\emptyset}_{R} - E^{\emptyset}_{L} = (0.52 - 0.34)V = +018V$ (**1**)
Since e.m.f of the cell corresponding to the above reaction is positive, the reaction is spontaneous and hence Cu^{2+} disproportionates in aqueous solution. (**0.5**)
Equation for disproportionation of silver (I) ions:
$2Ag^+(aq) \rightarrow Ag(s) + Ag^{2+}(aq)$ (**0.5**)
The cell diagram corresponding to the above disproportionation reaction is
$Ag^+(aq)|Ag^{2+}(aq)||Ag^+(aq)|Ag(s)$ (**0.5**)
From which; $E^{\emptyset}_{cell} = E^{\emptyset}_{R} - E^{\emptyset}_{L} = (0.8 - 1.98)V = -1.18V$ (**1**)
Since e.m.f of a cell corresponding to the above reaction is negative, the reaction is not spontaneous and hence Ag^+ ions do not disproportionate in aqueous solution. (**0.5**)

(ii) Blue solution of $CuSO_4$ (**0.75**)

$Cu_2O(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + Cu(s) + H_2O(l)$ (**0.75**)
Remark: The ionic form of the equation is acceptable. That is;
$Cu_2O(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s) + H_2O(l)$

(iii)
1. Kinetic factors (**0.5**)
2. Non-standard conditions (**0.5**)
3. Very small difference in $E^{\emptyset}$ values (**0.5**)

Remark: Allow 'activation energy' in place of **kinetic factors** and **ignore** one factor if both kinetic factors and activation energy are given separately as two different factors.

Question 3

(a)

(i) Solubility is the ability of a certain solute to be dissolved in a given solvent which is given as the amount of substance dissolved in one litre of saturated solution at given temperature. (**0.5**)

(ii) Saturated solution is the solution which cannot dissolve more solute without forming a precipitate at given temperature. (**0.5**)

(iii) Saturated point is the point at which a liquid cannot take up more of the solute at given temperature. (**0.5**)

(iv) Supersaturated solution is the solution with more solute beyond its saturated point.(**0.5**)

(v) Fractional precipitation is the method for separating elements or compounds with similar solubility by a series of analytical precipitations, each one improving the purity of the desired element. **(0.5)**

(b)

(i) Let the molar solubility of CaF_2 in water be x

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

$x \qquad\qquad 2x$ (**0.5**)

Then $K_{sp} = [Ca^{2+}][F^-]^2$ (**0.5**)

Substituting $4 \times 10^{-11} = x(2x)^2 = 4x^3$ (**0.5**)

From which $x = \sqrt[3]{\frac{4\times10^{-11}}{3}} = 2.15 \times 10^{-4}moldm^{-3}$ (**0.5**)

But molar mass of CaF_2 is $78g/mol$

Then using solubility (mass solubility)= Molar solubility × Molar mass

$$= 2.15 \times 10^{-4} \times 78 = 1.677 \times 10^{-2}gdm^{-3}$$

Hence solubility of CaF_2 in water is $1.677 \times 10^{-2}gdm^{-3}$ (**0.5**)

(ii) Let the molar solubility of CaF_2 in 0.01M NaF be x.

Then: $[Ca^{2+}] = x$ and $[F^-] = 2x + 0.01$ (**0.5**)

But since x comes from sparingly soluble electrolyte, its value after common ion effect can be neglected compared to $[F^-]$ which comes from the strong electrolyte, NaF (**0.5**)

That is $2x + 0.01 \approx 0.01$

It follows that:

$K_{sp} = [Ca^{2+}][F^-]^2 = x(0.01)^2 = 4 \times 10^{-11}$

From which $x = 4 \times 10^{-11}moldm^{-3}$ (**0.5**)

Then solubility = Molar solubility × Molar mass

$$= 4 \times 10^{-11}moldm^{-3} \times 78gdm^{-3} = 3.12 \times 10^{-5}gdm^{-3}$$

Hence solubility of CaF_2 in 0.01MNaF is $3.12 \times 10^{-5}gdm^{-3}$ (**0.5**)

(iii) From Ostwald dilution law:

$[F^-]$ from HF $= \sqrt{K_a[HF]}$ (**0.5**)

$$= \sqrt{5.6 \times 10^{-4} \times 1} = 0.02M$$ (**0.5**)

So if x represents molar solubility of CaF_2 in the HF;

$[Ca^{2+}] = x$

$[F^-] = 2x + 0.02 \approx 0.02$ (**0.5**)

(CaF_2 being sparingly soluble substance, its contribution to $[F^-]$ is negligible).

Then $K_{sp} = [Ca^{2+}][F^-]^2$

Substituting $4 \times 10^{-11} = x(0.02)^2$ (**0.5**)

From which $x = 1 \times 10^{-7}$ $moldm^{-3}$ (**0.5**)

Then solubility = Molar solubility × Molar mass $= 1 \times 10^{-7} \times 78 = 7.8 \times 10^{-6}gdm^{-3}$

Hence solubility of CaF_2 in 1MHF is $7.8 \times 10^{-6}gdm^{-3}$ (**0.5**)

(c)

(i) Is an organic compound (acid) that changes colour with change in pH (**0.5**)

(ii) Let HA be acid-base indicator which is weak acid.

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ (**1**)

Red Yellow

From the above equation;

$K_a = \frac{[H^+][A^-]}{[HA]}$ (**0.5**)

Or $[H^+] = \frac{[K_a][HA]}{[A^-]}$

Then; $-\log[H^+] = -\log\frac{K_a[HA]}{[A^-]}$ (**0.5**)

$-\log[H^+] = -\log K_a + \log\frac{[A^-]}{[HA]}$

Thus $\text{pH} = \text{pKa} + \log\frac{[\text{A}^-]}{[\text{HA}]}$………….. (i) (**1**)

The indicator becomes orange when a half of the indicator has been ionized, that is $[\text{A}^-] = [\text{HA}]$ (**0.5**)

And when $[\text{A}^-] = [\text{HA}]$, equation (i) above becomes;

$\text{pH} = \text{pKa} = -\log 10^{-4} = 4$ (**0.5**)

Hence the colour of the indicator becomes orange when pH is 4. (**0.5**)

(iii) No. (**0.25**)

This indicator is not good test for acid and base because $[\text{A}^-] = [\text{HA}]$ occurs at far below 7 such that it is possible for two acidic solutions with different pH (for example pH of 3 and pH of 5) to have different colour or for acidic solution with pH above 4 to have the same colour as that of basic solution; for example, the solution with pH of 5 will have the same colour as that of pH of 9. (**1.75**)

(iv) The indicator is suitable for titration between strong acid and weak base because the equivalence point of that titration occurs when the solution is acidic and the end point of the given indicator also occurs when the solution is acidic too. **(1.5)**

(v) Red colour (**0.25**)

pH of $10^{-2}\,\text{MHCl} = -\log 10^{-2} = 2$. And at pH of 2 (below the pH of 4), the position of equilibrium lie to the left hand side (un-ionised indicator side) and hence the indicator will show red colour. (**1.25**)

Question 4

(a)

(i) As oxidizing agent, halogens (X) undergo reduction according to the following equation:

$$\text{X}_2(\text{g, l or s}) + 2\text{e} \rightarrow 2\text{X}^-(\text{aq})$$

Due to increase in atomization energy, decrease in electron affinity and decrease in hydration energy, ability of halogens to undergo above reduction and therefore oxidizing power of halogens decreases on descending the halogen group. (**1**)

This can be proved by displacement reaction whereby halogens above the group, oxidises (displaces) below member from their salts and not the opposite. For example:

$\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$

But $\text{I}_2 + \text{Br}^- \rightarrow$ No reaction (**1**)

(ii) Due to increase of size of halide ions on descending the halogen group, their ability to donate electrons and therefore reducing power of hydrogen halides appear to increase in the same direction. (**1**)

The reaction between hydrogen halides and concentrated sulphuric acid which is good oxidizing agent proves this:

$\text{HF} + \text{H}_2\text{SO}_4 \rightarrow$ No reaction

$\text{HCl} + \text{H}_2\text{SO}_4 \rightarrow$ No reaction

$\text{HBr} + \text{H}_2\overset{+6}{\text{S}}\text{O}_4 \rightarrow \overset{0}{\text{Br}_2} + \overset{+4}{\text{S}}\text{O}_2 + \text{H}_2\text{O}$

$\text{HI} + \text{H}_2\overset{+6}{\text{S}}\text{O}_4 \rightarrow \overset{0}{\text{I}_2} + \text{H}_2\overset{-2}{\text{S}} + \text{H}_2\text{O}$ (**1**)

(b)

(i) **Chlorides**

Due to their similar covalent characters^(0.5)^ (as Be^{2+} and Al^{3+} has similar polarising power), chloride of beryllium and aluminium have the following similarities:

1. They both hydrolyse in water to give acidic solution. (**0.5**)
   $BeCl_2(\text{or } AlCl_3) + H_2O \rightarrow Be(OH)_2(\text{or } Al(OH)_3) + HCl$ **(0.5)**
2. They both capable of undergoing association(0.5); beryllium chloride associates into polymer while aluminium chloride associates into dimer.

$$nBeCl_2(\text{or } 2AlCl_3) \xrightarrow{\text{Association}} (BeCl_2)_n(\text{or } Al_2Cl_6)\ (\mathbf{0.5})$$

(ii) **Oxides**

Due to their similar degree of covalent characters(0.5), oxides of beryllium and aluminium have the following similarities:

1. They are both amphoteric **(0.5)**
   As acids: They can react with strong base like NaOH.
   $BeO(\text{or } Al_2O_3) + NaOH \rightarrow NaBeO_2(\text{or } NaAlO_2) + H_2O$ (**0.5**)
   As bases: They can react with strong acid like HCl
   $BeO(Al_2O_3) + HCl \rightarrow BeCl_2(\text{or } AlCl_3) + H_2O$ (**0.5**)
2. They are both persistent such that they are insoluble in water and they have no reaction with concentrated nitric acid. (**0.5**)

(iii) **Carbonates**

Due to similar polarising power(0.5) of Be^{2+} and Al^{3+}, Carbonates of both beryllium and aluminium they are so thermally unstable(0.5) that they do not exist at room temperature.
$BeCO_3(\text{or } Al_2(CO_3)_3) \xrightarrow[\text{Room temperature}]{} BeO(\text{or}Al_2O_3) + CO_2(g)$ (**0.5**)

(iv) **Carbides**

Due to similar polarising power(0.5) of Be^{2+} and Al^{3+}, their carbides have similar structure with distorted carbide ion, C^{4-},(0.5) such that they give methane on hydrolysis.
$Be_2C\ (\text{or } Al_4C_3) + H_2O \rightarrow BeO(\text{or } Al_2O_3) + CH_4$ (**0.5**)

(c)

(i) With dilute sulphuric acid, strontium forms insoluble layer of $SrSO_4$ which resists further reaction. However due to oxidizing power of sulphuric acid when is concentrated, the acid can react with underlying layer of unreacted strontium (**1**)

$Sr + H_2SO_4\ (\text{dilute}) \rightarrow \text{No reaction}$
$Sr + H_2SO_4\ (\text{concentrated}) \rightarrow SrSO_4 + SO_2 + H_2O$ (**1**)

(ii) Due to its smaller cationic radius, beryllium can form complex with OH^- ligands and hence reacting with dilute NaOH (**1**)

$Be + 2NaOH + 2H_2O \rightarrow Na_2[Be(OH)_2] + H_2$ (**1**)

(iii) Due to greater polarising power of Be^{2+}, BeO has enough degree of polarisation to make it slightly covalent and hence it becomes amphoteric unlike oxides of other earth metals which are strong ionic. So while BeO can react with both acids and bases, oxides of other earth metals reacts with acids only. (**1**)

With acids like HCl:
$BeO + 2HCl \rightarrow BeCl_2 + H_2O$
And $MO + 2HCl \rightarrow MCl_2 + H_2O$; where M is any earth metal.
With base like NaOH:

$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$

And $MO + 2HCl \rightarrow$ No reaction, where M is any earth metal except beryllium (**1**)

(iv) Silver bromide is so covalent in characters that has no enough concentration of Ag^+ to make complex with NH_3 ligands unlike silver chloride which contain smaller sized Cl^- with smaller polarizability than Br^- making AgCl more ionic. (**1**)

$AgCl + 2NH_3 \rightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]^+Cl^-}$

While $AgBr + NH_3 \rightarrow$ No reaction (**1**)

Question 5

(a) Water **(0.5)**

Reason:

Methyl group in methanol exerts **positive inductive effect** [(0.5)] which stabilizes the OH bond [(0.5)] and makes the methoxide ion more unstable [(0.5)] and hence acidic strength of methanol is decreased.

(b)

(i) Route 1 **(0.5)**

Reason: KOH gives OH^- [(0.5)] which has greater nucleophilicity[(0.5)] as it has higher negative charge intensity [(0.5)] than H_2O used in route 2.
As result, the **nucleophilic substitution reaction** [(0.5)] in rout 1 occurs at higher rate [(0.5)].

(ii) Route 2 (**0.5**)

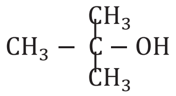
Reason:

The formation of alcohol from given reagents is the **nucleophilic substitution reaction** [(0.5)] which **compete with elimination reaction** [(0.5)]**.** KOH being stronger base [(0.5)] than H_2O, favours more formation of elimination product[(0.5)] (alkene) and therefore lowering the yield of alcohol[(0.5)]**.**

(c)

(i) $CH_3CH_2OH + CH_3COOH \xrightarrow{H^+} CH_3COOCH_2CH_3 + H_2O$ (**1**)

(ii)



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH + I_2 + NaOH \rightarrow \text{No reaction} \ (\mathbf{1})$$

(iii) Benzene − 1,4 − dioic acid + ethane − 1,2 − diol ⟶ Terylene + water (**1**)

Remarks:

1. Answer must be in words.
2. Alternative name for Terylene is Dacron.

(iv) Hexanedioic acid + hexane − 1,6 − diamine ⟶ Nylon − 6,6 + water (**1**)

(d)

(i) $[CoBr(NH_3)_5]SO_4$ (**1**)

(ii) $[Co(NH_3)_5(OSO_3)]Br$ (**1**)

(iii) $[CoCl(NH_3)_4(OH_2)]Br_2$ (**1**)

(iv) $[CoBr(NH_3)_4(OH_2)]Cl_2 \bullet H_2O$ (**1**)

(e)

(i) They are ionisation isomers with complex cation in each**. (1)**

Allow if you have mentioned just one of the following:

- They are ionisation isomers or
- They both contain complex cation

(ii) They both contain **complex cation (1)**

Don't allow if it just mentioned 'complex' without 'cation' or '

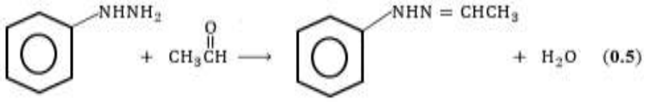
(iii) 6 **(0.5)**

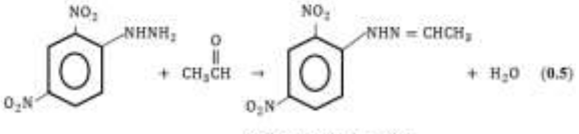
(iv) With solution of silver nitrate, (iii) gives light yellow precipitate of AgBr while (iv) gives white precipitate of AgBr (**1.5**)

Question 6

(a)

(i) With ethanal, 2,4-dinitrophenylhydrazine gives **yellow-orange precipitate** while phenylhydrazine does not. (**0.5**)





Yellow-orange precipate

Remark: Any other carbonyl compound (aldehyde or ketone) in place for ethanal is acceptable.

(ii) With solution of NaOH, $CH_3CH_2COCI_3$ gives **yellow precipitate** while $CH_3CH_2CCH_2CI_3$ does not (**0.5**)

$CH_3CH_2COCI_3 + NaOH \rightarrow CH_3CH_2COONa + CHI_3$**(0.5)**

Yellow precipitate

$CH_3CH_2COCH_2CI_3 + NaOH \longrightarrow$ No reaction **(0.5)**

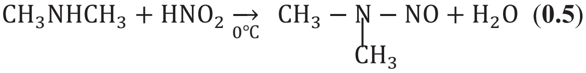
(iii) With drops (small amount) of water, CH_3CH_2COCl produces **white fumes** of hydrogen chloride gas while CH_3COOH does not. (**0.5**)

$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl(g)$ (**0.5**)
$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$ (**0.5**)

(iv) With cold nitrous acid, $CH_3CH_2NH_2$ gives **bubbles** of nitrogen gas while CH_3NHCH_3 gives yellow oil compound. (**0.5**)

$CH_3CH_2NH_2 + HNO_2 \xrightarrow[0°C]{} CH_3CH_2OH + N_2(g) + H_2O$

Bubbles (**0.5**)



$CH_3NHCH_3 + HNO_2 \xrightarrow[0°C]{} CH_3 - \underset{\substack{| \\ CH_3}}{N} - NO + H_2O$ (**0.5**)

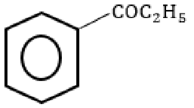
Yellow oil

(b)

(i) $CH_3COCH_3 + NH_2NH_2 \xrightarrow{KOH(aq)} CH_3CH_2CH_3 + N_2 + H_2O$ **(1.2)**

(ii) $CH_3CHO + HI \xrightarrow[150°C]{Red\ P} CH_3CH_3 + PI_3 + H_2O$ **(1.2)**

(iii)



$+ NaHSO_3 \rightarrow$ No reaction (1.2)

(iv) $CH_3COOH + NH_3 \xrightarrow[25°C]{} CH_3COONH_4$ **(1.2)**

(v) $C_6H_5OH + CH_3COOH \xrightarrow{H^+}$ No reaction **(1.2)**

(c) Since R is hydrocarbon;

$\%H = 100 - \%C = (100 - 85.7)\% = 14.3\%$

Constituent atoms	C	H
% age composition	85.7	14.3
Mass of each in 100g of R	85.7g	14.3g
Number of moles of each, $n = \frac{m}{M_r}$	$\frac{85.7g}{12g/mol}$ = 7.1417mol	$\frac{14.3g}{1g/mol}$ = 14.3 mol
Divide by smallest to get simpler ratio	$\frac{7.1417mol}{7.1417mol}$ = 1	$\frac{14.3\ mol}{7.1417mol}$ = 2

Empirical formula of R was CH_2 **(1.5)**

Then using Molar mass = 2g/mol × Vapour density

Molar mass of R = 2 × 28g/mol = 56g/mol **(0.5)**

Let molecular formula of R be $(CH_2)_n$

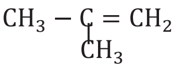
Then $12n + 2n = 14n = M_r = 56$ or $n = 4$

Hence the molecular formula of R is C_4H_8 **(0.5)**

The molecular formula, C_4H_8, suggest the general molecular formula of C_nH_{2n}. Thus R is aliphatic alkene with only one C = C. **(0.5)**

Since R has no geometrical isomers, it cannot be but-2-ene ($CH_3CH = CHCH_3$); it may be

(i) $CH_3CH_2CH = CH_2$ (ii)

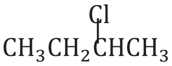


$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$ **(0.5)**

Reaction of R with NaOH(aq) gives alcohol (T) and since (ii) gives tertiary alcohol which resist to undergo oxidation; (T was easily oxidised) R cannot be (ii), must be (i)’ **(0.5)**

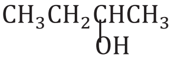
Hence: R must be but-1-ene ($CH_3CH_2CH = CH_2$) **(0.5)**

S is haloalkane with structure



$CH_3CH_2\overset{\displaystyle Cl}{\overset{|}{C}}HCH_3$

And T must be alcohol with the following structure



$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

Oxidation of secondary alcohol (T) gives ketone. Thus the structure of U is $CH_3CH_2COCH_3$ **(0.5)**

Reactions of U confirms that U must be ketone with terminal methyl group bonded to carbonyl group.

R is **alkene**$^{(0.25)}$ with the following structure: $CH_3CH_2CH = CH_2$ (**0.5**)

S is **haloalkane**$^{(0.25)}$ with the following structure:

$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$ (**0.5**)

T is **alcohol**$^{(0.25)}$ with the following structure:

$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$ (**0.5**)

U is **ketone**$^{(0.25)}$ with the following structure:

$CH_3CH_2COCH_3$ (**0.5**)

Solutions Examination Nine
CHEMISTRY 1E

Question 1

(a)

(i) Are levels used to describe electrons at their stationary states. **(0.5)**

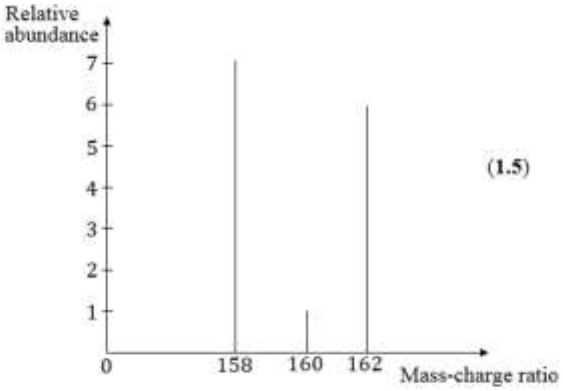
(ii) Is the frequency spectrum of separate lines with very little or no grouping at all which are formed during transition of electrons between quantized energy levels within an atom.**(0.5)**

(iii) Is an instrument which measures masses and relative concentrations of atoms or molecules. **(0.5)**

(b) Due to presence of isotopes, relative atomic mass is found from the weighted average of mass of different isotopes of silicon. Abundances (relative amounts) of these isotopes is different depending on the sources (region where silicon are is mined) and hence the mass will not be exactly the same. **(2)**

(c)

(i)



(1.5)

(ii) With two isotopes, bromine can form three different diatomic molecules (Br_2) as follows:

$^{79}Br - {}^{79}Br$ with peak at 158 ($M_1 = 158, I_1 = 6$)
$^{79}Br - {}^{81}Br$ with peak at 160 ($M_2 = 160, I_2 = 1$)
$^{81}Br - {}^{81}Br$ with peak at 162 ($M_3 = 162, I_3 = 5$) (**1**)

Then average molecular mass, $M_r = \frac{M_1I_1+M_2I_2+M_3I_3}{I_1+I_2+I_3}$ (**0.5**)

$= \frac{(158\times6)+(160\times1)+(162\times5)}{6+5+1}$ a.m.u= 159.83 a.m.u (**0.5**)

But since the bromine molecule is diatomic;

Average atomic mass $= \frac{\text{Average molecular mass}}{2}$ (**0.5**)

$$= \frac{159.83}{2} \text{a.m.u} = 79.915 \text{ a.m.u}$$

Hence the average atomic mass is 79.915 a.m.u (**0.5**)

(iii) Because it is weighted **average** of mass number of ^{79}Br and ^{81}Br isotopes. (**1**)

(iv) Let the relative abundance of ^{79}Br be y%

Then that of ^{81}Br will be (100-y)%

Then using $A_r = \frac{A_1P_1+A_2P_2}{100}$ (**0.5**)

Substituting $79.915 = \frac{79y+81(100-y)}{100}$ **(1)**
From which $y = 54.25$ and $100 - y = 45.75$
Hence the relative abundance is 54.25% for ^{79}Br and 45.75% for ^{81}Br **(1)**

Question 2

(a) **Supporting octet rule:**

When atoms combine together in accordance to the Octet rule, they get stable electronic structure of complete full filled electronic configuration. **(1)**
So in most cases, atoms obey octet rule when they combine with other atoms**(0.5)**. For example in $\ddot{\underset{\cdot\cdot}{O}} = C = \ddot{\underset{\cdot\cdot}{O}}$ (CO_2) both C and O have eight valence electrons as octet rule suggests.**(0.5)**
Opposing the rule:
There are number of molecules whose atoms do not obey octet rule in combining with other atoms in the molecule. **(0.5)**
This includes.

- Molecules with expanded octet like PCl_5 where P has 10 valence electrons instead of 8 electrons**(0.5)**
- Molecules with incomplete octet like $AlCl_3$ where Al has 6 valence electrons instead of eight. **(0.5)**
- Molecules with odd number of valence electrons like NO where N has seven valence electrons. **(0.5)**

(b)

(i) Delocalized electrons in metals are easily excited and on returning to the ground state or to lower energy excited state they emit radiations with wavelength in the visible spectrum which are recognized by eyes as definite colour and hence metals are coloured. **(1.5)**
Also the delocalized electrons are very mobile such that there is continuous successive excitation and de-excitation of electrons and is this oscillation of electrons that make metals to be shiny. **(1.5)**

(ii) Delocalized electrons in metals are flexible. So if the arrangement of atoms change, the delocalized electrons (electrons sea) can rearrange quickly and therefore the layers of metal atoms can slide past each other without breaking the metallic bond and hence metals become ductile and malleable. **(1.5)**

(iii) Delocalized electrons in metals can move freely within the structure of metal when a potential difference is applied and hence metals become good conductor of electricity. **(1.5)**

Question 3

(a) Boyle's law: $P \propto \frac{1}{V}$ at constant T and n **(0.25)**

Justification:
A decrease in V leads to an **increased gas molecules concentration** and thus an **increase in the number of collisions per second** with the walls of the container. More frequent collisions leads to greater pressure exerted by the gases in the container. **(1.25)**
Charles's law: $V \propto T$ at constant P and n **(0.25)**
Justification:
Initially an increase in T leads to an increase in kinetic energy and thus speed of gas molecules and frequency of collision is increased too. As result pressure (P) appears to increase at initial stages. The only way to prevent P from increasing under such conditions

is to increase V, which will decrease collision frequency despite the increased speed. **(1.25)**

Avogadro's law: V ∝ n at constant P and T **(0.25)**

Justification:

Initially, an increase in n leads to an increased gas molecules concentration and thus an increase in frequency of collision with the walls and thus pressure. The only way to prevent P from increasing under such conditions is to increase volume proportionally, which will keep concentration constant. **(1.25)**

(b) From ideal gas equation: $PV = nRT$ **(0.5)**

But $n = \frac{m}{M_r}$ **(0.5)** where m is the mass of the gas in grams

Then $PV = \left(\frac{m}{M_r}\right) RT$ **(0.5)**

Or $\frac{PM_r}{RT} = \frac{m}{v}$ **(0.5)**

But $\frac{m}{v}$ = Density of the gas in gdm^{-3}, ρ **(0.5)**

Hence $\rho = \frac{PM_r}{RT}$ **(0.5)**

(c) Using $n = \frac{m}{M_r}$;

Number of moles of $CH_4 = \frac{6.4g}{16g/mol} = 0.4$ mol **(0.25)**

Number of moles of $C_2H_6 = \frac{9g}{30g/mol} = 0.3$ mol **(0.25)**

From ideal gas equation:

$\frac{PV}{nT} = R$

Then $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$ **(0.5)**

But $T_1 = T_2 = T$ (Temperature is constant)

It follows that: $\frac{P_1V_1}{n_1} = \frac{P_2V_2}{n_2}$

Substituting; $\frac{0.5 \text{ atm} \times 2L}{0.4 \text{ mol}} = \frac{P_2 \times 1L}{0.3 \text{ mol}}$ **(1)**

From which $P_2 = 0.75$ atm

Hence the pressure is 0.75 atm **(0.5)**

Question 4

(a)

(i) Are properties of solution which depend on the relative amount of solute and solvent but not on the nature of the solute. Are properties of solution which are boiling point elevation, boiling point elevation, lowering in vapour pressure and osmotic pressure.**(1)**

(ii) Is the temperature at which vapour pressure exerted by liquid phase of a substance is equal to that exerted by its solid phase. Is the temperature at which liquid phase and solid phase of the substance co-exist at equilibrium. **(1)**

(iii) Is the component of the solution which does not produce vapour at the boiling point of solution. Non-volatile solutes are substances with low vapour pressure and high boiling point. **(1)**

(iv) Is the temperature at which vapour pressure of a substance is equal to atmospheric pressure (external pressure). Is the temperature at which liquid phase and gas phase of the substance are at equilibrium. **(1)**

(b)

(i) The addition of table salt which is non-volatile solute decreases the vapour pressure of water and hence boiling point of water is raised. **(1.5)**

(ii) The non-volatile solute decreases the vapour pressure of the solvent, making the solid phase to need lower temperature for its vapour pressure to be equal to the vapour pressure of liquid phase and hence the freezing point is lowered. **(1.5)**

(c) Using $\Delta T = iK_f m$ **(0.5)**

From which $i = \frac{\Delta T}{K_f m}$

Substituting $i = \frac{0.265}{1.86 \times 0.05} = 2.85$ **(0.5)**

Calcium nitrate dissociates according to the following equation:

$Ca(NO_3)_2(aq) \rightleftharpoons Ca^{2+}_{(aq)} + 2NO_3^-(aq); N = 3$ **(0.5)**

$$\text{Using } \alpha = \frac{i-1}{N-1} \ (\mathbf{0.5})$$

$$\text{Substituting } \alpha = \frac{2.85-1}{3-1} = 0.925 \ (\mathbf{0.5})$$

Hence the degree of dissociation is 0.925 or 92.5% **(0.5)**

Question 5

(a)

(i) Zinc hydroxide ($Zn(OH)_2$) **(1)**

(ii) $Zn(OH)_2 + 2HNO_3 \rightarrow Zn(NO_3)_2 + 2H_2O$ **(1)**

$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$ **(1)**

Remarks:

1. Allow $Na_2[Zn(OH)_4]$Insted of above products.
2. Accept any other correct example of amphoteric hydroxide.

(b)

(i) All hydrogencarbonates are water soluble due to their ability of making intermolecular hydrogen bonding with water molecules while most of carbonates are insoluble in water due to their high lattice energy and high degree of covalent characters as result of their high degree of polarisation. **(1.5)**

(ii) On heating; calcium carbonate gives effervescence of colourless gas (carbon dioxide) which turns lime water milky while sodium carbonate does not. **(0.5)**

$$CaCO_3(s) \underset{\Delta}{\rightarrow} CaO(s) + CO_2(g) (\mathbf{0.5})$$

$$Na_2CO_3(s) \underset{\Delta}{\rightarrow} \text{No reaction } (\mathbf{0.5})$$

(c)

(i) $2Fe(s) + 3Cl_2(g) \underset{\Delta}{\rightarrow} 2FeCl_3(s)$ **(1)**

(ii) $Fe(s) + 2HCl(aq) \rightarrow FeCl_2(g) + H_2(g)$ **(1)**

(iii) $2K(s) + Cl_2(g) \rightarrow 2KCl(s)$ **(1)**

(iv) $Ca(s) + Cl_2(g) \rightarrow CaCl_2(g)$ **(1)**

Question 6

(a) Equation for combustion of cyclohexane:

$C_6H_{12}(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$ **(1)**

Using $\Delta H_r^{\emptyset} = \sum \Delta H_f^{\emptyset}\text{(Products)} - \sum \Delta H_f^{\emptyset}\text{(Reactants)}$

Then $\Delta H_c^{\emptyset}(C_6H_{12}) = 6\Delta H_f^{\emptyset}(CO_2) + 6\Delta H_f^{\emptyset}(H_2O) - 9\Delta H_f^{\emptyset}(O_2) - \Delta H_f^{\emptyset}(C_6H_{12})$ **(0.5)**

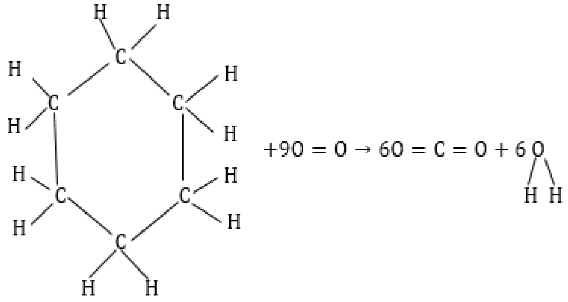
But $\Delta H_f^{\emptyset}(O_2) = 0$

Then substituting: $\Delta H_c^{\emptyset}(C_6H_{12}) = (6 \times -393) + (6 \times -285.6) - (-156)$ **(1)**

From which $\Delta H_c^{\emptyset} = -3915.6\text{kJ/mol}$

Hence standard enthalpy of combustion of cyclohexane is -3915.6kJ/mol **(0.5)**

(b) Equation for combustion cyclohexane showing all bonds broken and bonds formed;



(1)

Using $\Delta H_r = \sum \text{B.E (reactants)} - \sum \text{B.E(Product)}$

Then $\Delta H_r = 6(C-C) + 12(C-H) + 9(O=O) - 12(C=O) - 12(O-H)$ **(1)**

Substituting:

$$\Delta H_r = (6 \times 347) + (12 \times 412) + (9 \times 498) - (12 \times 805) - (12 \times 464)$$
$$= -3720\ \text{kJ/mol}$$ **(0.5)**

Hence the theoretical enthalpy of combustion of cyclohexane is $-3720\ \text{kJ/mol}$ **(0.5)**

(c) Total enthalpy of vapourisation of six moles of water

$$= 6 \times 40.7\text{kJ/mol} = 244.2\ \text{kJ/mol}$$ **(0.5)**

Then the corrected value of enthalpy of combustion = Theoretical enthalpy of combustion + Enthalpy of vapourisation of cyclohexane – Enthalpy of vapourisation of six moles of H_2O

$= (-3720 + 30 - 244.2) = -3934.2\text{kJ/mol}$ **(1)**

Hence the correct value of enthalpy of combustion is -3934.2kJ/mol**(0.5)**

(d) Apart from (a), none of the answers can be considered as standard enthalpy of combustion of cyclohexane because bond enthalpy calculation can only involve gaseous species and the fact that bond energies are based on average values for similar molecules. The value obtained in (b) has greater error compared to the standard value obtained in (a) because it ignores state changes while in (c) the error is very small due to corrections applied to take into account the state changes. **(2)**

Question 7

(a)

(i) **White fumes** (of hydrogen chloride gas). **(0.5)**

Remark: The response; hydrogen chloride gas is observed. (The question asked about observation and not chemical composition of the 'physical observation'. So **award zero score**, if the student just mention HCl gas without mentioning physical observation (mentioning HCl not necessary)).

(ii) HCl being gaseous is removed from the equilibrium system and thus the position of equilibrium shifts to the right. **(1.5)**

(b) In the Haber process, ammonia is produced as per equation:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\ \Delta H = \text{negative}$ **(0.5)**
The following conditions are applied to increase the yield of ammonia:

1. Very high pressure in the range of 200atm to 500atm **(0.5)**

   This shifts the position of equilibrium to the ammonia side (right hand side) as the production of ammonia per above equation is accompanied with significant reduction of volume. **(1)**

2. Relative low temperature of 450°C. **(0.5)**

   The reaction is exothermic. So applying low temperature shifts the position of equilibrium to the ammonia side. However below 400°C no ammonia is produced. **(1)**

3. Catalyst based on finely divided reduced iron promoted by alumina. **(0.5)**

   The low temperature favours production of ammonia but at very slow rate. So it is necessary to introduce catalyst which gives sufficient reaction rate in spite of relatively low temperature. **(1)**

(c) Given that:

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g);\ K_c = 10^2$....... (i)
From which:
$K_c = \frac{[NO]}{[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}} = K_1 = 10^2$ **(0.5)**
$2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g); K_c = 10^3$........ (ii)
From which:
$K_c = \frac{[N_2O_4]}{[NO]^2[O_2]} = K_2 = 10^3$ **(0.5)**
$N_2O_4(g) \rightleftharpoons 2NO_2(g);\ K_c = 10^4$ .... (iii)
From which: $K_c = \frac{[NO_2]^2}{[N_2O_4]} = K_3 = 10^4$ **(0.5)**
Taking $2(i) + (ii) + (iii)$ gives
$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ which is the same as given equation whose K_c is unknown.
Thus the K_C of the given equation will be given by the following relationship:
Required $K_c = (k_1)^2k_2k_3(\mathbf{1})$
$= (10^2)^2 \times 10^3 \times 10^4 = 10^{11}$
Hence the equilibrium constant is $10^{11}(\mathbf{0.5})$

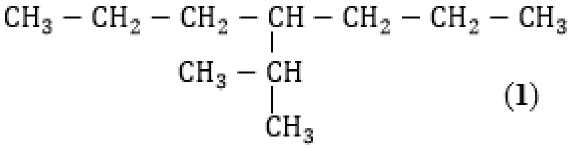
Question 8

(a)
(i) Is the bonding of atoms of the **same element** into very long and stable chain. (**0.5**)
(ii) Is an electron-poor specie with tendency to accept an electron **pair** from electron-rich specie called nucleophile. (**0.5**)
(iii) Is an organic molecule with positively charged carbon. (**0.5**)

(iv) Is the addition reaction whereby an electrophile is added first to carbon atom followed by a nucleophile. (**0.5**)

(b)

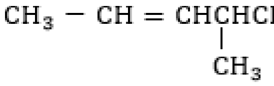
(i)



$$CH_3-CH_2-CH_2-\underset{\substack{|\\ CH_3-CH\\ |\\ CH_3}}{CH}-CH_2-CH_2-CH_3$$

(1)

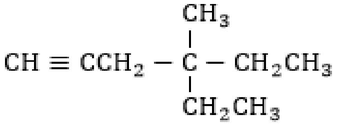
(ii)



$$CH_3-CH=CH\underset{\substack{|\\ CH_3}}{C}HCH_3$$

(1)

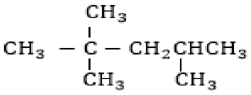
(iii)



$$CH\equiv CCH_2-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_2CH_3}}{C}}-CH_2CH_3$$

(1)

(iv)



$$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH_2\underset{\substack{|\\ CH_3}}{C}HCH_3$$

(1)

(c)

(i) Potassium permanganate test: Ethylbenzene decolorizes purple colouration of acidified potassium permanganate while ethane does not. **(1)**

Remark: Liquid bromine test is acceptable: Under presence of anhydrous aluminium bromide, ethylbenzene decolourises reddish brown colouration of liquid bromine while ethane does not. **(1)**

(ii) Ammonical silver nitrate test: But-1-yne gives white precipitate with ammonical silver nitrate solution while but-2-yne does not. **(1)**

Remark: Any one of the following tests is acceptable:

- Ammonical silver hydroxide test
- Ammonical copper (I) nitrate test
- Ammonical copper (I) hydroxide test
- Any relevant test

(d) Ethane is formed when two methyl radicals combine in the termination step. **(1)**

That is $CH_4 + Cl^{\square} \rightarrow H_3C^{\square} + HCl$(Propagation step) **(1)**
Then $H_3C^{\square} + H_3C^{\square} \rightarrow CH_3CH_3$(Termination step) **(1)**

(e)

(i) Both water and alkene like ethene are nucleophiles.

Nucleophilic character of water is explained by presence of lone pair while that of ethene is explained by the presence of pie bond. **(1.5)**

(ii) The reaction is made possible by adding concentrated sulphuric acid which act as an acidic medium to initiate the reaction despite the fact that the two reactants are both nucleophiles **(1)**

That is $CH_2 = CH_2 + H_2SO_4(\text{Conc}) \overset{A_E}{\rightarrow} CH_3CH_2(O_3SOH)$ (Initiation) (0.75)

Then $CH_3CH_2(O_3SOH) + H_2O \overset{S_N}{\rightarrow} CH_3CH_2OH + H_2\,SO_4$ (Formation of product and regeneration of catalyst) **(0.75)**

Question 9

(a)

(i)

(ii)

Comment:

Will deactivate electrophilic substitution reaction in benzene ring because it has π − bonded carbon (or atom) which is directly bonded to benzene ring. **(1)**

(b)

(i) H_2O in the aqueous medium being more polar than alcohol, causes more polarisation of positively charged carbon bonded to chlorine. As the carbon becomes more positive charge nucleophilic substitution reaction which leads to the alcohol formation is more favored than elimination reaction which leads to the formation of alkene. **(1.5)**

(ii) Under presence of water in the solution, the Griginard reagent would react to form alkane. So to prevent the formation of alkane, it must be prepared under anhydrous conditions**.** **(1.5)**

$$RMgX + H_2O \rightarrow RH + Mg(OH)X$$

Griginard reagent Alkane

(iii) To precipitate the chloride, the Cl in given chlorohydrocarbons must be substituted by nucleophile. In 1- chloropropene the Cl to be substituted is bonded to pie bonded carbon which is nucleophile too and hence there is very large repulsion between two nucleophiles which prevents the reaction to occur unlike in 1-chloropropane. **(1.5)**

(iv) In hydroxybenzene, electrophilic substitution reaction has been activated by presence of OH group which is activator (activate the benzene ring through positive mesomerism) and thus making it capable of reacting with bromine water unlike unsubstituted benzene**.** **(1.5)**

(c) .

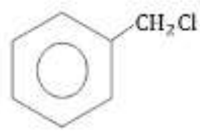
Constituent elements	C	H	Cl
% age composition	66.4	5.5	28.1
Mass of each in 100g of the compound	66.4g	5.5g	28.1g
Number of moles of each; $n = \frac{m}{M_r}$	$\frac{66.4g}{12gmol^{-1}}$ $= 5.533$ mol	$\frac{5.5g}{1gmol^{-1}}$ $= 5.5$ mol	$\frac{28g}{35.5gmol^{-1}}$ $= 0.7915$ mol
Divide by the smallest to get simple ratio	$\frac{5.533 \text{ mol}}{0.7915 \text{ mol}} = 7$	$\frac{5.5 \text{ mol}}{0.7915 \text{ mol}} = 7$	$\frac{0.7915 \text{ mol}}{0.7915 \text{ mol}} = 1$

(i) The empirical formula is C_7H_7Cl **(1.5)**
Let the molecular formula be $(C_7H_7Cl)_n$
Then $84n + 7n + 35.5n = M_r = 63 \times 2 = 126$
From which $n = 1$

(ii) The molecular formula is C_7H_7Cl **(0.5)**

(iii) Isomers:

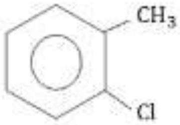
1.



(0.25)

Name: (choromethyl)benzene **(0.25)**

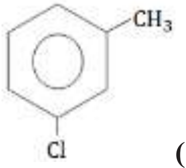
2.



(0.25)

Name: 2-chlorotoluene **(0.25)**

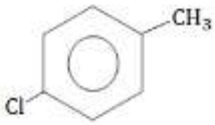
3. .



(0.25)

Name: 3-chlorotoluene **(0.25)**

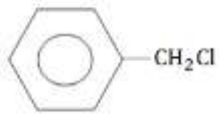
4. .



(0.25)

Name: 4-chlorotoluene **(0.25)**

(iv)



(0.5)

Explanation:
In this isomer, Cl is not directly bonded to benzene and thus its lone pairs are not involved in mesomerism unlike other isomers where Cl are involved in mesomerism leading to the formation of $C = Cl$ which is too difficult to break. **(1.5)**

Question 10

(a)

(i) Is the reaction of soil solution which represents the degree of acidity or basicity caused by the relative concentration of hydronium ions, H_3O^+, (acidity) or hydroxide ions, OH^-, (basicity) present in the soil. **(0.5)**

(ii) Is the reversible reaction which involves an interchange between ion in soil solution and another ion on surface of soil colloid. **(0.5)**

(iii) Is the phenomenon of coalescence and formation of flocs or loose aggregate. **(0.5)**

(iv) Are very small organic and inorganic particles present in the soil which are responsible for potential fertility of the soil. **(0.5)**

(v) Is the process of increasing salt content of the soil. **(0.5)**

(b)

(i) Number of exchangeable base cations = $(20 + 38 + 4 + 6 + 2)\text{meq} = 70\text{meq}$ **(1)**

Using; percentage base saturation = $\frac{\text{number of exchangeable base cations}}{\text{CEC of the soil}} \times 100\%$ **(1)**

$= \frac{70}{96} \times 100\% \quad = 72.9\%$

Hence the percentage base saturation is 72.9% **(1)**

(ii) Using $\text{meq} = \text{number of mmol} \times \text{amount of ionic charge}$ **(1)**

Substituting; 38= number of mmol × 2 **(0.5)**

From which amount of Ca^{2+} in mmol= $\frac{38}{2}$ or 19 mmol **(0.5)**

But number of mmol= $\frac{\text{mass in milligrams}}{\text{molar mass}}$

Substituting $19 = \frac{\text{mass in milligrams}}{40}$ **(0.5)**

Mass in milligrams = 19×40 or

760 milligrams or 0.76g

Hence the mass of Ca in 100g of oven dried soil is 0.76g **(1)**

(c)

Ozone formation

The ozone in stratosphere is produced through photochemical reactions involving O_2 as outlined below:

1. When O_2 in the stratosphere absorbs ultraviolet radiation with wavelength less than 240nm, it dissociates into two oxygen atoms. **(0.5)**

$O_2(g) \xrightarrow{\text{uv light}} 2\,O(g)$ …………………………….. (i) **(0.5)**

2. Then, the resulting oxygen atoms combine with O_2 molecules to form ozone. **(0.5)**

$O(g) + O_2(g) \rightarrow O_3(g)$ ……………………… (ii) **(0.5)**

Overall reaction equation: $3O_2\ (g) \rightarrow 2O_3\ (g)$ **(0.5)**

Ozone depletion

Ozone depletion is mainly caused by chlorofluorocarbons (CFCs). Gaseous CFCs released into the troposphere rise to upper atmosphere (stratosphere) through atmosphere mixing, where they are dissociated by high energy solar radiation (higher than that found in troposphere). **(0.5)**

That is $CFCl_3\ (g) \xrightarrow{UV} CFCl_2^{\bullet}(g) + Cl^{\bullet}(g)$ **(0.5)**

(Or $CF_2Cl_2(g) \xrightarrow{UV} CF_2Cl^{\bullet}(g) + Cl^{\bullet}(g)$)

The chlorine atom, a free radical, then participate in a **chain reaction mechanism** as follows:

Step 1:

$Cl^{\bullet}(g) + O_3(g) \xrightarrow{UV} ClO^{\bullet}(g) + O_2(g)$……………..... (i) **(0.5)**

Step 2:

$ClO^{\bullet} + ClO^{\bullet} \rightarrow ClOOCl$ …………………..……….. (iii) **(0.5)**

Step 3:

$ClOOCl \xrightarrow{UV} ClOO^{\bullet} + Cl^{\bullet}$ ………………………. (iv) **(0.5)**

Step 4:

$ClOO^{\bullet} \xrightarrow{UV} Cl^{\bullet} + O_2$ ………….……………..…... (v) **(0.5)**

Overall reaction equation: $2O_3\ (g) \rightarrow 3O_2(g)$ **(0.5)**

Solutions Examination Ten
CHEMISTRY 2E

Question 1

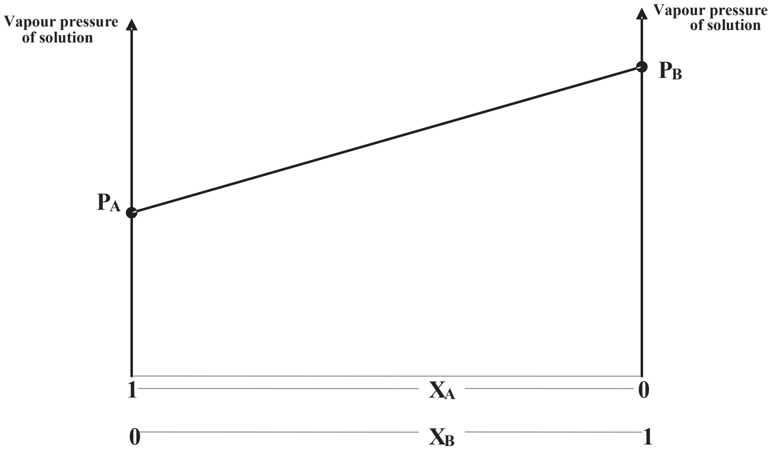
(a) Intermolecular forces in A and B should be equal in such a way that intermolecular forces in the solution is equal to intermolecular forces in pure A and pure B. **(1)**

A … … … … … … … . . … A = B … … … … … . . … … . . B = A … … … … … … … B(**0.5**)

Where; … … … … … … … … . …. represents intermolecular forces.

(b)

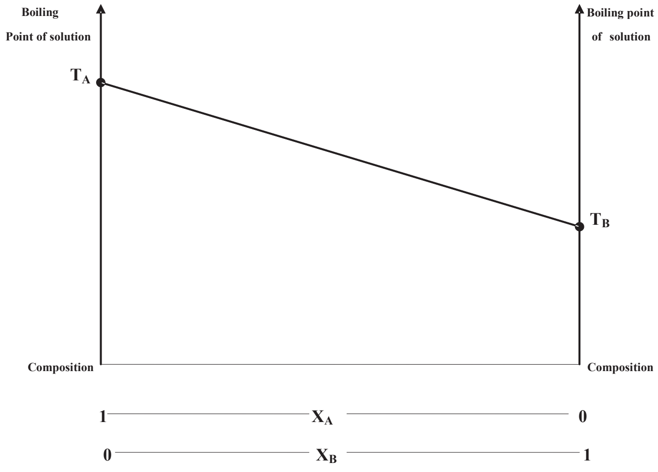
(i)



(2)

Where **P_A** is the vapour pressure of pure **A**
P_B is the vapour pressure of pure **B**

(ii)



(2)

Where **T_A** is the boiling point of pure **A**
T_B is the boiling point of pure **B**

(iii) The solution will boil in such a way that the vapour formed is richer in **B** (more volatile component). So on successive distillation and condensation the pure **B** is obtained as distillate in collector and pure **A** remain in the distillation flask as residue.**(1.5)**

(c)

(i) Using $\frac{n_c}{n_w} = \frac{P_c}{P_w}$ (For immiscible liquids) **(0.5)**

Where n_c and n_w is the number of moles of Chlorobenzene and water respectively in the distillate

P_c and P_w is the vapour pressure of Chlorobenzene and water respectively at 91°C

$\frac{n_c}{n_w} = \frac{760-540}{540} = \frac{11}{27}$ or $n_c : n_w = 11:27$ **(0.5)**

$\%n_c \left(\frac{11}{11+27}\right) \times 100\% = 28.9\%$

$\%n_w = (100 - 28.9)\% = 71.1\%$

Hence the mole composition of distillate is 28.9% Chlorobenzene and 71.1%water **(1)**

(ii) Using $\frac{m_c}{m_w} = \frac{P_c M_c}{P_w M_w}$ **(0.5)**

Where M_c and M_w are molar masses of Chlorobenzene and water respectively

m_c and m_w are masses of Chlorobenzene and water respectively in the distillate.

Then $\frac{m_c}{m_w} = \frac{(760-540)\times 112.5}{540\times 18} = \frac{275}{108}$ **(0.5)**

$m_c : m_w = 275:108$

$\% m_c = \left(\frac{275}{275+108}\right) \times 100\% = 71.8\%$

$\% m_w = (100 - 71.8)\% = 28.2\%$

Hence the mass composition of the distillate is 71.8% Chlorobenzene and 28.2% water.**(1)**

(iii) If 90% of chlorobenzene has been steam distilled:

Mass of chlorobenzene in the distillate = $\frac{90}{100}\times 20g = 18g$ **(0.5)**

If m_T is the total mass of the distillate

If follows that $\frac{71.8 m_T}{100} = 18g$ or $m_T = \frac{100\times 18g}{71.8} = 25g$ **(0.5)**

Using $V = \frac{m}{\rho}$

Total volume of distillate = $\frac{25}{1.1}cm^3 = 22.72cm^3$

Hence total volume of distillate obtained is 22.72 cm^3 **(1)**

Remark: In this calculation it has been assumed that the density of the mixture of two immiscible liquids is equal to the density of Chlorobenzene ($1.1g/cm^3$) because density of pure water is 1g/ cm^3 so the density of the mixture must lie between 1 and 1.1g/ cm^3; Chlorobenzene having grater proportional by mass the density of the mixture must be very close to 1.1g/ cm^3.

(d)

(i) Let C_1 and C_2 be concentration of phenol in water and chloroform respectively.

C_1	8.836	15.322	23.876
C_2	23.876	71.534	173.900
$\frac{C_1}{C_2}$	0.370	0.214	0.137
$\frac{C_1}{\sqrt{C_2}}$	1.808	1.812	1.811

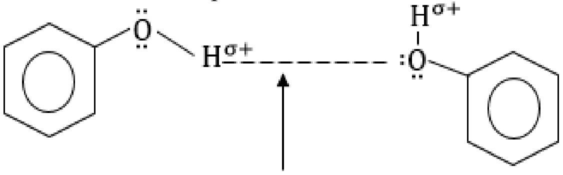
(3)

Since $\frac{C_1}{C_2}$ is not constant while $\frac{C_1}{\sqrt{C_2}}$ is constant of approximated value of 1.8, phenol dimerises in chloroform (**2**)

Remark: Distribute:

1. **0.5 mark** for ach correct entry of $\frac{C_1}{C_2}$ or $\frac{C_1}{\sqrt{C_2}}$ (**Allow** if molar concentration are used instead of mass concentration where the $\frac{C_1}{\sqrt{C_2}}$ constant value will be 0.187).
2. **2 marks** for correct conclusion with clear comment to justify the conclusion. **Deduct 1 mark** if the correct conclusion was given without giving the clear comment to support the conclusion. (The comment must base on difference in $\frac{C_1}{C_2}$ value and $\frac{C_1}{\sqrt{C_2}}$ value).

Dimerization of phenol is possible due to very strong hydrogen bonding existing between its molecules when the phenol is in chloroform.



Hydrogen bonding to enable the dimerisation (**2**)

Question 2

(a)

(i) Electrode is a solid electric conductor through which an electric current enters or leaves an electric cell or other medium. (**0.5**)

Remark: The definition which specify that the electrode must be **metal** (The definition which start with, "is a metal…….") is not acceptable. (The electrode not necessary to be metal. Some non-metals like carbon (graphite) are very good electrode).

(ii) Anode is the electrode at which oxidation occurs. (**0.5**)

Remark: The definition which implies that anode is **positive** electrode is not acceptable. (In electrochemical cell, anode is negative electrode).

(iii) Transport number is the fraction of the total current carried by ions. (**0.5**)

(iv) Conductance ratio is the ratio of conductivity at given concentration to that at infinite dilution. (**0.5**)

(b)

(i) Mass of hydrogen gas in 22400 cm^3 = 2g (**0.5**)

Thus mass of hydrogen in 56 $cm^3 = \frac{56}{2400} \times 2g = 5 \times 10^{-3}g$ (**0.5**)

Therefore mass of hydrogen gas liberated in electrolysis is $5 \times 10^{-3}g$

Then $z = \frac{m}{Q} = \frac{m}{It} = \frac{5\times10^{-3}g\,C^{-1}\,(0.5)}{0.27\times0.5\times3600} = 1.0288 \times 10^{-5}gC^{-1}$

Hence the electrochemical equivalent of hydrogen is $1.0288 \times 10^{-5}gC^{-1}$ (**0.5**)

(ii) Using equivalent weight, $E = \frac{\text{Atomic mass}}{\text{Magnitude of ionic charge}}$ (**0.5**)

Then equivalent weight of hydrogen, $E_1 = \frac{1}{1} = 1$ (**0.25**)

And equivalent weight of aluminium; $E_2 = \frac{27}{3} = 9$ (**0.25**)

But from (i); electrochemical equivalent of hydrogen,

$Z_1 = 1.0288 \times 10^{-5} gC^{-1}$ and $\frac{E}{Z} = \text{Constant}$

Then $\frac{E_1}{z_1} = \frac{E_2}{z_2}$

And substituting $\frac{1}{1.0288\times10^{-5}} = \frac{9}{z_2}$ **(0.5)**

From which $z_2 = 9.2592 \times 10^{-5} gC^{-1}$

Hence the electrochemical equivalent of aluminium is $9.2592 \times 10^{-5} gC^{-1}$ **(0.5)**

(c) Equilibrium constant of a cell, K_c can be found from the following equation:

$E^{\emptyset}_{cell} = \frac{0.0591}{n} \log K_c$ **(0.5)**

Where n is the number of electrons transferred in the balanced cell reaction. **(0.25)**

But for Daniel cell:

Anode reaction: $Zn(s) \rightleftharpoons Zn^{2+} + 2e$

Cathode reaction: $Cu^{2+}(aq) + 2e \rightarrow Cu\ (s)$

Cell reaction: $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ **(0.5)**

Thus $n = 2$ **(0.5)**

Also $E^{\emptyset}_{cell} = E^{\emptyset}_{Cu^{2+}/Cu} - E^{\emptyset}_{Zn^{2+}/Zn}$ **(0.75)**

Then using $E^{\emptyset}_{red} = -E^{\emptyset}_{oxid}$

$E^{\emptyset}_{Cu^{2+}/Cu} = -E^{\emptyset}_{Cu^{2+}/Cu} = -(-0.337V) = +0.337V$ **(0.5)**

And $E^{\emptyset}_{Zn^{2+}/Zn} = -E^{\emptyset}_{Zn^{2+}/Zn} = -0.765V$ **(0.5)**

Thus $E^{\emptyset}_{cell} = \left(0.337 - (-0.765)\right)V = 1.102V$ **(0.5)**

Then substituting $1.102V = \frac{0.0591}{2} \log K_c$ **(0.5)**

From which $K_c = 1.96 \times 10^{37}$

Hence the equilibrium constant for the cell is 1.96×10^{37} **(0.5)**

Let the rate law for the reaction be the following:

$R = k[HgCl_2]^m[C_2O_4^{2-}]^n$ **(0.5)**

(d)

(i) But we are given with the rate of formation of Cl^- and from stoichiometry of the reaction;

$R = \frac{1}{2}\frac{d[Cl^-]}{dt}$ **(0.75)**

Thus $\frac{1}{2}\frac{d[Cl^-]}{dt} = k[HgCl_2]^m[C_2O_4^{2-}]^n$

Or $\frac{d[Cl^-]}{dt} = 2k[HgCl_2]^m[C_2O_4^{2-}]^n$ **(0.75)**

Then substituting given data for ach experiment:

$0.52 \times 10^{-4} = 2k[0.0836]^m[0.202]^n$ ……. (i)

$2.08 \times 10^{-4} = 2k[0.0836]^m[0.404]^n$ ……. (ii)

$1.06 \times 10^{-4} = 2k[0.0418]^m[0.404]^n$ ……. (iii)

Taking $\frac{(ii)}{(i)}$ gives $\frac{2.08\times10^{-4}}{0.52\times10^{-4}} = \left(\frac{0.404}{0.202}\right)^n$

Or $4 = 2^n$ or $2^2 = 2^n$ or $n = 2$ **(0.75)**

Taking $\frac{(ii)}{(iii)}$ gives $\frac{2.08\times10^{-4}}{1.06\times10^{-4}} = \left(\frac{0.0836}{0.0418}\right)^m$

Or $2 = 2^m$ or $m = 1$ **(0.75)**

Hence the rate law is;

$R = k[HgCl_2][C_2O_4^{2-}]^2$ **(0.5)**

(ii) From (i); $R = k[HgCl_2][C_2O_4^{2-}]^2$

$R = \frac{1}{2}\frac{d[Cl^-]}{dt}$

Then $\frac{1}{2}\frac{d[Cl^-]}{dt} = k[HgCl_2][C_2O_4^{2-}]^2$ (**0.75**)

Substituting given data for experiment 1 gives;

$\frac{1}{2} \times 0.52 \times 10^{-4} molL^{-1}min^{-1} = k(0.0836 molL^{-1})(0.202 molL^{-1})^2$ (**0.75**)

From which $k = 7.62 \times 10^{-3} L^2mol^{-2}min^{-1}$

Hence the specific rate constant is $7.62 \times 10^{-3} L^2mol^{-2}min^{-1}$ (**0.5**)

(iii) From stoichiometry of the given equation:

$-\frac{d[C_2O_4^{2-}]}{dt} = \frac{1}{2}\frac{d[Cl^-]}{dt}$ (**0.5**)

Substituting; $-\frac{d[C_2O_4^{2-}]}{dt} = \frac{1}{2} \times 0.52 \times 10^{-4} molL^{-1}min^{-1}$

Then $-\frac{d[C_2O_4^{2-}]}{dt} = 2.6 \times 10^{-5} molL^{-1}min^{-1}$ (**0.5**)

Where the negative sign indicates that the concentration of $C_2O_4^{2-}$ is decreasing as the reaction proceed.

Hence the numerical value for the rate of disappearance of $C_2O_4^{2-}$ is 2.6×10^{-5} (**0.5**)

(iv) From $\frac{d[Cl^-]}{dt} = 2k[HgCl_2][C_2O_4^{2-}]^2$ (**0.5**)

Substituting given data for experiment 4 and obtain value of k

$1.27 \times 10^{-4} = 2 \times 7.62 \times 10^{-3} \times 0.0316 \times [C_2O_4^{2-}]^2$ (**0.5**)

From which $[C_2O_4^{2-}] = 0.514M$

Hence initial concentration of $C_2O_4^{2-}$ was 0.514M(**0.5**)

Question 3

(a)

(i) Solubility is the ability of a certain solute to be dissolved in a given solvent which is given as the amount of the substance dissolved in one litre of saturated solution.**(1.5)**

Solubility product is an equilibrium constant which is given as the product of concentration of ions in a **saturated solution** of sparingly soluble electrolyte, each raised to the power of their stoichiometric coefficients in the balanced chemical equation. (**1.5**)

(ii) Since dissolving sparingly soluble substance is endothermic process, the value of solubility product increases with an increase in temperature. **(2)**

(b) AgBr being highly covalent in character as result of very large polarizing power of Ag^+, does not dissolve in water which is polar solvent (it readily form yellow precipitate in water). However in aqueous ammonia, it tends to form soluble complex which appears to dissolve. (**2**)

$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+ + Br^-$

Insoluble Soluble (**1**)

Remark: To get full score, an examinee must give reasons for both low solubility of AgBr in water and its high solubility in ammonia solution.

Distribute:

(i) 1 mark for giving a reason for low solubility of AgBr in pure water.

(ii) 2 marks for giving a reason for high solubility of AgBr in ammonia solution.

Deduct 1 mark if the formula of the complex $[Ag(NH_3)_2]^+$ is not included in the explanation (Not necessary to include the equation of the complex formation but the formula of the complex must be included).

(c) If x is the molar solubility of AgBr

Then; $AgBr(s) \rightleftharpoons \underset{x}{Ag^+(aq)} + \underset{x}{Br^-(aq)}$ **(0.5)**

$K_{sp} = [Ag^+][Br^-] = x^2$ **(0.5)**

From which $x = \sqrt{K_{sp}} = \sqrt{3.33 \times 10^{-13}} = 5.744 \times 10^{-7}M$ **(0.5)**

The solubility of AgBr = Molar solubility × Molar mass

$= 5.744 \times 10^{-7} \times 188g/dm^3 = 1.1 \times 10^{-4}g/dm^3$**(0.5)**

Thus mass of AgBr dissolved in 50mL $= \frac{50}{1000} \times 1.1 \times 10^{-4}g^{(\mathbf{0.5})} = 5.5 \times 10^{-6}g$

Hence mass of AgBr is $5.5 \times 10^{-6}g$ **(0.5)**

$K_{sp} = [Ag^+][Br^-] = 3.3 \times 10^{-13}$ ...... (i) **(0.5)**

And $K = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$....... (ii) **(0.5)**

AgBr dissolves in $NH_3(aq)$ according to the following equation:

$AgBr(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Br^-(aq)$

At Equilibrium $10 - 2x$ x x **(1)**

Where x is the molar solubility of AgBr in $NH_3(aq)$

Then $K_s = \frac{[Ag(NH_3)_2]^+[Br^-]}{[NH_3]^2} = \frac{x^2}{(10-2x)^2}$ **(1)**

But $K_{sp} \times K = \frac{[Ag(NH_3)_2]^+[Ag^+][Br^-]}{[Ag^+][NH_3]^2} = \frac{[Ag(NH_3)_2^+][Br^-]}{[NH_3]^2} = K_s$ **(1.5)**

Thus $K_s = K_{sp} \times K = 3.3 \times 10^{-13} \times 1.7 \times 10^7$ **(1)**

Then $\frac{x^2}{(10-2x)^2} = 5.61 \times 10^{-6}$ **(0.5)**

From which $x^2 + 2.244 \times 10^{-4}x - 5.61 \times 10^{-6} = 0$; and $x = 0.0236$ **(1)**

Then mass solubility of AgBr in $NH_3(aq) = 0.0236 \times 188gdm^{-3} = 4.4368gdm^{-3}$ **(1)**

And mass of AgBr dissolved in 50mL $= \frac{50}{1000} \times 4.4368gdm^{-3(\mathbf{0.5})} = 0.22g$

Hence mass of AgBr dissolved was 0.22g **(0.5)**

Question 4

(a) According to Mendeleeff's periodic law, properties of elements are determined by their **atomic weights (masses)** while Modern periodic law suggested that the properties are determined by **atomic number. (1)**

Remark: An examinee is not required to distinguish by just stating the two laws. **Award zero score** if the examinee just stated the two laws instead of giving the main difference (after understanding the two laws).

(b)

(i) $1s^2 2s^2 2p^6 3s^2 3p^5$ **(0.75)**

Remark: $[Ne]3s^2 3p^5$ is acceptable.

(ii) The block letter is the letter of sub energy level with greatest energy which is 3p-subenergy level. Hence the element is fond at **p-block. (0.75)**

(iii) With five electrons in 3p-subenergy level there is one **unpaired electron** in the atom and hence the element is **paramagnetic. (0.75)**

(iv) The outermost electronic configuration of the element is $3s^2 3p^5$ which has $2 + 5 = 7$ valence electrons. Thus the element will principally gain **one** electron to get stable octet electronic structure of noble gases and hence its principle **oxidation number is -1 (0.75)**

Remark: The answer must include negative sign.

(c)

(i) **O (0.25)**

Reason: It has smaller atomic size, greater effective nuclear attractive force and more unstable electronic configuration than other elements except G. it has also smaller repulsion between outer and inner electrons than G. (**0.75**)

(ii) **G** (**0.25**)

Reason: It has smallest atomic size accompanied with greatest effective nuclear attractive force. (**0.75**)

(iii) **I (0.25)**

Reason: It has largest atomic size, very small nuclear charge accompanied with very large screening effect. (**0.75**)

(iv) **I** and **G (0.25)**

Reason: I is most electropositive while G is most electronegative. **(0.75)**

(v) **A** and **I** (**0.25**)

Reason: They have lower **atomization and ionisation energy** than other elements. (**0.75**)

(vi) **H and P (0.25)**

Reason: They have very stable electronic configuration of completely full filled (paired) electronic structure. (**0.75**)

(d) **Chief ore:**

The chief ore is tinstone (cassiterite), SnO_2 (**0.5**)
Concentration of ore:
The powdered tinstone is concentrated by gravity separation through washing with running water (which remove lighter matters) and magnetic separates to remove magnetic impurities (**1.25**)
of ore:
The concentrated ore is heated in a current of air where impurities like Sulphur and arsenic are removed as volatile SO_2 and AS_2O_3. Iron and copper pyrites change to their oxides and sulphates (**1.25**)

Leaching and washing
The roasted ore is treated with water where $CuSO_4$ and $FeSO_4$ are washed away from the main ore. Further lighter ferric oxide is washed away leaving behind heavier ore particles known as black tin containing 60% to 70% tin (**1.5**)
Smelting:
Black tin (SnO_2) is mixed with carbon and smelted in a reverberatory furnace. The ore is reduced to metallic state while SiO_2 is removed as slag (**1**)
$SnO_2 + 2C \xrightarrow[1200°C]{} Sn + 2CO$ (**0.5**)
$CaCO_3 \xrightarrow[\Delta]{} CaO + CO_2$ (**0.5**)

$CaO + SiO_2 \rightarrow CaSiO_3$ (Slag) (**0.5**)

Purification:

To obtain a tin in very high purity, electrolytic refining is employed. **(0.5)**

- In this method, impure tin is made anode and thin sheet of pure tin is made cathode. The electrolyte is made of H_2SiF_6, $SnSO_4$ and H_2SO_4. (**1**)
- On passing electric current, tin is dissolved from anode and get deposited on the cathode. (**1**)

At anode: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e$ (**0.25**)
At cathode: $Sn^{2+}(aq) + 2e \rightarrow Sn(s)$ (**0.25**)

Question 5

(a)

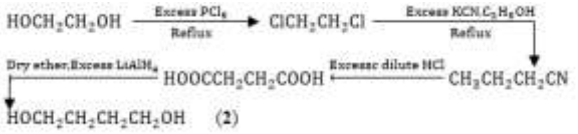
(i) In phenol there is a weaker hydrogen bonding because its lone pairs are delocalized in mesomerism as the OH is directly bonded to $\pi -$ bonded carbon in benzene ring unlike in benzyl alcohol. **(1)**

(ii) $LiAlH_4$ contains **nucleophilic hydride ion** which **repels to nucleophilic $\pi -$ bond** in $C = C$ or $C \equiv C$ of alkene and alkyne respectively. **(1)**

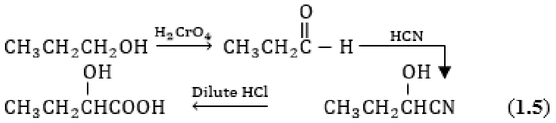
(iii) Disease-causing microorganisms are made by **organic compounds** and therefore they **dissolve easily** in **alcohol** which is **organic solvent** rather than in water which is **inorganic solvent. (1)**

(b)

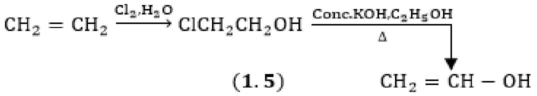
(i)



(ii)



(iii)

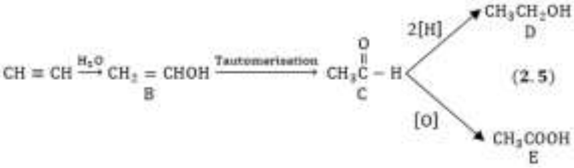


Remark: Distribute 0.5 mark for each correct step in (i), (ii) and (iii).

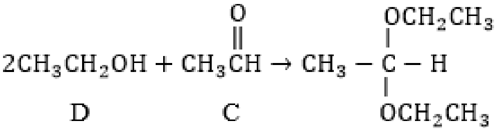
(c)

- Since A is hydrocarbon with two carbons, it can be either ethane, ethene or ethyne (**0.5**)
- For hydrocarbon to react with water, it must be unsaturated. Thus A cannot be ethane, it must be either ethene or ethyne **(0.5)**
- Molecular formula C_2H_4O, confirms general molecular formula of $C_nH_{2n}O$. Thus the compound B may be unsaturated alcohol with $C = C$ or carbonyl compound (aldehyde) (**0.5**)
- Since alkene (ethene) gives alcohol (ethanol) with water, A cannot be ethene, it must be ethyne.**(0.5)**

Hence A is the alkyne of the following structure:



$CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_3 + H_2O$
D E F **(1)**

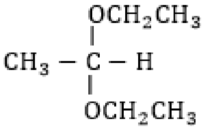


$$\underset{D}{2CH_3CH_2OH} + \underset{C}{CH_3\overset{\overset{O}{\|}}{C}H} \rightarrow CH_3 - \underset{\underset{OCH_2CH_3}{|}}{\overset{\overset{OCH_2CH_3}{|}}{C}} - H$$ **(1)**

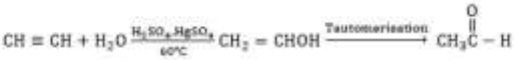
A is **alkyne** with structure CH ≡ CH (**0.5**)
B is **enol** with structure $CH_2 = CH - OH$ (**0.5**)

C is **aldehyde** with structure $CH_3 - \overset{\overset{O}{\|}}{C} - H$ (**0.5**)
D is **alcohol** with structure CH_3COOH (**0.5**)
E is **carboxylic acid** with structure CH_3COOH (**0.5**)
F is **ester** with structure $CH_3COOCH_2CH_3$ (**0.5**)

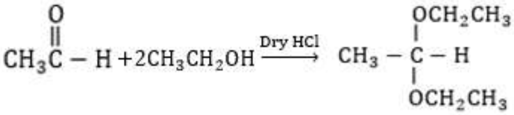
G is acetal with structure



$$CH_3 - \underset{\underset{OCH_2CH_3}{|}}{\overset{\overset{OCH_2CH_3}{|}}{C}} - H$$ **(0.5)**



$$CH \equiv CH + H_2O \xrightarrow[60^\circ C]{H_2SO_4, HgSO_4} CH_2 = CHOH \xrightarrow{\text{Tautomerisation}} CH_3\overset{\overset{O}{\|}}{C} - H$$ (1)



$$CH_3\overset{\overset{O}{\|}}{C} - H + 2CH_3CH_2OH \xrightarrow{\text{Dry HCl}} CH_3 - \underset{\underset{OCH_2CH_3}{|}}{\overset{\overset{OCH_2CH_3}{|}}{C}} - H$$ (1)

Functional isomer of F is $CH_3CH_2CH_2COOH$ (**0.5**)
Functional isomer of G is $CH_3\underset{\underset{OH}{|}}{C}HCH_2\underset{\underset{OH}{|}}{C}HCH_2CH_3$ (**0.5**)

Question 6

(a)

(i) Is the addition reaction whereby nucleophile is added first to carbon atom followed by an electrophile. (**0.5**)

Example: $CH_3 - \overset{\overset{O}{\|}}{C} - H + HCN \xrightarrow{S_N} CH_3\overset{\overset{OH}{|}}{C}H - CN$ (**0.5**)

(ii) Is the chemical reaction between carboxylic acid and alcohol under presence of acidic medium to give ester and water only. (**0.5**)

Example: (0.5)

$$CH_3COOH + CH_3CH_2OH \xrightarrow{H_2SO_4(\text{Conc.})} CH_3COOCH_2CH_3 + H_2O$$

(iii) Is the chemical reaction between organic compound and ammonia to give commonly either amines or amides. (**0.5**)

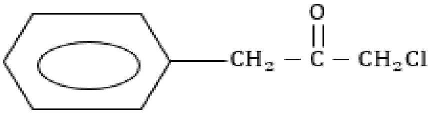
Example: $CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$ (**0.5**)

(iv) Is the chemical reaction between an amide and bromine under presence of an alkaline solution which involves the removal of carbonyl group from the amide resulting to the formation of an amine. (**0.5**)

Example: $CH_3CH_2CONH_2 + Br_2 + KOH \rightarrow CH_3CH_2NH_2 + K_2CO_3 + KBr + H_2O$ (**0.5**)

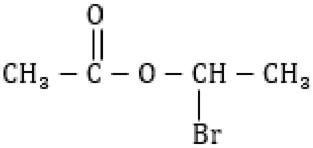
(b)

(i)



(1)

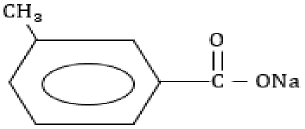
(ii)



$$\overset{\displaystyle O}{\overset{\|}{CH_3 - C}} - O - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$$

(1)

(iii)



(1)

(c)

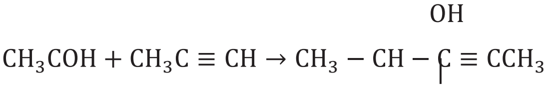
(i) $HCOONa + NaOH \xrightarrow[\Delta]{} H_2 + Na_2CO_3$ (**1**)

(ii) $CH_3CH_2NC \xrightarrow{Na/CH_3CH_2OH} CH_3CH_2NHCH_3$ (**1**)

(iii) $C_6H_5OH + CH_3COOH \xrightarrow{H^+}$ No reaction (**1**) (C_6H_5OH is phenol which has no chemical reaction with carboxylic acid)

(iv) $CH_3COCH_3 + NH_2NH_2 \xrightarrow{KOH(aq)} CH_3CH_2CH_3 + N_2 + H_2O$ (**1**)

(v)



$$CH_3COH + CH_3C \equiv CH \rightarrow CH_3 - CH - \underset{|}{\overset{OH}{C}} \equiv CCH_3$$

(**1**)

Note: CH_3COH is ethanal.

(vi) $CH_3OCOH + [Ag(NH_3)_2]NO_3 \rightarrow CH_3COONH_4 + HNO_3 + NH_3 + Ag$ (**1**)

Note: CH_3OCOH is methyl methanoate (ester).

(d)

(i) Potassium permanganate test: Ethanedioic acid decolourises purple colouration of acidified potassium permanganate heated to temperature of about 70°C while ethanoic acid does not. (**1**)

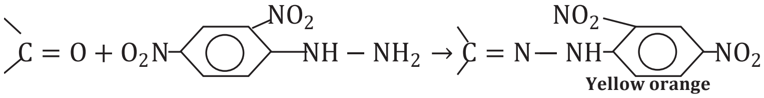
(ii) Potassium permanganate test: Ethyl methanoate decolourises purple colouration of acidified potassium permanganate while ethyl ethanoate does not. (**1**)

(e)

(i) CH_3CH_2CHO and CH_3COCH_3 (**1**)

(ii) Position isomerism (**0.5**)

(iii) On mixing with Brady's reagent and gently heating of the mixture, they give yellow precipitate. **(1)**



(0.5)

(iv) Class: Enol (Unsaturated alcohol with $C = C$) **(1)**

Formula $CH_3CH = CHOH$ **(0.5)**
Remark: Any position isomer of the above compound is acceptable.
Types of isomerism: Function isomerism **(0.5)**

Solutions Examination Eleven
CHEMISTRY 1F

Question 1

(a)

(i) Radiant energy is emitted or absorbed in small packets as quanta. (**1**)

(ii) It is not passible at any moment to predict accurately both position and momentum of an electron in an atom simultaneously. (**1**)

(iii)

1. It does not explain the spectrum of multi-electron atoms. (**0.5**)
2. It does not explain the relative intensity of spectral lines. (**0.5**)
3. It does not explain why covalent bonding makes a molecule stable. (**0.5**)
4. It viewed an electron as placed at certain fixed distance from nucleus which is against Heisenberg's uncertainty principle. (**0.5**)
5. No clear justification was given for the quantization of angular momentum of electron and presence of stationary states. (**0.5**)
6. It suggested that electron move in circular orbit in two dimensions which is against quantum mechanical atomic model which suggests that the motion is in three dimensions on the elliptical path. (**0.5**)
7. It does not explain presence of hyperfine spectral lines. (**0.5**)
8. It does not explain Zeeman and Stark effect. (**0.5**)

Remark: Any four shortcomings with maximum score of 2 marks.

(b)

(i) Is the energy required to remove completely the most loosely bound electron each from one mole of gaseous atom or ion at given conditions of temperature and pressure. It is the measure of strength of nuclear attractive force in an atom. **(1)**

(ii) When electron jump from one energy level to another, the energy change (ΔE) is given by:

$\Delta E = hf = \frac{hc}{\lambda}\ \left(f = \frac{c}{\lambda}\right)$ (**0.25**)

But from Rydberg equation;

$\frac{1}{\lambda} = R_H\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$ (**0.25**)

Then $\Delta E = hcR_H\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$ (**0.25**)

When an electron is ionised in hydrogen atom, the electron jumps from $n = 1$ to infinity (convergence limit where $n = \infty$).

Thus $n_1 = 1$ and $n_2 = \infty$

Substituting:

$\Delta E = 6.626 \times 10^{-34} \times 3 \times 10^8 \times 1.097 \times 10^7\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$ (**0.25**)

$= 2.1806 \times 10^{-18}\text{J/electron}$ (**0.5**)

But from the definition of ionisation energy, it must be per mole of electrons

And 1 mol of $e^- \equiv 6.02 \times 10^{23}\text{electron/mol}$

Thus the ionisation energy

$= 2.1806 \times 10^{-18}\text{J/electron} \times 6.02 \times 10^{23}\text{electron/mol}$

$1312721.2\text{J/mol} = 1312.7212\text{kJ/mol}$

The ionisation energy of hydrogen is 1312.7212kJ/mol. (**0.5**)

(c) Using Rydberg equation:

$\frac{1}{\lambda} = \mathrm{R_H}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$ (**0.5**)

For first line in the Balmer series;

$n_1 = 2, n_2 = 3$ and $\lambda = \lambda_B = 6863\mathrm{A^O}$

$\frac{1}{\lambda_B} = \mathrm{R_H}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5}{36}\mathrm{R_H}$……(i) (**0.5**)

For first line in Lyman series:

$n_1 = 1, n_2 = 2$ and $\lambda = \lambda_L = 6863\mathrm{A^O}$

$\frac{1}{\lambda_L} = \mathrm{R_H}\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3}{4}\mathrm{R_H}$……(ii) (**0.5**)

Taking $\frac{(i)}{(ii)}$ gives; $\frac{\lambda_L}{\lambda_B} = \frac{5}{36} \times \frac{4}{3} = \frac{5}{27}$ (**0.5**)

Or $\lambda_L = \frac{5}{27}\lambda_B = \frac{5}{27} \times 6863\mathrm{A^O} = 1271\mathrm{A^O}$

The wavelength is $1271\mathrm{A^O}$ (**1**)

Question 2

(a) Is the type of bond that is formed by transfer of electrons from metals to non-metals. (**0.5**)

Example: During the formation of NaCl crystal, Cl gain an electron from Na resulting to the formation of Na^+ and Cl^- in the crystal. (**0.5**)

Remark: The definition; *Is the strong electrostatic force of attraction between cation and anion in a crystal,* is acceptable.

(b)

(i) **Similarity**

They both involve sharing of electrons. (**0.5**)

Difference

In (normal) covalent bonding, shared electrons comes from all bonded atom where by each atom contribute single electron while in coordinate bonding all shared electrons comes from single atom. (**0.5**)

(ii) **Similarity**

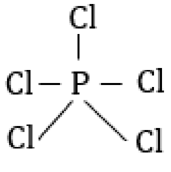
They are both covalent bonds which form molecular orbital through overlapping of atomic orbitals. (**0.5**)

Difference

Sigma bond is formed by maximum overlap of atomic orbitals in head to head (end to end) style and is stronger than pi bond which is formed by minimum overlap of atomic orbitals in side way (lateral) style .(**0.5**)

(c)

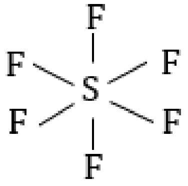
(i)



(**0.5**)

So with **five sigma bonds** without any lone pair in the phosphorous, the type of **hybridisation is sp^3d (0.5)**

(ii)



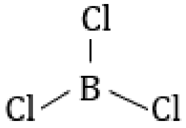
(0.5)

So with **six sigma bonds** without any lone pair in the sulphur, the type of **hybridisation is sp^3d^2 (0.5)**

(iii) $O = C = O$ **(0.5)**

So with **two sigma bonds** without any lone pair in the carbon, the type of **hybridisation is sp. (0.5)**

(iv)



(0.5)

So with **three sigma bonds** without any lone pair in the boron, the type of **hybridisation is sp^2. (0.5)**

(d) With **three** bonded electron pairs and **one** lone pair in each central atom of PCl_3 (phosphorous is the central atom) and NH_3 (nitrogen is the central atom) whereby the lone pair exert stronger repulsion than the bonded pair, the four electron pairs will be arranged around the central atom (according to VSEPR theory) in trigonal pyramidal so as to minimize repulsion between them. **(1)**

In case of PCl_5, all five electron pairs around the phosphorous (central atom) are bonded exerting equal amount of repulsion and therefore in accordance to VSEPR theory the electron pair will be arranged as far as possible in trigonal bipyramidal so as to minimize repulsion (**0.5**)
Hence:
The molecular geometry of $\mathbf{NH_3}$ and $\mathbf{PCl_3}$ is **trigonal pyramidal. (1)**
The molecular geometry of PCl_5 is **trigonal bipyramidal. (0.5)**
Remark: 'Distorted tetrahedral' or simply 'pyramid' for trigonal pyramidal is acceptable.

Question 3

(a)

(i) Is the volume of one mole of a gas at temperature of 0°C (273K) and pressure of 1 atm (760 mmHg) (**0.5**)

(ii) Is the law which express the total pressure exerted by mixture of two or more gases in terms of their partial pressures. (**0.5**)

(b)

(i) Consider two gases: gas 1 and gas 2.

Then from fundamental gas equation:

$P_1V_1 = \frac{N_1M_1C_1^2}{3}$ ……………… (i)

$P_2V_2 = \frac{N_2M_2C_2^2}{3}$ ……………… (ii) (**0.25**)

But kinetic energy of one molecule of gas is given by:

$K.E = \frac{1}{2}mc^2$

From which $mc^2 = 2K.E$

Then equation (i) and (ii) becomes:

$P_1V_1 = \frac{N_1K.E_1}{3}$ ……………… (ii)

$P_2V_2 = \frac{N_2K.E_2}{3}$ ……………… (iii) (**0.25**)

But from one of assumptions of kinetic theory of gases;

$K.E \propto T$ or $K.E = kT$ (Where k is the constant for proportionality). (**0.25**)

It follows that:

$P_1V_1 = \frac{N_1kT_1}{3}$ ……………… (iv)

$P_2V_2 = \frac{N_2kT_2}{3}$ ……………… (v) (**0.25**)

If temperature (T) and pressure (P) are kept constant (As suggested by Avogadro); that is

$P_1 = P_1 = P$ and $T_1 = T_2 = T$ (**0.25**)

$PV_1 = \frac{2N_1kT}{3}$ ……………… (vi)

$PV_2 = \frac{2N_2kT}{3}$ ……………… (vii) (**0.25**)

Taking $\frac{(vi)}{(vii)}$ gives; $\frac{V_1}{V_2} = \frac{N_1}{N_2}$ (**0.25**)

Or $\frac{V_1}{N_1} = \frac{V_2}{N_2}$

That is $\frac{V}{N} = \text{Constant}$

Or $V = \text{Constant} \times N$

Hence $V \propto N$ (Avogadro's law) (**0.25**)

(ii) From fundamental gas equation; $PV = \frac{N}{3}mc^2$ (**0.25**)

But $mc^2 = 2K.E$

Then $PV = \frac{2}{3}NK.E$ (**0.25**)

But from one of assumptions of kinetic theory of gases;

$K.E \propto T$ or $K.E = kT$

Then $PV = \frac{2}{3}NkT$

But from $n = \frac{N}{N_A}$; $N = nN_A$

Then $PV = \frac{2}{3}nN_AkT$ (**0.25**)

But $\frac{2N_Ak}{3}$ gives another constant, R (universal molar gas constant)

Hence $PV = nRT$ (Ideal gas equation) (**0.25**)

(c) Equation for the reaction:

$SO_2(g) + 2H_2S \rightarrow 3S(s) + 2H_2O(l)$

From which mole ratio of SO_2 to H_2S is 1:2

Since mole ratio = Volume ratio (Avogadro's law), volume of H_2S reacted twice the volume of SO_2 (**0.5**)

That is V_{H_2S} reacted $= 2V_{SO_2} = 2 \times 10\text{cm}^3 = 20\ \text{cm}^3$ (**0.5**)

But total volume of H_2S was $30\ \text{cm}^3$

Then V_{H_2S} unreacted $= (30 - 20)\ \text{cm}^3 = 10\text{cm}^3$ (**0.5**)

So after the reaction, $10\ \text{cm}^3$ of H_2S will determine the final pressure in the vessel. (**0.5**)

But at s.t.p: $n = \frac{\text{V in cm}^3}{22400\ \text{cm}^3/\text{mol}}$ (**0.5**)

Then n_{H_2S} unreacted $= \frac{10\ \text{cm}^3}{22400\ \text{cm}^3/\text{mol}} = \frac{1}{2240}\text{mol}$ (**0.5**)

Also from $P = \frac{nRT}{V}$; (**0.5**)

If V represents final volume (of container),

$V_f = (10 + 30)\text{cm}^3 = 40\ \text{cm}^3 = 0.04\ \text{dm}^3$ (**0.5**)

Then final pressure, $P_f = \frac{n_{H_2S}\ \text{unreacted} \times RT}{V_f}$ (**0.5**)

$$= \frac{1 \times 0.082 \times 273}{2240 \times 0.04}\text{atm}(\mathbf{0.5})$$

$$= 0.25\ \text{atm}$$

Hence the final pressure after the reaction has ended is 0.25atm. (**1**)

Question 4

(a)

(i) Is the process of measuring freezing point depression so as determine molar mass of non – volatile solute. **(0.5)**

(ii) Is the process of measuring boiling point elevation so as to determine molar mass of the non-volatile solute. **(0.5)**

(b) $0.01\text{MBa}_3(\text{PO}_4)_2 < 0.01\text{MLi}_3\text{PO}_4 < 0.01\text{MNa}_2\text{SO}_4 < 0.01\text{MKCl} < 0.01\text{MC}_2\text{H}_5\text{OH}$ **(0.5)**

Reason:

Freezing points of given solutions are lower than that of pure water and the depression varies directly proportional to the number of particle (concentration) of solute formed after ionisation. The number decreases in order of $Ba_3(PO_4)_2$, Li_3PO_4, Na_2SO_4, KCl and finally C_2H_5OH which does not ionise at all and hence the freezing points of solutions follow the reverse order. **(1.5)**

(c)

(i) Non-volatile ions and compounds present in the water in the beef lower the freezing point of the beef below −1 °C. (**1**)

(ii) Unlike glycerine which is non-electrolyte (covalent), NaCl being strong ionic (electrolyte) ionises almost completely to give twice as much as its number of moles.**(1)**

(d)

(iii) Using freezing point depression, $\Delta T = K_f m$

Where $m = \frac{n_{su}}{m_{sv}\ \text{in kg}} = \frac{m_{su}}{M_{su} \times m_{sv}\ \text{in kg}}$

Then $\Delta T = \frac{K_f \times m_{su}}{M_{su} \times m_{sv}\text{in kg}}$ $(\mathbf{1.5})$

Where:

m_{su} = mass of solute = 22.5g

M_{su} = molar mass of solute = 342g/mol

m_{sv} = mass of solvent = 450g = 0.45kg

Substituting $\Delta T = \frac{1.86 \times 22.5}{342 \times 0.45}°\text{C} = 0.27°\text{C}$**(1.5)**

Then the freezing point, $T_f = 0°C - \Delta T = (0 - 0.27)°C = -0.27°C$
Then freezing point of solution is $-0.27°C$ **(1)**

(iv) The potassium chloride solution has **larger** freezing point than cane sugar solution and hence the ice **will first separate in the potassium chloride solution. (1)**

Question 5

(a)

(i) With the limited(small) amount of carbon dioxide, calcium hydroxide forms insoluble calcium carbonate which dissolves when the carbon dioxide present in excess due to the formation of soluble calcium bicarbonate. **(0.5)**

That is $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$ **(0.5)**
Then $CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$ **(0.5)**
(Or $Ca(OH)_2 + 2CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$)

(ii) With concentrated HNO_3, aluminium forms very thin insoluble layer of Al_2O_3 over surface of the metal. The impervious protective oxide layer prevents further reaction between the aluminium and the acid. (**1**)

$$4Al + 12HNO_3(conc) \rightarrow 2Al_2O_3 + 12NO_2 + 6H_2O \ (\mathbf{0.5})$$

(iii) Potassium nitrate undergoes thermal decomposition into its corresponding nitrite while magnesium nitrate having higher degree of polarisation its nitrate undergoes further decomposition to give nitrogen dioxide which appears as brown fumes. **(1)**

$$\text{That is } 2KNO_3 \underset{\Delta}{\rightarrow} 2KNO_2 + O_2 \ \mathbf{(0.25)}$$
$$\text{While } 2Mg(NO_3)_2 \underset{\Delta}{\rightarrow} 2MgO + 4NO_2 + O_2 \ \mathbf{(0.25)}$$

(iv) In aqueous solution, $CuSO_4$ undergoes cationic hydrolysis resulting to the formation of acidic solution which is responsible for evolving CO_2 gas from the bicarbonate and the gas appears as effervescence of colourless gas. **(1)**

$$CuSO_4 + 2H_2O \rightarrow Cu(OH)_2 + 2H^+ + SO_4^{2-}$$
$$\text{Then } 2H^+ + 2HCO_3^- \rightarrow 2CO_2 + 2H_2O \quad (\mathbf{0.5})$$

(b)

(i) To **ensure complete oxidation** of iron to $FeCl_3$ whereby neither undecomposed iron remains nor incomplete oxidation of iron to undesired $FeCl_2$ occurs. **(1)**

(ii) To avoid hydrolysis of the iron (III) chloride whereby iron (III) hydroxide would be formed. **(1)**

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

(c)

1. In the production of sodium and chlorine by Downs' process **(0.5)**
2. In the production of sodium hydroxide by chlor-alkali process **(0.5)**
3. In production of hydrogen chloride gas **(0.5)**
4. In dehumidifiers and air conditioning **(0.5)**
5. In agricultural fertilizer **(0.5)**

Remark: Any four uses with maximum score of 4 marks.

Question 6

(a) The total energy change resulting from a chemical reaction is dependent only on the initial and final state of reactants and is independent of the routes. (**1**)

(b)

(i) It is wrong to use the phrase “heat change” instead of “heat evolved”. **(0.5)**

Explanation
Using the word “change” which actually may be positive or negative change, implies that the combustion may be either endothermic or exothermic which is not correct because combustions are commonly exothermic. **(0.75)**

(ii) It is wrong to exclude the phrase “one mole” (of water) in the definition. **(0.5)**

Explanation
The amount of heat evolved in the neutralisation reaction depends on the amount of acid and base reacted and hence the amount of water produced. To make the data uniform enthalpy of neutralisation is always given per one mole of water.**(0.75)**

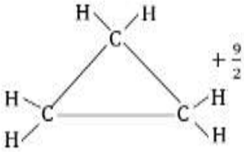
(iii) It is wrong to state “one mole of hydrogen” instead of “one mole of unsaturated compound”.

Explanation
Enthalpy of hydrogenation is always given per one mole of the compound that has undergone complete hydrogenation. One mole of compound like alkyne need two moles of H_2 for its complete combustion, so defining the enthalpy of hydrogenation in terms of one mole of H_2 will correspond to 0.5 mole of the alkyne which is not correct. **(0.75)**

(v) It is wrong to give a definition with an idea that “any valence electron” is removed during ionisation instead of the idea of an electron which is least tightly (most loosely) held by nuclear attractive force.

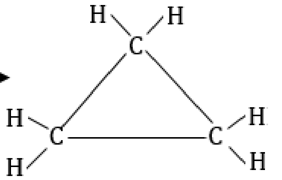
Explanation
Two different valence electrons in an atom may require different amount of energy during the ionisation. For example, boron has 3 valence electrons with outermost electronic configuration of $2S^2 2P_x^1$ whereby smaller amount of energy is required to remove $2P_x$ electron than 2s electron and hence (first) ionisation energy of boron reflect the energy required to remove the $2P_x$ electron and not any valence electron. **(0.75)**

(c) Chemical equation to show combustion of cyclopropane



$+\frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O$ **(0.5)**

Using $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$ **(0.25)**
$\Delta H_c(C_2H_6) = 3\Delta H_f(CO_2) + 3\Delta H_f(H_2O) - 3\Delta H_f(C_2H_6) - \frac{9}{2}\Delta H_f(O_2)$ **(0.25)**
But:
$\Delta H_c(\text{Carbon}) = \Delta H_f(CO_2) = -393.5$ kJ/mol **(0.25)**
$\Delta H_c(\text{Hydrogen}) = \Delta H_f(H_2O) = -286$ kJ/mol **(0.25)**
$\Delta H_f(O_2) = 0$
Substituting: $-2091 = (3 \times -393.5) + (3 \times -286) - \Delta H_f(C_3H_6)$
From which $-\Delta H_f(C_3H_6) = 52.5$ kJ/mol **(0.5)**
The chemical equation to show the formation of cyclopropane

$3C_{(s)} + 3H_{2}{}_{(g)} \longrightarrow$  **(0.5)**

In reactants side:

(3×720) kJ/mol = 2160kJ/mol was absorbed in sublimating 3 moles of C. **(0.5)**

(3×432)kJ/mol = 1296 kJ/mol was absorbed in dissociating 3 moles of H_2. **(0.5)**

In products side:

(6×414) kJ/mol = 24 kJ/mol was released in forming six C − H bond. **(0.5)**

Unknown energy was released in forming three C − C bonds.

Thus: Total energy absorbed in the reactants side

= (2160 + 1296) kJ/mol = 3456 kJ/mol

Total energy released in the product side = 2484 + 3(C − C)

Then using:

ΔH_r = Total heat absorbed in reactants side − Total heat released in products side

52.5 kJ/mol = (3456 − 2484) kJ/mol −3(C − C) **(0.5)**

From which; C − C = 306.5 kJ/mol

The mean C − C bond energy is 306.5 kJ/mol **(0.5)**

Question 7

(a)

(i) When a reaction has (almost) zero heat of the reaction. **(0.5)**

(ii) No scenario. **(0.5)**

(iii) **First scenario:** When the reaction does not involve gas. **(0.5)**

Second scenario: When reaction (even if it is involving gases) is not accompanied with change of number of gas particles. **(0.5)**

(b)

(i) $K_c = \frac{[CO_2]^4}{[C_2H_6]^2[O_2]^7}$ **(0.5)**

$K_p = \frac{(P_{CO_2})^4}{(P_{C_2H_6})^2(P_{O_2})^7}$ **(0.5)**

(ii)

$K_p = \frac{(P_{CO_2})^4}{(P_{C_2H_6})^2(P_{O_2})^7}$ **(0.5)**

But from ideal gas equation; P = [ ]RT

Then $K_p = \frac{([CO_2]RT)^4}{([C_2H_6]RT)^2([O_2]RT)^7}$ **(0.5)**

$K_p = \frac{[CO_2]^4}{[C_2H_6]^2[O_2]^7} \times (RT)^{4-(2+7)}$ **(0.5)**

But $\frac{[CO_2]^4}{[C_2H_6]^2[O_2]^7} = K_c$

Hence $K_p = K_c(RT)^{-5}$ **(0.5)**

(c)

- Once equilibrium has been attained the concentration of carbon dioxide gas (CO_2) remain unchanged and hence the pressure become constant. **(1)**
- The current of blown air displace $CO_2(g)$ from the line kiln thus removing the carbon dioxide and hence the position of chemical equilibrium will shift to the right by producing more quick lime CaO. **(1)**

Mass of $CaCO_3$ decomposed $= \frac{70}{100} \times 20g = 15g$ **(0.5)**
But from the mole ratio of the given reaction equation, 100g (1mol) of decomposed $CaCO_3$, gives 44g (1mol) of $CO_2(g)$;
Thus 15g of decomposed $CaCO_3$ gives $\frac{15\times44}{100}g = 6.6g$ of $CO_2(g)$ **(0.5)**
From ideal gas equation;

$$PV = nRT$$

From which;

$$P = \frac{nRT}{V} = \frac{mRT}{M_rV}$$

It follows that;

$$P_{CO_2} = \frac{6.6\times0.082\times1000}{44\times15}atm = 0.82atm \ \textbf{(1)}$$

But from the given reaction equation;

$$K_p = P_{CO_2} = 0.82atm$$

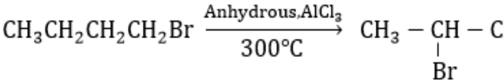
The value of K_p is 0.82atm **(1)**

Question 8

(a)

(i) Is the organic reaction whereby atoms or group of atoms rearrange themselves in the molecule under influence of reagent or condition resulting to the formation of new compound with the same atomic composition as the original one. (**0.5**)

Example:



$$CH_3CH_2CH_2CH_2Br \xrightarrow[300°C]{Anhydrous, AlCl_3} CH_3-\underset{\substack{|\\ Br}}{CH}-CH_2CH_3$$

(**0.5**)

(ii) Are organic compounds in the same homologous series with the same molecular formula but differ in the nature of alkyl groups attached to polyvalent atom of functional group. (**0.5**)

Example:
$CH_3-O-CH_2CH_3$ and $CH_3CH_2-O-CH_2CH_3$ (**0.5**) are metamers.

(b) There are two possible structures of X.

First structure:
$CH_2 = C(CH_3)CH_2CH_3$
Name: 2-methylbut-1-ene **(1)**
Second structure:
$(CH_3)_2C = CHCH_3$
Name: 2-methybut-2-ene **(1)**
Y is hydrogen bromide **(1)**
Z is water-sulphuric acid mixture **(1)**
W is hydrogen chloride **(1)**

(c) Unbranched alkene with molecular formula of C_4H_8 may have one of the following structures :

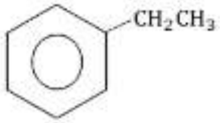
(i) $CH_3CH = CHCH_3$(2 − butene) **(0.5)**

(ii) $CH_3CH_2CH = CH_2$(1 − butene) **(0.5)**

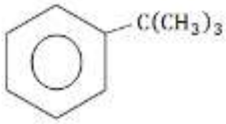
Thus A may be either 2-butene or 1-butene
On addition of bromine water, 2-butene gives;
$CH_3CH(OH)CHBrCH_3$ while 1 − butene gives $CH_3CH_2CH(OH)CH_2Br$ **(1)**
Thus B may be either $CH_3CH(OH)CHBrCH_3$ or $CH_3CH_2CH(OH)CH_2Br$ **(0.5)**
Dehydration of $CH_3CH(OH)CHBrCH_3$ gives either
$CH_2 = CHCHBrCH_3$or $CH_3CH = CBrCH_3$ **(1)**
Neither $CH_2 = CHCHBrCH_3$nor $CH_3CH = CBrCH_3$ gives propanal on ozonolysis. Thus B cannot be $CH_3CH(OH)CHBrCH_3$ **(1)**
Dehydration of $CH_3CH_2CH(OH)CH_2Br$ gives either $CH_3CH_2CH = CHBr$ which gives propanal upon ozonolysis or $CH_3CH = CHCH_2Br$ which gives ethanal upon ozonolysis.**(1)**
Thus B must be $CH_3CH_2CH(OH)CH_2Br$ which comes from 1-butene (A) **(0.5)**
Hence:
A is 1- butene with the structure, $CH_3CH_2CH = CH_2$ **(0.5)**
B is bromoalcohol with the structure, $CH_3CH_2CH(OH)CH_2Br$ **(0.5)**
C is bromoalkene with the structure, $CH_3CH = CHCH_2Br$ **(0.5)**
D is bromoalkene with the structure, $CH_3CH_2CH = CHBr$ **(0.5)**

Question 9

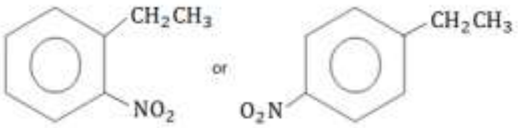
(a) Structure of A



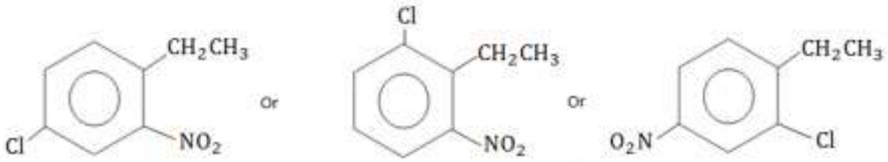
Structure of E



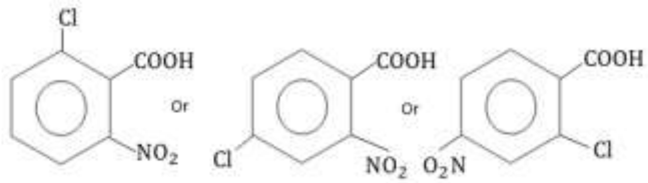
Structure of B



Structure of C



Structure of D

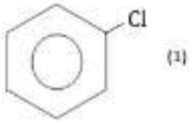


Structure of F

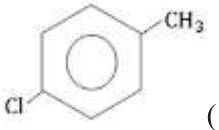
Structure of G

(b)

(i) Benzene gives:

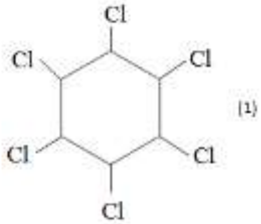


Toluene gives:

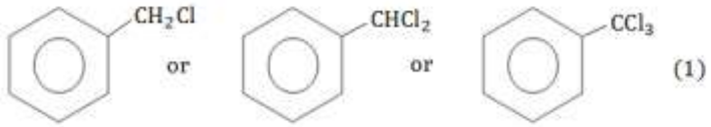


(1)

(ii) Benzene gives:



Toluene gives:



(c)

(i)

1. Preparation of alcohol **(0.5)**

   Example:

   $CH_3CH_2Cl + NaOH(aq) \xrightarrow[25℃]{} CH_3CH_2OH + NaCl$ **(0.5)**

2. Preparation of amine **(0.5)**

Example:

$CH_3CH_2Cl + NH_3 \xrightarrow{\text{Alcohol,Heat}} CH_3CH_2NH_2 + HCl$ **(0.5)**

3. Formation of ester

   Example: $CH_3CH_2COOAg + CH_3CH_2Cl \longrightarrow CH_3CH_2COOCH_2CH_3 + AgCl$ **(0.5)**
4. Formation of ether **(0.5)**
   Example:
   $CH_3CH_2Cl + CH_3CH_2ONa \longrightarrow CH_3CH_2OCH_2CH_3 + NaCl$ **(0.5)**

(ii)
1. They are carcinogens. **(0.5)**
2. They are environmental pollutant. **(0.5)**

Question 10

(a)
(i) Is the interchange between an anion in a soil solution and another anion on the surface of sesquioxide clay at low pH. **(0.5)**
(ii) Is the maximum quantity of total cations, of any class, that a soil is capable of holding at a given pH value, available for exchange with soil solution. **(0.5)**
(iii) Is any organic or inorganic material of natural or synthetic origin (other than liming materials) that is added to a soil to supply one or more plant nutrients essential to the growth of plants. **(0.5)**
(iv) Is the application of calcium and magnesium rich materials with anions capable of producing hydroxide ions (OH^-) to neutralize acidity of the solution. **(0.5)**

(b) $H^+$from soil reacts with OH^- from NaOH according to the following equation:

H^+(aq) (aq)+ OH^- (aq)→ H_2O **(0.5)**
Number of moles of NaOH = Number of moles of OH^-
$= \frac{10}{100} \times 0.1 = 1 \times 10^{-3}$mol**(0.5)**
But from above equation, mole ration of H^+ to OH^- is 1:1
Then number of moles of exchangeable H^+ from 5g of oven dry soil was 1×10^{-3}mol $= 1$mmol**(0.5)**
Using, number of meq =number of mol × ammount of ionic charge**(0.5)**
Number of meq of H^+= 1× 1meq = 1meq per 5g of oven dry soil **(0.5)**
And number of meq per 100g of oven dry soil $= \frac{1\times100}{5}$ meq = 20meq**(0.5)**
Thus number of acidic cations = 20meq/100g oven dried soil **(0.5)**
But number of base cations + number of acidic cations = CEC of the soil**(0.5)**
Then number of base cation +20meq = 25meq
From which; number of base cation =(25-20)meq = 5meq**(0.5)**
Using: percentage base saturation $= \frac{\text{number of base cation}}{\text{CEC of the soill}} \times 100\%$**(0.5)**
$= \frac{5}{25} \times 100\%^{(\mathbf{0.5})} = 20\%$

(i) Hence the percentage base saturation of the soil sample is 20%**(0.5)**

From (i) above concentration of H^+ is 20meq/100g oven dried soil
Then the number of meq in 75g of oven dried soil $= \frac{75}{100} \times 20$ meq $= 15$meq

(ii) Hence the concentration of H^+in 75g of oven dried soil is 15meq **(1)**
(iii) The soil is acidic and therefore liming is required. **(1)**

(c)

(i) Ozone layer is the thin part of stratosphere which consist of elemental oxygen in the form of trioxygen molecules. It filters (absorbs) harmful ultraviolet radiations from sunlight which are highly energetic and would damage both plants and animals exposed to it on the Earth's surface. **(2)**

(ii)

3. Increased rate of skin cancer **(0.75)**
4. Increased rate of eye cataracts **(0.75)**
5. Weakening of immune system **(0.75)**
6. Damage to crops **(0.75)**
7. Reduction in primary products (plankton) in the ocean **(0.75)**

Remark: Any four effects with maximum score of 3 marks.

Solutions Examination Twelve
CHEMISTRY 2F

Question 1

(a)

(i) Decrease in concentration makes the solution more ideal while increase in concentration makes the solution to deviate more from ideal behaviour. **(1)**

(ii) If the intermolecular forces in the solution are similar to intermolecular forces in pure components the solution will be more ideal while different intermolecular forces in the solution compared to those present in the pure components makes the solution to show greater deviation from ideal behaviour. **(1.5)**

(b)

(i) The Van't Hoff's factor approaches the ideal value when the salt undergoes complete ionisation. $FeCl_3$ having higher degree of polarisation as result of greater polarising power of smaller sized and higher changed Al^{3+} than Na^+in NaCl, is more covalent in character and hence it has lower degree of ionisation than NaCl. **(1.5)**

(ii) The Van't Hoff's factor is large when the degree of dissociation (or ionisation) is large too. When the solution is more concentrated, the degree of dissociation is lowered and therefore the Van't Hoff's factor becomes smaller. **(1.5)**

(iii) Whether is through formation of precipitate of lead (II) chloride whereby two moles of chloride ions form one mole of lead (II) chloride precipitate or through formation of complex whereby four moles of chloride ions form one mole of complex ($[PbCl_4]^{2-}$), the introduction of lead (II) ions decreases number of solute particles which means less lowering in vapour pressure and hence increase in vapour pressure.**(1.5)**

(c)

(i) Not ideal solution. **(0.5)**

Explanation
An ideal solution would have a vapour pressure at any mole fraction of H_2O between that of pure propanol and pure water (between 74torr and 71.9torr). The vapor pressures of the solution are not between these limits so it is not an ideal solution. **(1)**

(ii) From the data, the vapour pressures of the various solutions are greater than in the ideal solution (positive deviation from Raoult's law). This occurs when the intermolecular forces in solution are weaker than the intermolecular forces in pure solvent and pure solute. This will cause the solution making process endothermic (positive) and hence the enthalpy of solution (ΔH_{soln}) will be positive. **(1.5)**

(iii) Weaker **(0.25)**

Explanation
The interactions between propanol and water molecules are weaker than between the pure substances since the solution exhibits a positive deviation from Raoult's law. **(0.75)**

(iv) When $X_{H_2O} = 0.54$ the vapour pressure is highest as compared to the other solutions. Since a solution boils when the vapour pressure of the solution equals the external pressure, then the solution with $X_{H_2O} = 0.54$ should have the lowest normal boiling point; this solution will have a vapour pressure equal to 1 atm at a lower temperature as compared to the other solutions. **(1.5)**
Special name: Azeotropic mixture (minimum boiling azeotrope). **(0.5)**

(d) $n_{Acetone} = \frac{50g}{58gmol^{-1}} = 0.862mol$ **(0.5)**

$n_{Methanol} = \frac{50g}{32gmol^{-1}} = 1.5625mol$ **(0.5)**

$n_T = n_{Acetone} + n_{Methanol} = 2.4245mol$

$X_{Acetone} = \frac{n_{Acetone}}{n_T} = \frac{0.862mol}{2.4245mol} = 0.36$ **(0.5)**

$X_{Methanol} = \frac{n_{Methanol}}{n_T} = \frac{1.5625mol}{2.4245mol} = 0.64$ **(0.5)**

From Raoult's law;

$P_{soln} = X_{Acetone}P^{\circ}_{Acetone} + X_{Methanol}P^{\circ}_{Methanol}$ **(0.5)**

$= 0.36 \times 271torr + 0.64 \times 143torr$ **(0.5)**

$= 189.08torr$

The vapour pressure of the solution is approximately 189torr (0.5)

$$X^V_{Acetone} = \frac{X_{Acetone}P^{\circ}_{Acetone}}{P_{soln}} = \frac{0.36 \times 271torr}{189torr} \quad (\mathbf{0.5})$$

$= 0.52$ **(0.5)**

And $X^V_{Methanol} = 1 - X^V_{Acetone}$ **(0.5)**

$= 1 - 0.52 = 0.48$ **(0.5)**

The vapour composition for acetone and methanol in terms of mole fractions are 0.52 and 0.48 respectively. (1)

Explanation on the discrepancies:

The observed vapour pressure is smaller than the calculated vapour pressure from Raoult's law suggesting that the solution shows negative deviation from Raoult's law. **(1)**

Question 2

(a)

(i) Collision frequency is the number of collisions between particles per second.(**0.5**)

Remarks:

1. The definition; *Is the term used to express the rate of collision between particles,* is acceptable.
2. **"….per unit time"** instead of, "….per **second**" can be used.

(ii) Effective collision is the collision between proper oriented reacting particles with enough energy to overcome activation energy. (**0.5**)

(iii) Collision energy is the combined energy of colliding particles. (**0.5**)

(iv) Activation energy is the minimum amount energy required to activate atoms or molecules to a state in which they can undergo chemical reaction. (**0.5**)

Remark: The definition; *Is the minimum energy required for the reaction to take place,* is **not** acceptable. (That is the definition of **threshold energy, not** activation energy).

(b) The rate law of the **slowest step** (step 2) which is the **rate determining step** is; (**0.5**)

$R = k_3[N_2O_2][O_2]$ (**1**)

Eliminating the intermediate, N_2O_2 ($[N_2O_2]$) so as to get the rate law of the overall reaction by using the fact that: $k_1[NO]^2 = k_2[N_2O_2]$ ($R_b = R_f$ for rapid equilibrium in step 1 (fast step)) (**1**)

From which $[N_2O_2] = \frac{k_1}{k_2}[NO]^2$ (**0.5**)

Thus $R = \frac{k_3 \times k_1}{k_2}[NO]^2[O_2]$ (**0.5**)

But $\frac{k_3 \times k_1}{k_2}$ gives another modified constant, k(**0.5**)

Hence $R = k[NO]^2[O_2]$ and the proposed mechanism is consistence with the given rate equation. (**1**)

(c) **No;** reactions with large equilibrium constant are not necessary to be very fast. (**0.5**)

Reason:
Equilibrium constant is the measure of relative concentration of reactants and products at equilibrium. So even slow reactions with greater concentration of products than that of reactants have large equilibrium constants. (**1.5**)

(d)

(i) Galvanization **(0.25)**

In this method, iron is covered with another metal like zinc which form protective layer to prevent iron from rusting. The protective metal must be stronger reducing agent than iron for the method to be more efficient. **(0.75)**

(ii) Cathodic protection **(0.25)**

In this method iron is connected to more reactive metal like magnesium and zinc whereby the iron (weaker reductant) acts as cathode while the more reactive metal (stronger reductant) acts as anode of the galvanic cell. In this galvanic cell arrangement, iron behaving as cathode will not get oxidized and hence it is prevented from rusting. **(0.75)**
Remark: Any two well explained methods are acceptable.

(e) From Kohlrausch's law:

$\Lambda_\infty(\text{AgCl}) = \Lambda_\infty(\text{AgNO}_3) + \Lambda_\infty(\text{NaCl}) - \Lambda_\infty(\text{NaNO}_3)$ (**0.5**)
Substituting:
$\Lambda_\infty(\text{AgCl}) = (116.5 + 110.3 - 105.22)\Omega^{-1}\text{cm}^2\text{mol}^{-1}$
$= 121.6\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (**0.5**)
Using: $K_{(\text{solution})} = K_{(\text{AgCl})} + K_{(H_2O)}$ (**0.5**)
From which;
$K_{(\text{AgCl})} = K_{(\text{solution})} - K_{(H_2O)}$
$= (2.4 - 1.16) \times 10^{-6}\Omega^{-1}\text{cm}^{-1} = 1.24 \times 10^{-6}\Omega^{-1}\text{cm}^{-1}$ (**1**)
But for sparingly soluble substance like AgCl;
Molar conductivity at infinite dilution= Molar conductivity of saturated solution
$= 121.6\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (**0.5**)
Then using $\Lambda_m = KV$;
$V = \frac{\Lambda_m}{K}$ (**0.5**)
$= \frac{121.6}{1.24\times10^{-6}}\text{cm}^3\text{mol}^{-1} = \frac{121.6}{1.24\times10^{-6}\times1000} = 98064.516\text{dm}^3\text{mol}^{-1}$(**0.5**)
Using $[\quad] = \frac{1}{V}$;
Then molar solubility of AgCl
$= \frac{1}{98064.516}\text{moldm}^{-3} = 1.0197 \times 10^{-5}\ \text{moldm}^{-3}$(**1**)
And its solubility = Molar solubility × Molar mass
$= 1.0197 \times 10^{-5} \times 143.5\ \text{gdm}^{-3}$ (**0.5**)
$= 1.4633 \times 10^{-3}\ \text{gdm}^{-3}$

Thus solubility of AgCl is 1.4633×10^{-3} gdm^{-3} (**0.5**)
Also $\text{AgCl(s)} \rightleftharpoons \text{Ag}^{+}\text{(aq)} + \text{Cl}^{-}\text{(aq)}$
Thus $K_{sp} = [\text{Ag}^{+}][\text{Cl}^{-}]$ (**0.5**)
But from stoichiometry of thee above equation:
Molar solubility of AgCl $= [\text{Ag}^{+}] = [\text{Cl}^{-}]$ (**0.5**)
Hence $K_{sp} = (1.0197 \times 10^{-5})^{2}$ **(0.5)**
$= 1.0398 \times 10^{-10}\ \text{mol}^{2}\text{dm}^{-6}$
Thus solubility product of AgCl is $1.0398 \times 10^{-10}\ \text{mol}^{2}\text{dm}^{-6}$ (**0.5**)

Question 3

(a)
(i) Is the solution which can maintain its pH value on addition of **small amount** of acid or base. (**1**)
(ii) Is the relative ability of buffer solution to resist pH change on addition of acid or base. (**1**)
(iii) Is the range of pH at which a buffer solution can maintain its pH value on addition of small amount of acid or base. (**1**)
(iv) Is the reagent which is completely used in the reaction and therefore determine the amount of product formed. (**1**)

(b) Given that:

Volume of CaCl_2 = Volume of $\text{Na}_2\text{CO}_3 = \text{Vdm}^3$
Then using $n = MV$;
Number of moles of $\text{CaCl}_2 = 0.1\text{V mol}$ (**0.25**)
Number of moles of $\text{Na}_2\text{CO}_3 = 0.1\text{V mol}$ (**0.25**)
Na_2CO_3 reacts with CaCl_2 to give CaCO_3 according to the following equation:
$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$ (**0.5**)
From which mole ratio is 1:1 and because number of moles of CaCl_2 is equal to the number of moles of Na_2CO_3 (0.1V mol); nothing present in excess (**0.5**)
Also from the reaction equation; mole ratio of CaCl_2 (or Na_2CO_3) to CaCO_3 is 1: 1; thus number of moles of CaCO_3 produced was also 0.1V mol. (**0.5**)
Using $[\ ] = \frac{n}{V}$;
Number of moles of CaCO_3 produced in 1 dm^3 of the solution

$$= \frac{0.1\ \text{V mol}}{(\text{V+V})\text{dm}^3} = 0.05\ \text{moldm}^{-3}\ (\mathbf{0.5})$$

Then using mass concentration in gdm^{-3} = Molar concentration × Molar mass
Mass of solid CaCO_3 produced (just before being dissolved in the solution)

$$= 0.05 \times 100 = 5\ \text{gdm}^{-3}\ (\mathbf{0.5})$$

The produced CaCO_3 dissolves only slightly according to the following equation:

$$\begin{array}{lll} \text{CaCO}_3\text{(s)} \rightleftharpoons & \text{Ca}^{2+}\text{(aq)} + & \text{CO}_3^{2-}\text{(aq)} \\ & x & x\ \ (\mathbf{0.5}) \end{array}$$

where x is the molar solubility of CaCO_3
Then using $K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = x^2$ (**0.5**)
From which $x = \sqrt{K_{sp}} = \sqrt{1.69 \times 10^{-8}\text{mol}^2\text{dm}^{-6}} = 1.3 \times 10^{-4}\text{moldm}^{-3}$ (**0.5**)
Then using mass solubility = Molar solubility × Molar mass
Mass solubility of $\text{CaCO}_3 = 1.3 \times 10^{-4} \times 100 = 0.013\ \text{gdm}^{-3}$ (**0.5**)
And thus mass of the precipitation in 1dm^{-3} of the solution $= (5 - 0.013)\text{gdm}^{-3}$ (**0.5**)

$$= 4.987\text{gdm}^{-3}$$

Hence the mass concentration of $CaCO_3$ precipitate $4.987gdm^{-3}$ (**0.5**)

(c) Since HCOOK contain weak acid cation (K^+) and strong base anion (CH_3COO^-), undergoes **anionic salt hydrolysis**$^{(0.5)}$ whose $[H_3O^+]$ is given by the following equation:

$[H_3O^+] = \sqrt{\frac{K_aK_w}{[salt]}}$ (**0.5**)
Where $K_a = \log^{-1}(-pK_a) = 2.4 \times 10^{-4}$ (**0.25**)
$K_w = 1 \times 10^{-14}$
$[salt] = [HCOOK] = 0.001M$ (**0.25**)
$[H_3O^+] = \sqrt{\frac{2.4\times10^{-4}\times10^{-14}}{0.001}}\,(\mathbf{0.5}) = 5.01 \times 10^{-8}M$
Hence the concentration of $H_3O^+$is $5.01 \times 10^{-8}M$ (**1**)

(d) Reaction equation: $NH_4OH + HCl \rightarrow NH_4Cl + H_2O$ **(0.5)**

From which mole ratio of NH_4OH to HCl is 1:1 (**0.5**)
Then because$[NH_4OH] = [HCl]$, at neutralization point; equal volume of NH_4OH and HCl must be used. (**0.5**)
Thus
Volume of $NH_4OH(aq)$ = Volume of $HCl(aq) = Vdm^3$
And $n_{NH_4OH} = n_{HCl} = 0.01Vmol\ (n = MV)$ (**1**)
But mole ratio of NH_4OH(or HCl) to NH_4Cl is 1:1
Thus number of moles of NH_4Cl produced was also $0.01Vmol$ (**1**)
The produced NH_4Cl contain strong acid cation and weak base anion and therefore undergo **cationic salt hydrolysis**$^{(0.5)}$ whose pH value is given by the following equation:
$pH = -\log\sqrt{K_h[salt]}$ (**0.5**)
where $K_h = K_a$ of $NH_4^+ = 5.7 \times 10^{-10}moldm^{-3}$ (**0.5**)
And $[salt] = \frac{\text{Number of moles of } NH_4Cl}{\text{Total volume of solution}} = \frac{0.01Vmol}{(V+V)dm^3} = 0.005\ moldm^{-3}$ (**1**)
Then $pH = -\log\sqrt{5.7 \times 10^{-10} \times 0.005}\,(\mathbf{0.5})$
$= 5.77$
Hence pH at the neutralization point is 5.77 **(0.5)**

Question 4

(a)
(i) Properties of elements are periodic function of their atomic numbers. **(1)**
(ii) When elements are arranged in the increasing order of their atomic masses, the eighth element resembles the first in physical and chemical properties. **(1)**
(iii) When elements are arranged in the increasing order of their atomic masses, the eighth element resembles the first in physical and chemical properties. **(1)**

(b)
(i) Atomic radius

Across the period: Generally atomic radius decreases as you go across the period (from left to right) due to increase in nuclear attractive force as result of increase of number of protons (nuclear charge) while number of shells and hence screening effect remain constant. **(1)**
Down the group: Atomic radius increases as you descend the group due to increase in screening effect as result of an increase in number of shells in the same trend. **(1)**

(ii) Ionization energy

Across the period: Generally ionisation energy increases as you go across the period from left to right due to the increase in nuclear charge as result of an increase in number of protons and hence the outer electron(s) become more strongly attracted as you go in the same direction. **(1)**

Down the group: Generally ionisation energy decreases as you descend the group due to increase in distance of the most loosely electron from the nucleus and increase in screening effect as result of an increase in number of shells in the same direction. **(1)**

(iii) Electronegativity

Across the period: As you go across the period from left to right, the electronegativity increases due to increase in the size of nuclear charge as result of an increase in number of protons in the same direction. (1)

Down the group: As you go down a group, electronegativity decreases due to an increase in distance from the nucleus of an atom to the bonding pair of electrons and an increase in screening effect as result of an increase in number of inner electrons in the same direction. **(1)**

(iv) Electron affinity

Across the period: Generally electron affinity increases as you go gross the period from left to right due to decrease in atomic size and increase in effective nuclear attractive force in the same direction. **(1)**

Down the group: Generally first electron affinity decreases on descending the group due to increase in atomic size and increase in screening effect in the same direction. **(1)**

(c)

(vi) Lithium being on the top of group IA has smallest cationic radius and therefore greatest polarizing power. This makes compounds of lithium to have greater degree of polarisation and hence more covalent in characters than compounds of other elements in the group. **(1)**

(vii) On heating $MgCl_2$ undergo partial hydrolysis with water molecules (steam) to be removed yielding basic magnesium chloride and hydrogen chloride gas. (**1**)

$$MgCl_2 \bullet 6H_2O \underset{\Delta}{\rightarrow} Mg(OH)Cl + HCl + 5H_2O \quad (\mathbf{0.5})$$

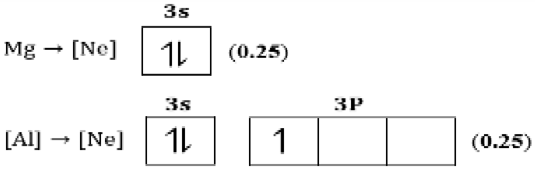
(viii) In aqueous solution, $CuSO_4$ undergoes cationic hydrolysis resulting to the formation of acidic solution which is responsible for evolving CO_2 gas from the bicarbonate and the gas appears as effervescence of colourless gas. **(1)**

$$CuSO_4 + 2H_2O \rightarrow Cu(OH)_2 + 2H^+ + SO_4^{2-}$$
$$\text{Then } 2H^+ + 2HCO_3^- \rightarrow 2CO_2 + 2H_2O \quad (\mathbf{0.5})$$

(ix) Li^+ being smaller than Na^+, has greater polarising power and therefore Li_2CO_3 has greater degree of polarisation making it less thermally stable than Na_2CO_3.(**1**)

$$Li_2CO_3 \underset{\Delta}{\rightarrow} Li_2O + CO_2 \quad (\mathbf{0.5})$$
$$Na_2CO_3 \underset{\Delta}{\rightarrow} \text{No reaction}$$

(x) Consider electronic configuration of Mg and Al:



From above electronic configurations, it can be concluded that first ionisation energy of Al is smaller than that of Mg due to the following reasons:

1. With all of its orbitals paired, Mg has more stable electronic configuration. (**0.5**)
2. The 3s-electron to be removed from Mg experience weaker screening effect than 3p-electron to be removed in Al (**0.5**)
3. The 3p-electron to be removed from Al is of greater distance from the nucleus than the 3s-electron in Mg. (**0.5**)

(xi) HI which would be formed is good reducing agent, thus it oxidised by concentrated H_2SO_4 which has oxidising property to I_2. **(1)**

$NaI + H_2SO_4 \text{ (conc)} \rightarrow NaHSO_4 + HI$
Then $HI + H_2SO_4 \text{ (conc)} \rightarrow H_2S + H_2O + I_2$ **(0.5)**
Thus overall reaction equation becomes;
$NaI + H_2SO_4 \text{ (conc)} \rightarrow NaHSO_4 + H_2O + I_2 + H_2S$

Question 5

(a)

(i) Is the **neutral substance** whose at least one of its ions consists of central atom and several ligands bonded to it by dative bond. **(0.5)**

Remark: It is **inappropriate** to provide the following definition: *Is the one that is formed by central atom and several ligands bonded to it by dative bond.* (That is the definition of complex, not complex (or coordination) compound).

(ii) Is the positively charged specie that consist of central metal atom and several ligands bonded to it by dative bond. **(0.5)**

Remark: The definition; *Is the complex that has net positive charge,* is not allowed.

(b)

(i) Coordination number for **each** complex is 6 (**1**)

Remark: +6 is **not** acceptable. (Coordination number (unlike oxidation number) must be positive. So including the +ve sign, implies that coordination number may be negative which is wrong).

(ii) IUPAC name of $[Fe(SO_4)(NO)_2(CO)Br(OH)]$ is;
bromocarbonylhydroxodinitrosylsulphatoiron (IV) (**1**)

IUPAC name of $[Ni(CN)(H_2O)(C_2O_4)(NH_3)(SO_3)]^{4-}$ is;
ammineaquacynooxalatosulphitonickelate (I) ion (**1**)
Remark: The complex name must appear as a single word.

(iii) Geometrical shape for **each** complex is octahedral (**1**)
(iv) Electronic configuration of Fe^{4+} is $[Ar]3d^4$ (**0.5**)

Electronic configuration of Ni^{+} is $[Ar]3d^7 4s^1$ (**0.5**)
Remarks:

1. Fe^{4+} is the central ion in the first complex.

2. Ni^+ is the central ion in the second complex.
3. **Accept** $[Ar]4s^13d^7$ for Ni^+
4. **Accept** $[Ar]3d^44s^0$ or $[Ar]4s^03d^4$ for Fe^{4+}.

(c)

(i) In concentrated hydrochloric acid, there is enough concentration of Cl^- to form soluble complex with Pb^{2+} and hence $PbCl_2$ appears to dissolve in the concentrated hydrochloric acid (**0.5**)

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ ………… (i) **(0.25)**
Insoluble
Then $Pb^{2+}(aq) + 4Cl^-(aq) \rightarrow [PbCl_4]^{2-}(aq)$…...(ii)**(0.25)**
Where the formation of the complex in (ii) is equivalent to removal of Pb^{2+} in equilibrium (i) and therefore the position of the equilibrium (i) will shift to the right hand side by dissolving more $PbCl_2$ (**0.5**)

(ii) In aqueous solution, copper (II) sulphate exists in complex form as $[Cu(H_2O)_4]SO_4$.

In small amount of ammonia solution, the complex undergoes ligand substitution reaction with OH^- from $NH_3(aq)$ leading to the formation of **neutral complex** which are commonly insoluble and both OH^- and H_2O being **weak ligands** the complex has **light colour** which is pale blue (**0.5**)
$[Cu(H_2O)_4]^{2+} + \quad 2OH^- \rightleftharpoons \quad [Cu(H_2O)_2(OH)_2] + 2H_2O$….(i)
($\downarrow$from $CuSO_4(aq)$)$\downarrow$(from $NH_3(aq)$) Insoluble) (**0.25**)
In large amount of ammonia solution, the tetraaqua complex undergoes ligand substitution reaction with NH_3 to form **complex ion** which are commonly soluble and the NH_3 being **strong ligand,** the complex has **deep colour** which is deep blue. (**0.5**)
$[Cu(H_2O)_4]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2H_2O$ … (ii)
Soluble (**0.25**)
(This second reaction shifts the position of equilibrium in (i) to the left and hence the precipitate appear to dissolve).
Remarks:

1. **Don't allow** the following equation instead of the first chemical equation;

   $CuSO_4(aq) + 2NH_4OH(aq) \rightarrow (NH_4)_2SO_4(aq) + Cu(OH)_2(s)$
   (Although the above equation is correct, it is **inappropriate** because the only way to explain the difference in colour (pale and deep blue colour) is through complex formation).

2. **Accept** the following equation instead of the first chemical equation:

   $[Cu(H_2O)_4]SO_4 + 2NH_4OH \rightleftharpoons [Cu(H_2O)_2(OH)_2] + (NH_4)_2SO_4$

3. **Accept** the following equation instead of the second chemical equation

   $[Cu(H_2O)_4]SO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

(iii) Al^{3+} can form **soluble complex** with solution of NaOH and therefore $Al(OH)_3$ dissolves in it. (**0.5**)

$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$ ……. (i)(**0.25**)
$Al^{3+}(aq) + 4OH^-(aq) \rightarrow [Al(OH)_4]^-$ ……... (ii)(**0.25**)
$\downarrow$
From NaOH(aq) Soluble

The formation of complex in (ii), lowers the concentration of Al^{3+} in the equilibrium of reaction (i) shifting the position of equilibrium to the right hand side by dissolving more $Al(OH)_3(s)$. (**0.5**)
Remark: **Accept** the following chemical equation instead of the second equation;

$$Al^{3+}(aq) + 6OH^-(aq) \rightarrow [Al(OH)_6]^{3-}$$

(iv) In water which is polar solvent, iodine is sparingly soluble due to its covalent characters and large atomic size which makes difficult for it to interact with water molecules.$^{(\mathbf{0.5})}$With solution of KI, iodine forms the complex ion which is soluble (**0.5**)

$$\underset{\text{From KI}}{\overset{}{\underset{\downarrow}{I^-(aq)}}} \quad + \quad I_2 \quad \rightarrow \quad \underset{\text{Soluble}}{[I_3]^-} \quad (\mathbf{0.5})$$

Remark: Accept the following chemical equation instead of the above equation.

$$KI\ (aq) + I_2 \rightarrow K[I_3]$$

(d) Hydrocarbon which does not react with chlorine in dark but reacts under presence of ultra-violet light is alkane.

- Thus P must be alkane (**0.5**)

Alkane which gives only two monochlorinated products is the one with three carbons.

- Thus P must be propane of the following structure (**0.5**)

$CH_3 - CH_2 - CH_3$

Monochlorination of propane may give either 1-chloropropane or 2-chloropropane (**0.5**)

- Thus P and Q may be either 1-chloropropane or 2-chloropropane (**0.5**)

On treatment with aqueous NaOH, 1-chloropropane gives propanol (primary alcohol) which gives carboxylic acid on oxidation (**0.5**)

- Thus S is ethanoic acid and therefore Q cannot be 2-chloropropane, it must be 1-chloropropane (**0.5**)

On treatment with aqueous NaOH, 2-chloropropane gives propan-2-ol which gives ketone on oxidation (**0.5**)

- Thus T is propanone and R is 2-chloropropane (**0.5**)

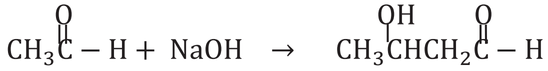
Hence:
Structure of P is $CH_3CH_2CH_3$(**0.5**)
Structure of Q is $CH_3CH_2CH_2Cl$(**0.5**)
Structure of R is $CH_3CH(Cl)CH_3$(**0.5**)
Structure of S is CH_3CH_2COOH(**0.5**)
Structure of T is CH_3COCH_3 (**0.5**)
$2CH_3CH_2CH_3 + 2Cl_2 \xrightarrow{uv} CH_3CH_2CH_2Cl + CH_3CH(Cl)CH_3 + 2HCl$ (**0.5**)
$CH_3CH_2Cl + NaOH(aq) \rightarrow CH_3CH_2OH + NaCl$ (**0.5**)
Then $CH_3CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2COOH + H_2O$(**0.5**)
And $CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$ (**0.5**)

Question 6

(a)

(i) Is the reaction between carbonyl compound with α-hydrogen and alkaline solution to form new compound which has both hydroxyl group and carbonyl group in the same compound. **(0.5)**

Example:

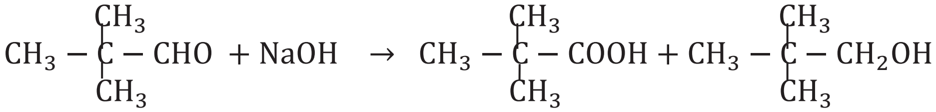


$$CH_3\overset{O}{\overset{\|}{C}}-H+ NaOH \rightarrow CH_3\overset{OH}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}-H$$

(0.5)

(ii) Is the disproportionation reaction which occurs between carbonyl compound without α–hydrogen and alkaline solution to form carboxylic acid and alcohol.**(0.5)**

Example:



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CHO+NaOH \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-COOH+CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2OH$$

(0.5)

(b) The molecular formula, C_3H_8O, suggest that the general molecular formula of $C_nH_{2n+2}O^{(0.25)}$ Thus A may be either alcohol or ether. (**0.25**)

Since A reacts with sodium metal to give hydrogen gas, it cannot be ether; it can be alcohol. (**0.5**)
Evolvement of HCl by PCl_5, confirm that there is OH group in A and therefore A must be **alcohol**$^{(0.25)}$ with the following structural formula:
$CH_3CH_2CH_2OH$ (Structure of A) (**0.25**)
Reaction alcohol (A) with Na give alkoxide. Thus B is the **alkoxide**$^{(0.25)}$ with the following structural formula;
$CH_3CH_2CH_2ONa$ (Structure of B) (**0.25**)
Reaction of alcohol A with PCl_5 gives haloalkane (chloroalkane). Thus C is the **haloalkane**$^{(0.25)}$ with the following structural formula;
$CH_3CH_2CH_2Cl$ (Structure of C) (**0.25**)
Reaction of haloalkane (C) with ZnCl/copper couple in alcohol gives alkane. Thus D is **alkane**$^{(0.25)}$ with the following structural formula:
$CH_3CH_2CH_3$ (structure of D) (**0.25**)
Reaction of haloalkane (C) with Mg in dry ether gives Grignard reagent. Thus E is the **Grignard reagent**$^{(0.25)}$ with the following structural formula:
$CH_3CH_2CH_2MgCl$ (Structure of E) (**0.25**)
Reaction of Grignard reagent (E) with CO_2 gives the following organometallic compound (F)
$CH_3CH_2CH_2C(O)-OMgCl$ (structure of F) (**0.25**)
Acidic hydrolysis of F gives the following **carboxylic acid (0.25)**
$CH_3CH_2CH_2COOH$ (Structure of G) (**0.25**)
Chemical equations:
$2CH_3CH_2CH_2OH+2Na \rightarrow 2CH_3CH_2CH_2ONa+H_2$

(A) **(B)** **(0.5)**

$CH_3CH_2CH_2OH+PCl_5 \rightarrow CH_3CH_2CH_2Cl+POCl_3+HCl$

(A) **(C)** **(0.5)**

$CH_3CH_2CH_2Cl + [H] \xrightarrow{Zn/Cu,,Alcohol} CH_3CH_2CH_3 + HCl$
(C) **(D)** (**0.5**)

$CH_3CH_2CH_2Cl + Mg \xrightarrow{Dry\ ether} CH_3CH_2CH_2MgCl$ (**0.5**)
(A) **(E)**

$CH_3CH_2CH_2MgCl + CO_2 \rightarrow CH_3CH_2CH_2COOMgCl$ (**0.5**)
(E) **(F)**

$CH_3CH_2CH_2COOMgCl + H_2O \xrightarrow{H^+} CH_3CH_2CH_2COOH + Mg(OH)_2Cl$
(F) **(G)** (**0.25**

(ii) $CH_3 - O - CH_2CH_3$ (**0.75**)

Remark: $CH_3 - CH(OH) - CH_3$ is **not** acceptable. Both $CH_3CH_2CH_2OH$ and $CH_3CH(OH) - CH_3$ are alcohols which will react in the same way.

(c)

(i) Acidified $KMnO_4$ is oxidizing agent, it would oxidize the given aldehyde to carboxylic acid. **(1)**

Correction: $CH_3CH_2CHO \xrightarrow{LiAlH_4, Dry\ ether} CH_3CH_2CH_2OH$ **(1)**

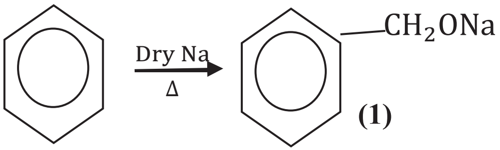
(ii) Carboxylic acid cannot react with alcohol (Esterification) in absence of acidic medium (sulphuric acid). **(1)**

Correction:

$CH_3CH_2COOH \xrightarrow{CH_3OH,H^+} CH_3CH_2COOCH_3$ **(1)**

(iii) Sodium bicarbonate ($NaHCO_3$) cannot react with alcohol because both have similar basic characters. **(1)**

Correction:

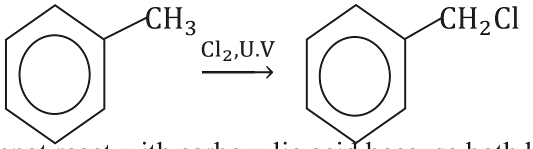


(1)

(iv) Presence of $AlCl_3$ (Lewis acid) favours occurrence of electrophilic substitution reaction in benzene ring (and not free radical substitution reaction in the side chain).**(1)**

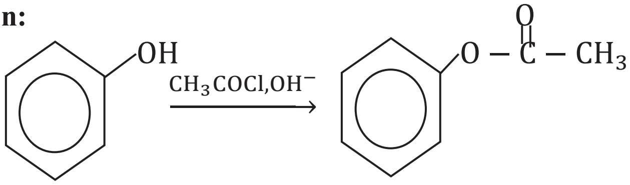
Correction:

(1)



(v) Phenol cannot react with carboxylic acid because both have similar acid characters.**(1)**

Correction:



(1)

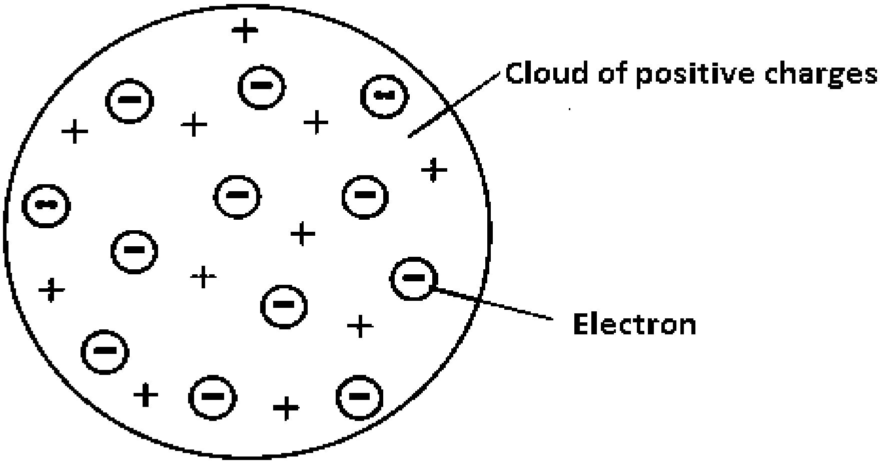
Solutions Examination Thirteen
CHEMISTRY 1G

Question 1

(a)

(i) This is because the model suggested that the atom to be full of some positive fluid like a **pudding** in which electrons were embedded like **plums** on that pudding. **(1)**

(ii) According to Thomson; "An atom possesses a spherical shape in which the positive charge is uniformly distributed with electrons embedded over it" **(0.75)**



(0.75)

(iii)

Advantages:

1. It explains satisfactorily how heating a substance starts radiating light. **(0.75)**
2. It explains neutral character of an atom. **(0.75)**

Disadvantages:

1. It does not explain the stability of an atom. **(0.75)**
2. It is not supported by Rutherford's $\propto -$ scattering experiment. **(0.75)**

Remark: Accept any two correct disadvantages.

(b)

(i) 3 **(0.5)**
(ii) 0 **(0.5)**
(iii) 5 **(0.5)**
(iv) 1 **(0.5)**

(c)

(i) If electrons were transferred to the plastic, the plastic has extra electrons and becomes negative, since electrons are negative. If my fingers lost electrons, they would have more protons than electrons and become positive. Positive and negative attract. **(1.5)**

(ii) Since the balloon has extra electrons from being rubbed on your hair, the balloon is negatively charged. When you bring it over to the wall, the negative balloon repels the negative electrons in the wall and leaves an area of positive charge. The negative balloon is then attracted to the positive wall. **(1.5)**

Question 2

(a)

(i) In normal covalent bond, shared electrons are contributed by each bonded atom while in coordinate bond all shared electrons are contributed by a single atom.

(ii) Sigma bond. (**0.25**)

Reason:
Sigma bond has **greater region of overlapping** and is commonly formed between **hybrid orbitals** which have **lower energy content.** (**0.75**)

(b)

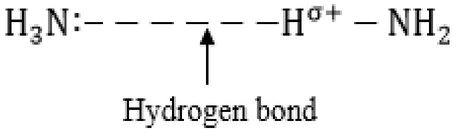
(i) **Conditions:**

1. Hydrogen atom must be bonded to strong electronegative atom, mainly N, O or F.(**0.25**)

   This ensures the formation of strong partial positive charge in hydrogen atom. (**0.25**)

2. The strong electronegative atom must possess at least one lone pair. (**0.25**)

   This ensures strong electrostatic force of attraction between the partial positively hydrogen atom and negatively charged lone pair. (**0.25**)
   For example in NH_3, N is more electronegative than H and it has lone pair and therefore hydrogen bond between molecules of NH_3.



(**0.5**)

Remark: To get full score**,** an examinee must do the following:

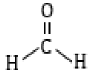
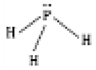
1. State the two conditions followed by brief explanation in each for more clarification.
2. Give relevant example to illustrate the stated conditions.

(The question asked to ‘describe’ the conditions and not simply to write down (or to give) the conditions).

(ii) **Difference to other intermolecular forces**

Hydrogen bond is stronger than other intermolecular forces because hydrogen having very small size, its positive charge is highly concentrated in small region making it to have exceptionally strong attraction to negative charge of lone pairs. (**0.5**)

(c)

Molecule	**Geometrical shape**	**Name of the structure**	**Type of hybridisation**
CO_2	$O = C = O$	Linear	sp
CH_2O		Trigonal planar	sp^2
PH_3		Trigonal pyramidal	sp^3

(**4.5**)

Question 3

(a)

(i) Volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature. (**1**)

(ii) The rate of diffusion of gases at given temperature and pressure varies inversely proportional to the square root of their densities. (**1**)

(b)

1. A gas consists of very small particles in a random motion of which there is a collision between gas molecules (particles) themselves and the collision between gas molecules and the walls of the container thus exerting a pressure. (**0.5**)
2. Force of gravity has no effect on the motion of gas molecules. (**0.5**)
3. Intermolecular forces of attraction are negligible in the motion of gas molecules.(**0.5**)
4. Kinetic energy of gas molecules varies directly proportional to the absolute temperature. (**0.5**)
5. The collision between gas molecules and walls of the container is completely elastic.(**0.5**)
6. Volume of a gas molecules is negligible compared to the volume of the whole gas or the volume of the container.(**0.5**)

Remark: To get full score, an examinee must give at least **five** correct postulates with 0.5 mark for each postulate.

(c)

(i) From its definition, compressibility factor (Z) is given by;

$Z = \frac{\text{Real volume}}{\text{Ideal volume}}$ **(0.5)**

If V represents real volume, the formula becomes: $Z = \frac{V}{\text{Ideal volume}}$

But ideal volume can be calculated from ideal gas equation with measured (actual) P, T and n

That is $V = \frac{nRT}{P}$ **(0.5)** (From $PV = nRT$)

Where V is the ideal volume.

Then the formula $Z = \frac{V}{\text{ideal volume}}$ becomes $Z = \frac{V}{\frac{nRT}{P}} = \frac{PV}{nRT}$

Thus the compressibility factor, $Z = \frac{PV}{nRT}$ **(0.5)**

Where:

P is the measured (real) pressure

V is the measured (real) volume

n is the measured number of moles

(ii) For ideal behaviour, $Z = 1$ **(0.5)**

For the positive deviation, $Z > 1$ **(0.5)**

For the negative deviation, $Z < 1$ **(0.5)**

(d) Using Gay-Lussac's law to calculate the expected pressure of CO_2 at 1401K.

That is $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ or $P_2 = \left(\frac{T_2}{T_1}\right)P_1$ **(0.5)**

Where $P_1 = 10\text{ atm}, T_1 = 701\text{K}, T_2 = 1401\text{K}$

Then $P_2 = \frac{1401 \times 10}{701}\text{atm} = 19.9857\text{ atm}$ **(1)**

Using $i = \frac{\text{Observed pressure}}{\text{Expected pressure}} = \frac{22.5\text{ atm}}{19.9857\text{ atm}} = 1.1258$ **(0.5)**

CO_2 decompose according to the following equation:

$CO_2(g) \rightleftharpoons CO\,(g) + \frac{1}{2}O_2(g)$; $N = 1.5$ **(0.5)**

Then using $\alpha = \frac{i-1}{N-1} = \frac{1.1258-1}{1.5-1}$ **(0.5)**

$= 0.2516$ or 25.16%

Hence the percent of CO_2 that decomposes was 25.16%. **(0.5)**

Question 4

(a)

(i)

1. Lowering in vapour pressure **(0.5)**
2. Freezing point depression **(0.5)**
3. Boiling point elevation **(0.5)**

(ii)

1. Beckmann's method **(0.5)**
2. Landsberger's method **(0.5)**

(iii) Diluted solution **(0.5)**

Explanation

Better result of determination of molar mass by colligative properties are obtained when the solution is almost ideal and the solution containing non-volatile solution becomes almost ideal when it is dilute. **(1)**

(iv) **Reason to oppose:**

It is difficult to measure osmotic pressure as it requires a more advanced apparatus and hence the experiment cannot be carried out as an ordinary laboratory process. **(0.5)**

Reason to support:

1. The osmotic pressure measurements are taken around room temperature. **(0.5)**
2. The molarity of the solution is used in measuring osmotic pressure instead of molality. It is easier to measure molarity than molality. **(0.5)**
3. It is useful for determination of molar mass of biomolecules (polymers) as they are generally not stable at higher temperatures. **(0.5)**
4. It is useful for determination of molar mass of substances with large molar mass as the osmotic pressure is measurable for those substances unlike boiling point elevation and freezing point depression. **(0.5)**

Remark: Any **one** opposing reason and **two** supporting reasons are enough to gain maximum score of 1.5 marks.

(b) Calcium chloride ionises according to the following equation:

$$CaCl_2(aq) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq);\ N = 3$$

Thus assuming complete ionisation, Van't Hoff's factor, $i = N = 3$ $(\mathbf{0.5})$

Using $\Delta T = iK_b m = 3 \times 1.22°C kg/mol \times 3.725 mol/kg = 13.6°C$ $(\mathbf{0.75})$

Boiling point of the solution, $\mathbf{T_b} = (\mathbf{78.5 + 13.6})°C = \mathbf{92.1}°C$ $(\mathbf{0.75})$

Also $\Delta T = iK_f m = 3 \times 1.99°C kg/mol \times 3.725 mol/kg = 22.2°C$ $(\mathbf{0.5})$

Freezing point of the solution, $\mathbf{T_f} = (\mathbf{-117.3 - 22.2})°C = \mathbf{-139.5}°C$ $(\mathbf{0.5})$

(ii) Practical boiling point will be smaller while practical freezing point will be greater than their respective calculated values. **(0.5)**

Explanation

Practically calcium chloride has some covalent character; so it will not ionise completely making number of dissociated solute particles smaller. Fewer solute particles as result of that pairing between ions ($Ca^{2+}$and Cl^-) means smaller of both boiling point elevation and freezing point depression which in turn means lower boiling point and higher freezing point. **(1)**

Question 5

(a) Basic oxides: MgO **(0.5)**

Acidic oxide: Mn_2O_7, CrO_3 **(0.5)**
Amphoteric oxides: ZnO, Al_2O_3, MnO_2 **(0.5)**

(b)
(i) By direct heating of the metal with oxygen. **(0.5)**
(ii) Other alkali metals have smaller polarising power such that they may form peroxides (and even superoxides for metals below sodium) apart from normal oxide unlike lithium which form normal oxide only. **(1)**
(iii) To avoid the formation of peroxides and superoxides, normal oxides of those metals are prepared by reducing their nitrite or nitrate by free metal. **(1)**

Taking the preparation of K_2O as an example;

$$2KNO_3 + 10K \longrightarrow 6K_2O + N_2 \text{ } \mathbf{(0.5)}$$

(c) Salts which hydrolyse in water are $ZnSO_4$ and $AlCl_3$ **(0.5)**

Equations:
$ZnSO_4\,(s) + 2H_2O(l) \rightarrow Zn(OH)_2(s) + 2H^+(aq) + SO_4^-(aq)$ **(0.75)**
$AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3H^+(aq) + 3Cl^-(aq)$ **(0.75)**

(d) **In extraction of metals**

Metal oxides may act as useful ore from which their respective metal are extracted. For example, bauxite is the oxide of aluminium ($Al_2O_3.XH_2O$) is used for extracting aluminium and haematite (Fe_2O_3) for iron. **(1)**
Furthermore metallic oxides like CaO and FeO are useful in removing gangue (earthy impurities) in blast furnace. For example, CaO is used to eliminate sand, SiO_2 (gangue) as slag. **(1)**

In soil liming

Metal oxides are used to eliminate excess acid in the soil and to increase fertility of the soil through soil liming. For example, calcium oxide and magnesium oxide are good liming materials.**(1.5)**

Question 6

(a)
(i) Is the amount of heat evolved or absorbed in a reaction measured at given pressure. **(0.5)**
(ii) Is the amount of heat required by one mole of solid substance to change its state from a solid to a liquid, measured at given temperature and pressure. **(0.5)**
(iii) Is the reaction which can occur without the input of work from an external source. **(0.5)**
(iv) Is the chemical reaction which is accompanied with evolvement of heat to surroundings. **(0.5)**

(b)
(i) Reactants have weaker bonds than products. **(0.5)**
(ii) Reactants have stronger bonds than products. **(0.5)**

(c)
(i) Since the reaction accompanied with the temperature rise, it is exothermic.

Then; heat change, $\Delta H = -mc\Delta T$ **(0.5)**
But $m = \rho_{soln}V_{soln}$
Thus; $\Delta H = \rho_{soln}V_{soln}c\Delta T$ **(0.5)**
Substituting $\Delta H = 1gcm^{-3} \times 100cm^3 \times 4.18Jg^{-1}°C^{-1} \times 46.3°C$

$$= -19353.4J = -19.3534kJ \ \mathbf{(1)}$$

Number of moles of $CuSO_4 = \frac{100}{100}dm^3 \times 1moldm^{-3} = 0.1mol$ **(0.5)**
Then using;
Molar enthalpy change=$\frac{\text{Heat change}}{\text{Number of moles of }CuSO_4}$
Molar enthalpy change=$\frac{-19.3534kJ}{0.1mol}$ **(0.5)**
$= -193.534kJ/mol$
The molar enthalpy change for the reaction is $-193.534kJ/mol$ **(0.5)**

(ii) From the given equation; mole ratio of $CuSO_4$ to Mg is 1:1

Thus the minimum number of moles of Mg required is 0.1mol **(0.5)**
Using $m= nM_r$;
Mass of Mg $= 0.1mol \times 24gmol^{-1} = 2.4g$
The minimum quantity of magnesium required is 2.4g **(1)**

(iii) Number of moles of magnesium $n = \frac{0.8g}{24gmol^{-1}} = \frac{1}{30}mol$ **(0.5)**

Thus;
Number of moles of $CuSO_4$ = Number of moles of Mg $= \frac{1}{30}mol$
And;
Heat change = molar enthalpy change × Number of molar of $CuSO_4$
$= -193.534kJmol^{-1} \times {}^{1}/_{30}\ mol = -6.45kJ = 6450J$ **(0.5)**
From $\Delta H = -\rho_{soln}V_{soln}\ c\Delta T$
$-6450J = -1gcm^{-3} \times 100cm^3 \times 4.18Jg^{-1}°C^{-1} \times \Delta T$ **(0.5)**
From which; $\Delta T = 15.43°C$

Question 7

(a)

(i) Is the reaction which can proceed in both forward and backward reaction. **(0.5)**

A good example of this, is heating of a solid calcium carbonate in the closed vessel.

$$CaCO_3(s) \rightleftharpoons CaO(s) + O_2(g)(\mathbf{0.5})$$

(ii) Is the system of chemical equilibrium where by reagents involved in the system are in different phase. **(0.5)**

Example: The decomposition of solid ammonium chloride to form ammonia gas and hydrogen chloride gas.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)(\mathbf{0.5})$$

(b) When a chemical system is allowed to reach the equilibrium at a particular temperature, there is a fixed ratio of product of concentration of products to that of reactants raised to powers equals to stoichiometric coefficients regardless to the original concentration of the reagents present in the system. **(0.5)**

For the hypothetical reaction: $aA + bB \rightleftharpoons cC + dD$

Then according to equilibrium law; $\frac{[C]^c[D]^d}{[A]^a[B]^b} = \text{Constant }(K_c)$ **(0.5)**

(c)

(i) It is the balance of the rate of the two reactions (forward and reverse reaction) which are proceeding at the same time in opposite directions. **(0.75)**

(ii) $K_c = \frac{[R]^2}{[P][Q]^2}$**(0.5)**

(iii) $[P] = \frac{3.82\text{mol}}{10\text{dm}^3} = 0.382\text{moldm}^{-3}; [R] = \frac{5.24\text{mol}}{10\text{dm}^3} = 0.524\text{moldm}^{-3}$**(1)**

$K_c = 68.0\text{mol}^{-1}\text{dm}^3 = \frac{(0.524\text{moldm}^{-3})^2}{0.382\text{moldm}^{-3}\times[Q]^2}$**(1)**

From which; $[Q] = 0.103\text{moldm}^{-3}$**(0.5)**

(iv) The equilibrium amount of P will increase while the K_c value will decrease. **(1)**

(v) The equilibrium amount of P will increase. **(0.75)**

(vi) $K_c = \frac{[P][Q]^2}{[R]^2} = \frac{1}{\frac{[R]^2}{[P][Q]^2}} = \frac{1}{68.0\text{mol}^{-1}\text{dm}^3} = 0.0147\text{moldm}^{-3}$**(1.5)**

Question 8

(a)

(i) 5-ethylhexa-1,3-diene **(0.5)**
(ii) 4-hexen-1-yne or hex-4-en-1-yne **(0.5)**
(iii) 2-(2-chloroethyl)penta-1,3-diene **(0.5)**
(iv) 3,5-heptadien-1-yne or hepta-3,5-dien-1-yne **(0.5)**

(b) 2-methylpropane being more branched has smaller surface area and less compact package of carbon chains and therefore it has weaker Van-der-Waals dispersion forces. This makes 2-methylpropane to have lower boiling point than n-butane despite their equality in molecular mass. **(1.5)**

(c)

(i) CH_3Cl $(\mathbf{0.5})$
(ii) P is $CH_3CH(SO_3H)CH_3$ $(\mathbf{0.5})$
Q is $CH_3CH(OH)CH_3$ $(\mathbf{0.5})$
(iii) $CH_3C \equiv CCu$ $(\mathbf{0.5})$
(iv) $CH \equiv CH$ $(\mathbf{0.5})$

(d)

(i) Propene has higher boiling point **(0.25)**

Reason:
With greater molecular mass, propene has stronger Van-der-Waals dispersion forces. **(0.75)**

(ii) Benzene has higher boiling point **(0.25)**

Reason
With delocalised pie electrons, it is easier for benzene to form temporary dipole-dipole forces and hence stronger Van-der-Waals dispersion forces for it. **(0.75)**

(iii) Pentane has higher boiling point **(0.25)**

Reason:

With unbranched carbon chain, pentane has larger surface area and more compact arrangement of carbon chains making it to have stronger Van-der-Waals dispersion forces. **(0.75)**

(iv) Ethyne has higher boiling point

Reason:
With an increased number of weakly held pie electrons, it is easier for ethyne to form temporary dipole-dipole forces and hence stronger Van-der-Waals dispersion forces for it.**(0.75)**

(v) Cis-2-butene has higher boiling point **(0.25)**

Reason
In Cis-2-butene the same groups are at the same side with respect to the position of C=C and therefore there is no cancellation of dipole moment making it polar unlike in trans-2-butene where the group are at the opposite side. **(0.75)**

(e) Primary alkyl halides have the general molecular formula of RCH_2X, where R is alkyl group.

Thus with A being unbranched, its structure must be $CH_3CH_2CH_2CH_2Br$ **(1)**
Reaction equations:

$$\underset{\textbf{A}}{CH_3CH_2CH_2CH_2Br} + kOH \xrightarrow{\text{Alcohol}} \underset{\textbf{B}}{CH_3CH_2CH = CH_2} + KBr + H_2O \quad \textbf{(1)}$$

$$\underset{\textbf{B}}{CH_3CH_2CH = CH_2} + HBr \rightarrow \underset{\textbf{C}}{CH_3CH_2CHBrCH_3} \quad \textbf{(1)}$$

$$\underset{\textbf{C}}{2CH_3CH_2CHBrCH_3} + 2Na \xrightarrow{\text{Dryether}} \underset{\textbf{D}}{CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3} + 2NaBr$$

Question 9

(a)

(i) Is the haloalkane of which a carbon with halogen is also bonded to other two alkyl groups. **(0.5)**

(ii) Is the unsaturated aromatic hydrocarbon with molecular formula of C_6H_6 **(0.5)**

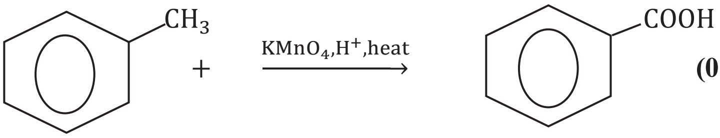
(iii) Is the organic compound which contain at least one benzene ring. **(0.5)**

(iv) Is the energy required to stop resonation (mesomerism) in the compound. **(0.5)**

(v) Is the type of mechanism of nucleophilic substitution reaction whereby there is only one molecule involved in the rate determining step. **(0.5)**

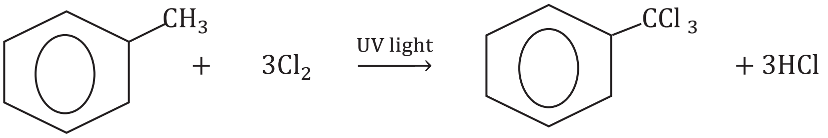
(b)

(i) **Oxidation** in the side chain will occur. **(0.5)**



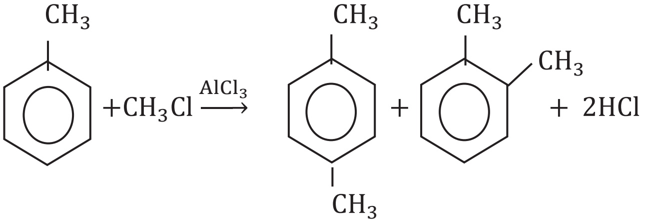
(0.75)

(ii) **Free radical substitution** reaction in the side chain will occur. **(0.5)**



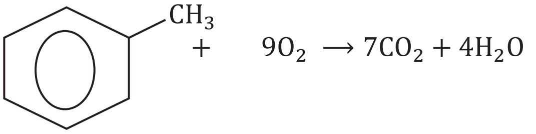
(0.75)

(iii) **Electrophilic substitution reaction** in benzene ring will occur. **(0.5)**



(0.75)

(iv) **Combustion** reaction will occur. **(0.5)**



$(\mathbf{0.75})$

(c)

(i) To precipitate the chloride, the Cl in given chlorohydrocarbons must be substituted by nucleophile. In 1- chloropropene the Cl to be substituted is bonded to pie bonded carbon which is nucleophile too and hence there is very large repulsion between two nucleophiles which prevents the reaction to occur unlike in 3-chloropropene. **(1.5)**

(ii) Firstly the intermediate tertiary (3°) carbenium ion, $(CH_3)_3C^+$ formed by t-butyl chloride is more stable than the primary (1°) carbenium ion, $CH_3CH_2CH_2CH_2^+$ formed by n-butyl chloride. $(\mathbf{0.75})$

Secondly the three alkyl groups surrounding carbon with Cl in $(CH_3)_3CCl$ exerts stronger steric hindrance than one alkyl group in $CH_3CH_2CH_2CH_2Cl$ **(0.75)**

The two factors make t-butyl chloride to undergo S_N1 mechanism while n-butyl chloride undergoes S_N1.

(iii) Some alkyl chlorides are so stable that their lifetime in environment is large enough to cause serious environmental problems. DDT for example is non-biogredable and causes the problem of biomagnification while CFC's causes serious problems of ozone depletion and global warming. **(1.5)**

(iv) The methyl group in toluene increases electron density in benzene ring through positive inductive effect making the toluene more reactive towards electrophile in electrophilic substitution reaction. **(0.75)**

Also the methyl group allow the toluene to undergo side chain reactions like oxidation reactions which are not common in benzene. **(0.75)**

(v) Due to their involvement in the mesomerism, pie bonds in benzene have too weak nucleophilic character to enable the formation of electrophile. So the presence of Lewis acid is essential in order to enable the formation of electrophile which will react with benzene. **(1.5)**

Question 10

(a)

1. Chemical oxidation and reduction (Redox method) (0.5)

Oxidation – reduction method is an important chemical treatment for sewage which have either reducing or oxidising character where the sewage is treated by either oxidising agent or reducing agent respectively. **(1)** Example: Oxidation of cyanide wastes from metal finishing industry using Cl in alkali solution. **(0.25)**

$2NaCN + 5Cl_2 + 8NaOH \rightarrow 10NaCl + 4H_2O + 2CO_2 + N_2$ **(0.25)**

2. **Acid – base neutralization (0.5)**

Acid-base neutralisation method is used to treat corrosive sewage are either strongly acidic (pH less than 2) or strongly basic (pH more than 12.5) by using either base or acid respectively. **(1)**

Example: Sewage containing nitric acid may be treated by using lime ($Ca(OH)_2$). **(0.25)**

$2HNO_3 + Ca(OH)_2 \longrightarrow Ca(NO_3)_2 + 2H_2O$ **(0.25)**

3. **Chemical precipitation (0.5)**

This technique can be applied to almost any liquid waste stream containing precipitatable hazardous constituent by properly adjusting pH, the solubility of toxic metals can be decreased, leading to formation of precipitate that can be removed by settling and filtration. **(1)**

Example: Hazardous Cr^{3+} can be precipitated out by using lime ($Ca(OH)_2$) or caustic soda (NaOH). **(0.25)**

$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3$ **(0.25)**

4. **Hydrolysis (0.5)**

Hydrolysis treatment can be given to those hazardous waste constituents which are very reactive with water. **(1)**

Example: Halides (or carbides or hydrides or alkoxides or active metals) may be treated by mixing with water. **(0.25)**

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ **(0.25)**

5. **Thermal incineration (0.5)**

This s a process that uses high temperature thermal oxidation to convert a waste to a less bulky, less toxic or less noxious material. It used to treat sewage which can undergo combustion. **(1)**

Example: Organic waste are treated by burning. **(0.25)**

Organic waste $+ O_2 \underset{\Delta}{\rightarrow} CO_2 + H_2O$ **(0.25)**

Remark: Any three methods are enough to award maximum score of 6 marks.

(b)

(i) Is the maximum quantity of total cations, of any class, that a soil is capable of holding at a given pH value, available for exchange with soil solution. **(0.5)**

(ii)

1. It is a measure of soil fertility **(0.5)**

   The more cation exchange capacity a soil has the more likely the soil will have fertility.**(0.5)**

2. It is a measure of nutrient retention capacity **(0.5)**

   Soil with large value of CEC has large nutrient retention capacity. **(0.5)**

3. It is a measure of the capacity of soil to protect ground water from cation contamination. **(0.5)**

   Soil with large value of CEC has good ability to protect ground water from cation contamination as it exerts more resistance for its cations to be leached away. **(0.5)**

(iii) Using;

Percentage base saturation $= \frac{\text{number of exchangeable base cations}}{\text{CEC of the soil}} \times 100\%(\mathbf{0.5})$

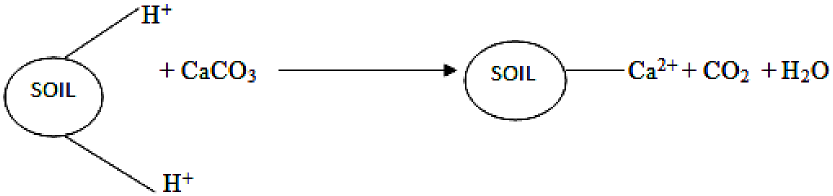
Before addition of $CaCO_3$

$70 = \frac{\text{Number of exchangeable base cation}}{40} \times 100(\mathbf{0.5})$

From which; number of exchangeable base cations is 28meq per 100g of the soil.

After addition of $CaCO_3$

When **$CaCO_3$** is added in order to raise percentage base saturation, Ca^{2+} from $CaCO_3$ exchange H^+ (acidic cation) according to the following equation:



(0.5)

Since 1eq of one cation= 1eq of any other cations:

1eq (0.5mol) of Ca^{2+} exchange 1eq (1mol) of H^+ and therefore total number of exchangeable cations (in eq) in the soil and hence CEC of the soil (in eq) remains the same even after addition of Ca^{2+}**(0.5)**

Let number of equivalents of added Ca^{2+} be xmeq/100g

Then, new total number of exchangeable base cations will be 28+x **(0.5)**

It follows that:

$90 = \left(\frac{28+x}{40}\right) \times 100$ or $28 + x = 36$ or $x = 8$ **(0.5)**

Thus amount of Ca^{2+} to be added is 8meq per 100g of soil

Using; number of meq $=$ number of mmol $\times$ amount of ionic charge

From which; number of mmol of $Ca^{2+} = \frac{\text{number of meq}}{\text{amount of ionic charge}} = \frac{8}{2} = 4\text{mmol}$**(0.5)**

And using; number of mol $= \frac{\text{mass in mg}}{\text{molar mass}}$

Then mass in mg = number of mol $\times$ molar mass $= 4 \times 40 = 160\text{mg}$**(0.5)**

Thus mass of Ca^{2+} to be added in 100g of the soil is 160mg or 0.16g **(0.5)**

And mass of Ca^{2+} to be added in 5000g (5kg) of the soil will be $\frac{5000\times0.16}{100}$g or 8g**(0.5)**

But 40 g of Ca^{2+} is contained in 100g of pure $CaCO_3$

Then 8g of Ca^{2+} will be contained in $\frac{8\times100}{40}$g or 20g of $CaCO_3$

Hence the mass of pure $CaCO_3$ required to meet the given requirements is 20g **(0.5)**

Solutions Examination Fourteen
CHEMISTRY 2G

Question 1

(a)

(i) If the volume of the container is suddenly increased, then the vapour pressure would decrease initially. This is because the amount of vapour remains the same, but the volume increases suddenly. As a result, the same amount of vapour is distributed in a larger volume. **(2)**

(ii) Since the temperature is constant, the rate of evaporation also remains constant. When the volume of the container is increased, the density of the vapour phase decreases. As a result, the rate of collisions of the vapour particles also decreases. Hence, the rate of condensation decreases initially. **(2)**

(iii) When equilibrium is restored finally, the rate of evaporation becomes equal to the rate of condensation. In this case, only the volume changes while the temperature remains constant. The vapour pressure depends on temperature and not on volume. Hence, the final vapour pressure will be equal to the original vapour pressure of the system. **(2)**

(b)

(i) Partial vapour pressure of a particular constituent (component) in a solution which contains two or more volatile miscible liquids is the product of its mole fraction and its vapour pressure of the pure liquid at given temperature. **(0.75)**

(ii)

1. Propanol-ethanol solution **(0.75)**
2. Toluene-benzene solution **(0.75)**
3. Heptane-hexane solution **(0.75)**

(iii)

1. Intermolecular forces between the components in the solution is the same as those intermolecular forces in pure components. **(0.75)**
2. The gaseous phase of the solution act as an ideal gas where the use ideal gas law is applicable. **(0.75)**

(c)

(i) From Raoult's law;

$P_{soln} = X_A^L P_A^\circ + X_B^L P_B^\circ$
Where $X_B^L = 1 - X_A^L$
Substituting;
$600 = 450X_A^L + (1 - X_A^L)700$ **(1)**
From which $X_A^L = 0.4$
And $X_B^L = 1 - 0.4 = 0.6$
Hence the composition by mole fraction is as follows;
Mole fraction of A is 0.4 **(0.75)**
Mole fraction of B is 0.6 **(0.75)**

(ii) In the vapour phase;

$$X_A^V = \frac{X_A^L P_A^\circ}{P_{soln}} = \frac{0.4 \times 450}{600} \ (\mathbf{0.5})$$
$$= 0.3$$
$$X_B^V = 1 - X_A^V = 1 - 0.3 = 0.7$$

Hence the vapour composition of the vapour phase by mole fraction is as follows;
Mole fraction of A is 0.3 **(0.75)**
Mole fraction of B is 0.7 **(0.75)**

(d) Let number of moles of uranium in the organic layer be n_o and number of moles of uranium in the water layer be n_w

Then from;

$$K_d = \frac{[\text{Uranium}]\text{in organic layer}}{[\text{Uranium}]\text{in water layer}} \ (\mathbf{0.5})$$

Substituting;

$$50 = \frac{\frac{n_o}{200}}{\frac{n_w}{500}} = \frac{500n_o}{200n_w} \ (\mathbf{1.5})$$

From which;

$$\frac{n_o}{n_w} = \frac{50 \times 200}{500} = 20 \ (\mathbf{1.5})$$

Hence the ratio of number of moles of uranium in organic solvent layer to water layer is 20:1 **(1)**

Question 2

(a)

(i) Is the electrode at which **reduction** occurs. (**0.5**)

Remark: It is **not** correct to define cathode as *the **negative** electrode*. **(**Cathode is negative electrode for **electrolytic cell** only. For **electrochemical cell,** cathode is **positive** electrode).

(ii) Is the electrode at which **oxidation** occurs. (**0.5**)

Remark: It is **not** correct to define anode as the **positive** electrode. (Anode is positive electrode for electrolytic cell only. For electrochemical cell anode is **negative** electrode).

(iii) Is the potential difference between the electric double layers which is formed when an electrode is in contact with solution containing 1M of its ions measured at 25℃ and 1 atm (standard conditions). (**0.5**)

Remark: It is allowed to define as *the electrode potential which is measured when an electrode is in contact with 1M solution of its ions at 25℃ and 1 atm (standard conditions).*

(iv) Is the **electrochemical cell** which consists of the same electrodes and the same electrolyte at different concentration which are connected by salt bridge. (**0.5**)

(b)

(i) Voltaic cell is a device which uses spontaneous chemical reactions to generate electricity while electrolytic cell is a device which uses electric current to produce non-spontaneous chemical reaction. (**1.5**)

(ii) This is due to its significances which are:

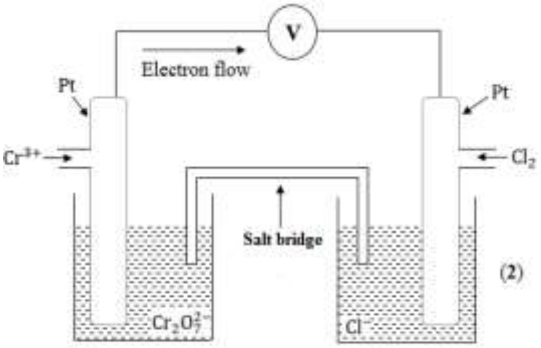
1. It allows the ions to migrate from cathode half-cell into the anode half-cell so as to complete the circuit.(**0.75**)
2. It prevents the diffusion of the electrolyte from one half-cell to the other thus maintaining the charge balance in the two half cells.(**0.75**)

(c)

(i) The cell diagram corresponding to the given cell reaction is:

$Cr^{3+}(1M) \mid Cr_2O_7^{2-}(1M) \parallel Cl_2(g) \mid Cl^-(1M)$ (**0.5**)
Thus $E^{\emptyset}_{cell} = E^{\emptyset}_{R} - E^{\emptyset}_{L}$ (**0.5**)
$= (1.36 - 1.33)V = 0.03V$ (**0.5**)
Hence the standard e.m.f is 0.03V (**0.5**)

(ii)



Remark: The diagram **must** include platinum (Pt) as inert electrode (in both cathode and anode as both Cr^{3+} and Cl_2 are not solid) with Cr^{3+} electrode at the left and Cl_2 electrode at the right.

(iii) Oxidation half reaction: (At anode)

$Cr^{2+} \rightarrow Cr^{3+} + e$ ……………….. (i) (**0.5**)
Reduction half reaction: (At cathode)
$S_4O_6^{2-} + 2e \rightarrow 2S_2O_3^{2-}$ ……….. (ii) (**0.5**)
Taking 2(i) + (ii) to get overall reaction equation;
$2Cr^{2+} + S_4O_6^{2-} \rightarrow Cr^{3+} + 2S_2O_3^{2-}$
From which, number of electron transferred, $n = 2$ (**0.5**)
Also using $E^{\emptyset}_{cell} = E^{\emptyset}_{cathode} - E^{\emptyset}_{anode}$
The e.m.f corresponding to given reaction;
$E^{\emptyset}_{cell} = 0.17V - (-0.5V) = 067V$ (**0.5**)
Using $E_{cell} = E^{\emptyset}_{cell} - \frac{0.0591}{n}\log R_Q$ (**0.5**)
But at equilibrium; $E_{cell} = 0$ and $R_Q = K_c$
It follows that: $0 = E^{\emptyset}_{cell} - \frac{0.0591}{n}\log K_c$ or $E^{\emptyset}_{cell} = \frac{0.0591}{n}\log K_C$ (**0.5**)
Substituting $0.67 = \frac{0.0591}{n}\log K_c$ (**0.5**)
$K_c = 4.71 \times 10^{22}$
Hence the equilibrium constant is 4.71×10^{22} (**0.5**)

(iv) The equilibrium constant is **very large** implying that the **operating time of the cell is large.** (**1**)

(d) Let the rate law to be; $R = k[A]^x[B]^y$ (**0.5**)

Then: $R_1 = k(0.185)^x(0.133)^y$ (**0.5**)
$R_2 = k(0.185)^x(0.266)^y$ (**0.5**)
$R_3 = k(0.370)^x(0.133)^y$ (**0.5**)
Taking $\frac{R_2}{R_1} = \frac{k(0.185)^x(0.266)^y}{k(0.185)^x(0.133)^y}$(**0.5**)

$\frac{R_2}{R_1} = \left(\frac{0.266}{0.133}\right)^y = 2^y$

Substituting $\frac{1.35\times10^{-3}}{3.35\times10^{-4}} = 2^y$ **(0.5)**

From which $4 = 2^2 = 2^y; y = 2$ **(0.5)**

Taking $\frac{R_3}{R_1} = \frac{k(0.370)^x(0.133)^y}{k(0.185)^x(0.133)^y}$

$\frac{R_3}{R_1} = \left(\frac{0.370}{0.185}\right)^x = 2^x$

Substituting $\frac{6.75\times10^{-4}}{3.35\times10^{-4}} = 2^x$ **(0.5)**

From which $2 = 2^1 = 2^x; x = 1$ **(0.5)**

Hence: The order of reaction with respect to A and B are 1 and 2 respectively. (**0.5**)

From $R_1 = k(0.185)^x(0.133)^y$

Substituting; $3.35 \times 10^{-4}Ms^{-1} = k(0.185)^1(0.133)^2$(**0.5**)

From which $k = 0.102\ M^{-2}s^{-1}$

Hence the value of rate constant is $0.102\ M^{-2}s^{-1}$ (**0.5**)

Question 3

(a)

Bronsted acids: HCO_3^-, H_2O **(1)**

Bronsted bases: $S^{2-}, HCO_3^-, H_2O, NH_3$ **(1)**

(b) **First component:** Weak electrolyte (**0.5**)

Explanation:

This is either weak acid or weak base which is used to provide the dynamic system of the chemical equilibrium. (**0.75**)

Second component: Strong salt (**0.5**)

Explanation:

The salt must contain either conjugate base of the acid or conjugate acid of the base of the first component. The strong salt which contain conjugate base of the weak acid, provides enough concentration of anions to combine with H^+ on addition of strong acid while strong salt which contain conjugate acid of the weak base provides enough concentration of cations to combine with OH^- on addition of strong acid. (**1.25**)

(c) Using n = [ ]V

Number of moles of $BaCl_2 = 0.5 \times 2 \times 10^{-3} = 1 \times 10^{-3}$moles **(0.5)**

Number of moles of $Na_2SO_4 = 1 \times 2 \times 10^{-4} = 2 \times 10^{-4}$moles (**0.5**)

Using $[\ ] = \frac{n}{V}$ and the fact both $BaCl_2$ and Na_2SO_4 are strong electrolytes:

$[BaCl_2] = [Ba^{2+}] = \frac{1\times10^{-3}mol}{(0.5+1)dm^3} = 6.67 \times 10^{-4}M$ **(0.5)**

$[Na_2SO_4] = [SO_4^{2-}] = \frac{2\times10^{-4}mol}{(0.5+1)dm^3} = 1.33 \times 10^{-4}M$ **(0.5)**

Then $Q_{sp} = [Ba^{2+}][SO_4^{2-}] = 6.67 \times 10^{-4} \times 1.33 \times 10^{-4}M = 8.87 \times 10^{-8}M^2$ (**0.5**)

Thus $Q_{sp} = 8.87 \times 10^{-8}M^2 > 1 \times 10^{-10}(K_{sp})$

$Q_{sp} > K_{sp}$, precipitate will be formed. (**0.5**)

Let molar solubility of $Ca(OH)_2$ in water (before addition of NaOH) be x

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

$$x \qquad\qquad 2x \quad (\mathbf{0.5})$$

$$K_{sp} = [Ca^{2+}][OH^-]^2 = x(2x)^2 = 4x^3 \quad (\mathbf{0.5})$$

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4.42\times10^{-5}}{4}} = 0.0223M \ (\mathbf{1})$$

After addition of NaOH:

Number of moles of NaOH added $= \frac{500}{1000} \times 0.4\ \text{mol} = 0.2\ \text{mol}$

$[NaOH] = [OH^-] = \frac{0.2\ \text{mol}}{(0.5+0.5)L} = 0.2\ M$ (**0.5**)

Again let new molar solubility of $Ca(OH)_2$ be x

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

$$x \qquad\qquad 2x + 0.2 \approx 0.2M$$

$$K_{sp} = [Ca^{2+}][OH^-]^2 = x(0.2)^2 \qquad (\mathbf{0.5})$$

$$x = \frac{K_{sp}}{0.04} = \frac{4.42\times10^{-5}}{0.04} = 1.105 \times 10^{-3}M \ (\mathbf{0.5})$$

Decrease in molar solubility after addition of NaOH

$= (0.0223 - 1.105 \times 10^{-3})M = 0.021195M$ (**0.5**)

Thus number of moles of $Ca(OH)_2$ precipitate formed in the litre of the solution is 0.021195 mol

Using $m = nM_r$;

Mass of the precipitate $= 0.021195 \times 74g = 1.57g$

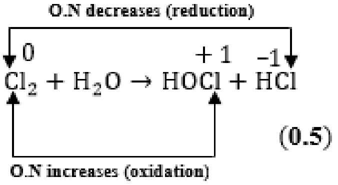
Hence the mass of precipitate is 1.57 g (**0.5**)

Question 4

(a)

(i) Is the redox reaction whereby both oxidation and reduction occurs in the same element. (**0.5**)

Thus in disproportionation reaction the oxidation state of the one particular element do both increases and decreases at the same time. For example:



(**0.5**)

(ii) Is the ability of smaller ion (cation) to distort the valence shell of larger ion (anion). (**0.5**)

It is the measure of electron attracting ability of cation whereby the cation with smaller size and higher charge is said to have greater polarising power. (**0.5**)

(iii) Is the energy absorbed when one mole of uninegative gaseous ions gain electrons to form one mole of binegative ion. (**0.5**)

It is the measure of atom's resistance to gain second electron due to repulsion between first added electron and new incoming electron whereby the atom with smaller sized uninegative ion accompanied with more unstable exerts smaller resistance and therefore it said to have smaller second electron affinity. (**0.5**)

(iv) Are compound of halogens in which the halogen has its maximum oxidation state. (**0.5**)

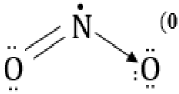
In perhali compounds, the oxidation state of halogen is +7. For example; sodium perchlorate $\left(\text{Na}\overset{+7}{\text{C}}\text{lO}_4\right)$ is perhali compound. (**0.5**)

Remark: An examinee is not to just **give** the meaning. The question asked to **explain** the meaning (not to **give** the meaning). So the examinee must add relevant information to explain the meaning for all parts of (a).

(b)

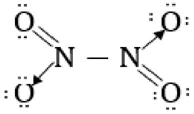
(i) With one unpaired electron in nitrogen, nitrogen dioxide is paramagnetic while in dinitrogen tetraoxide, all of electrons are paired and hence it becomes diamagnetic**(0.5)** as illustrated in their structures below:

Structure of NO_2:



(0.75)

Structure of N_2O_4:



(0.75)

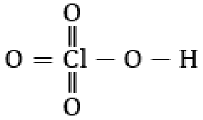
Remark: General explanation on paramagnetism like: nitrogen dioxide has unpaired electron while dinitrogen tetraoxide has not (has all of its electron paired) is **not** acceptable. To get full score an examinee must provide explanation which are very specific to NO_2 and N_2O_4 and they **must** be supported with their respective relevant structure. (It is obvious that **any** paramagnetic material has unpaired electron and diamagnetic material has not. So the key part of this question is to show presence and absence of unpaired electron).

(ii) Unlike Si, C (in CCl_4) has so **small atomic size** that cannot allow the incoming water molecule to attach in it and it has no **empty orbitals** for accepting lone pair of oxygen in water molecule and hence unlike $SiCl_4$, CCl_4 does not react with water. (**1.5**)

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ (**0.5**)
While $CCl_4 + H_2O \rightarrow$ No reaction

(iii) With greater number of oxygen atoms, there are more double bonds in $HClO_4$ to facilitate stronger mesomerism in it and therefore greater ability to donate H^+ and to stabilize the negatively ion formed after the donation of H^+ and hence making $HClO_4$ stronger acid than HNO_3. (**1.5**)

Structure of $HClO_4$:

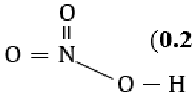


$$O=\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cl}}-O-H$$

(0.25)

(Has three $Cl=O$ bonds)

Structure of HNO_3:



(0.25)

(iv) B being more electronegative than Al, it easier for oxygen to take electron from Al than from B and therefore in $B(OH)_3$, the $B-O$ bond is less likely to break, releasing H^+ while in $Al(OH)_3$, it is easier for $Al-O$ bond (in $Al-O-H$) to break to release OH^- and therefore reducing the chance of releasing H^+ through $O-H$ cleavage in Al-O-H. (**1.5**)

Being stronger acid than $Al(OH)_3$, $B(OH)_3$ does not reacts with another acidic solution while $Al(OH)_3$ reacts.
$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$ while
$B(OH)_3 + 3HCl \rightarrow$ No reaction (**0.5**)

(v) Al^{3+} in $AlCl_3$ is strong acid cation and therefore $AlCl_3$ undergoes cationic salt hydrolysis to give acidic solution while CH_3COO^- in CH_3COONa is strong base anion and therefore CH_3COONa undergoes anionic salt hydrolysis to give basic solution (**1**)

$Al^{3+}(\text{From } AlCl_3) + 3H_2O \rightarrow Al(OH)_3 + 3H^+$ (**0.5**)
$CH_3COO^-(\text{from } CH_3COONa) + H_2O \rightarrow CH_3COOH + OH^-$ (**0.5**)

(vi) NH_4Cl contain NH_4^+ which is strong acid cation and therefore it undergoes cationic salt hydrolysis to give acidic solution which is responsible for evolving hydrogen gas in the reaction with magnesium metal. (**1**)

$NH_4^+ + H_2O \rightarrow NH_4OH + H^+$ **(0.5)**
Then $2H^+ + Mg \rightarrow Mg^{2+} + H_2$ **(0.5)**

(vii) Gives phosphoric acid and calcium sulphate by double displacement reaction according to the following equation: **(0.5)**

$Ca_3(PO_4)_2(s) + 3H_2SO_4(l) \longrightarrow 2H_3PO_4 + 3CaSO_4$ **(1.5)**
Remark: Alternative terms for double displacement are: double decomposition, double replacement or metathesis.

(viii) **No reaction** because potassium dichromate is not strong oxidizing agent enough to oxidize Cl^- in HCl which is very weak reducing agent. (**2**)

$$K_2Cr_2O_7 + HCl \rightarrow \text{No reaction}$$

Question 5

(a)
(i) Ammonium hexathiocyanatoferrate(III) (**1**)
(ii) Tris(oxalato)ferrate (III) ion (**1**)
(iii) Pentaamminechlorocobalt (III) bromide (**1**)
(iv) Diaquadithiosulphatocobalt(II) ion (**1**)
(v) Sodium tetrachlorooxomolybdate (IV) (**1**)

(b) Molar mass of $CrCl_3 \bullet 6H_2O$ is 266.5 g/mol

Using $n = \frac{m}{M_r}$;

Number of moles of $CrCl_3 \bullet 6H_2O = \frac{2.665g}{266.5g/mol} = 0.01$ mol (**0.5**)

Molar mass of AgCl is 143.5 g/mol

Then number of moles of AgCl produced $= \frac{2.87g}{143.5g/mol} = 0.02$ mol (**0.5**)

But Ag^+ (from $AgNO_3$) combines with Cl^- (from the complex compound) according to the equation:

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ (**0.5**)

From which mole ratio of AgCl to Cl^- is 1:1. Thus number of moles of Cl^- from 0.01 mol of $CrCl_3 \bullet 6H_2O$ (complex compound) was also 0.02 mol (**0.5**)

So 0.01 mol of $CrCl_3 \bullet 6H_2O$ produces 0.02 mol of Cl^- or 1 mol of $CrCl_3 \bullet 6H_2O$ produces 2 mol of Cl^- (**0.5**)

Hence Cl^- is coordinated to central metal ion as ligand and two Cl^- are free ions in the ionisation sphere. (**1**)

Also Cr^{3+} having a common coordination number of six, five H_2O must also be coordinated to central metal in as ligands in the coordination sphere so that with one Cl^-, coordination number of six is obtained. One H_2O remains as water of crystallization outside the coordination sphere. (**1**)

Hence the structure of compound is $[CrCl(H_2O)_5]Cl_2 \bullet H_2O$ (**1**)

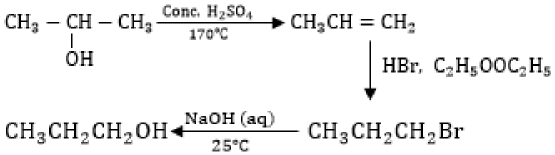
(c)

(i) Iodoform test (**0.25**)

Ethanol having terminal CH_3 − group bonded to carbon with OH give positive test by giving yellow precipitate of iodoform while methanol will give negative test because it does not contain terminal methyl group bonded to carbon with OH. (**0.75**)

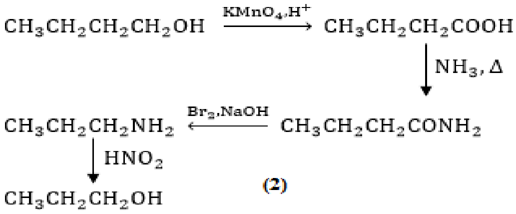
(d)

(i)



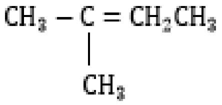
(**1.5**)

(ii)



(**2**)

(e) The alkene which gives propanone and ethanal on ozonolysis has the following structure:

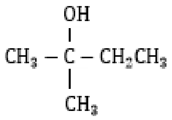


$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2CH_3$

(0.5)

Thus the above structure is of Q.

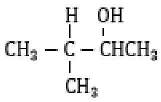
The compound which gives alkene (Q) on dehydration with concentrated H_2SO_4 is alcohol. Thus B must be an alcohol with five carbons (**0.75**) with one of the following structures:



$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$

2 – methylpropan – 2 – ol

(3° alcohol) **(0.5)**

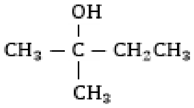


$CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{C}HCH_3$

3 – methylpropan – 2 – ol

(2° alcohol) **(0.5)**

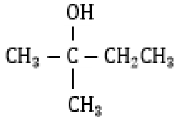
Since B reacts with hydrochloric acid immediately, it cannot be secondary (2°) alcohol, it must be tertiary (3°) alcohol with the following structure (**0.75**)



$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$

Hence:

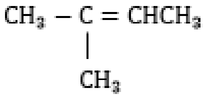
Structure of B is



$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$

(0.5)

Structure of Q is



$CH_3-\underset{\underset{CH_3}{|}}{C}=CHCH_3$ $(\mathbf{0.5})$

Question 6

(a)

(i) Methanal **(0.5)**

(ii) Propanone/acetone **(0.5)**

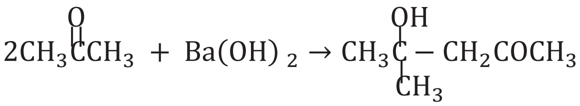
(iii) Ethanal **(0.5)**

(iv) 2-octanone/octan-2-one **(0.5)**

(b)

(i) $CH_3CH_2CONH_2 + Br_2 + KOH \rightarrow CH_3CH_2NH_2 + K_2CO_3 + KBr + H_2O(\mathbf{0.75})$

(ii)



$$2CH_3\overset{\overset{O}{\|}}{C}CH_3 + Ba(OH)_2 \rightarrow CH_3\overset{OH}{\underset{CH_3}{C}}-CH_2COCH_3$$

(0.75)

Remark: The carbonyl compound **must** be ketone. Aldehyde is not acceptable.

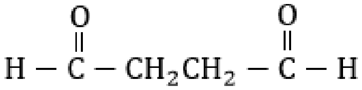
(iii) $CH_3CH_2NH_2 + CHCl_3 \xrightarrow{KOH(aq)} CH_3CH_2NC + KCl + H_2O(\mathbf{0.75})$

(iv) $HCHO + NaOH(aq) \rightarrow HCOOH + CH_3OH(\mathbf{0.75})$

(c)

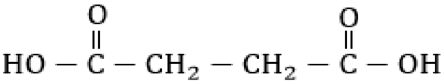
Composition by element	C	H	O
% composition	53.33	11.11	35.56
Mass of each in 100g of the compound	53.33g	11.11g	35.56g
Number of moles of each; $n = \frac{m}{M_r}$	$\frac{53.33g}{12g/mol}$ = 4.444 mol	$\frac{11.11g}{1g/mol}$ = 11.11mol	$\frac{35.56g}{16g/mol}$ = 2.2225mol
Divide by smaller number of moles to get simpler ratio	$\frac{4.444\ mol}{2.2225mol}$ = 2	$\frac{11.11mol}{2.2225mol}$ = 5	$\frac{2.2225mol}{2.2225mol}$ = 1

Thus the empirical formula of compound A is C_2H_5O (**2**)
Let the molecular formula of the compound be $(C_2H_5O)_n = C_{2n}H_{5n}O_n$
But number of carbon atoms per molecule is 4 (given)
Then $2n = 4\ ; n = 2$
Hence the molecular formula of the compound is $C_4H_{10}O_2$ (**1**)
The compound with two oxygen atoms per molecule that evolve hydrogen gas when reacted with sodium metal and can be oxidised is **diol.** (**0.5**)
Thus A must be diol.
Since B comes from oxidation of A which has 4 carbons, number of carbon atoms in A and B must be equal and therefore B has 4 carbons with the molecular formula $(C_2H_3O)_2 = C_4H_{10}O_2$ (**1**)
Since B forms condensation compound with 2,4-dinitrophenylhydrazine and reduces Fehling's solution, there is aldehyde group in B. (**0.5**)
Since B can undergo oxidation to give dicarboxylic acid, there two aldehyde groups in B, each coming from oxidation of $-CH_2 - OH$ group of diol.
Thus the two OH group in diol must be present in each end of carbon chain of the diol.(**0.5**)
Hence the structure of A is;
$HO - CH_2CH_2CH_2CH_2 - OH$
And structure of B is;



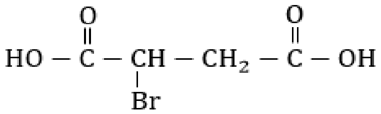
$$H - \overset{\overset{O}{\|}}{C} - CH_2CH_2 - \overset{\overset{O}{\|}}{C} - H$$

(empirical formula is C_2H_3O)
Oxidation of B gives the following dicarboxylic acid which is the structure of D;



$$HO - \overset{\overset{O}{\|}}{C} - CH_2 - CH_2 - \overset{\overset{O}{\|}}{C} - OH$$

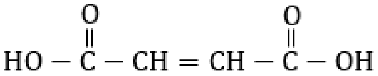
The mono-bromo derivative of D which gives dicarboxylic acid upon loss of hydrogen bromide is



$$HO-\overset{\overset{O}{\|}}{C}-\underset{\underset{Br}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

(structure of X) (**0.5**)

And therefore the structure of E (obtained after loss of hydrogen bromide in X) will be;



$$HO-\overset{\overset{O}{\|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}-OH$$

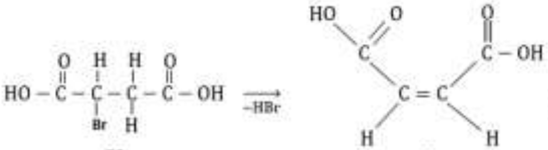
(Emprical formula is CHO as given) (**0.5**)

Hence:

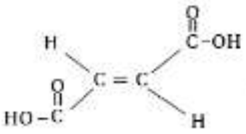
Molecular formula of A is $C_4H_{10}O_2$ (**0.5**)

Molecular formula of B is $C_4H_6O_2$ (**0.5**)

Molecular formula of E is $C_4H_4O_4$ (**0.5**)



X **E** (2)



(1)

Explanation

Since there is no free rotation between carbon atoms in $C=C$, the compound exist in two forms of cis-isomer and trans-isomer. (**1**)

Solutions Examination Fifteen
CHEMISTRY 1H

Question 1

(a)

(i) Is a particular arrangement of electrons in different orbitals of an atom.

(ii) Is the energy sublevel in which electron is placed and specifies the shape of an orbital of an electron.

(iii) Is the splitting of a spectral line of atoms or molecules subjected to the electric field.

(iv) Are levels used to describe electrons at their stationary states.

(b)

(i) 2 **(0.5)**

(ii) 0 **(0.5)**

(iii) $n = 3, l = 0, m = 0, s = +\frac{1}{2}$ **(0.75)**

(iv) 2

(v) $l = 2, m_l = -2, -1, 0, +1, +2$ **(0.75)**

(c)

(i) Using; $A_r = \frac{A_1P_1 + A_2P_2}{P_1 + P_2}$

Substituting; $A_r = \frac{(14\times95.12)+(15\times4.88)}{100} = 14.05\ (\mathbf{0.5})$

The relative atomic mas of nitrogen is 14.05 **(1)**

(ii)

A. Different mass-charge $(^{m}/_{z})$ratio **(0.75)**

B. Change in the amount of magnetic field **(0.75)**

(iii) No difference **(0.5)**

Explanation

Since the two isotopes have the same number of electrons and hence the same electronic configuration, no difference will be observed in their chemical reactions. **(1)**

Question 2

(a)

(i) Are electrostatic forces of attraction holding different molecules together.

(ii) An **interaction** between cation (positively charge ion) and anion (negatively charge ion) in ionic compound.

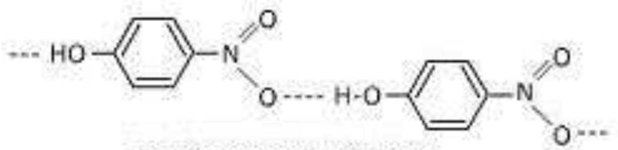
Remark: An examinee must give the definition of ionic bond**ing** and not ionic bond.

(iii) Are electrons outside noble gas core or pseudo-noble gas core.

(iv) Are electrostatic forces of attraction between induced dipoles.

(b)

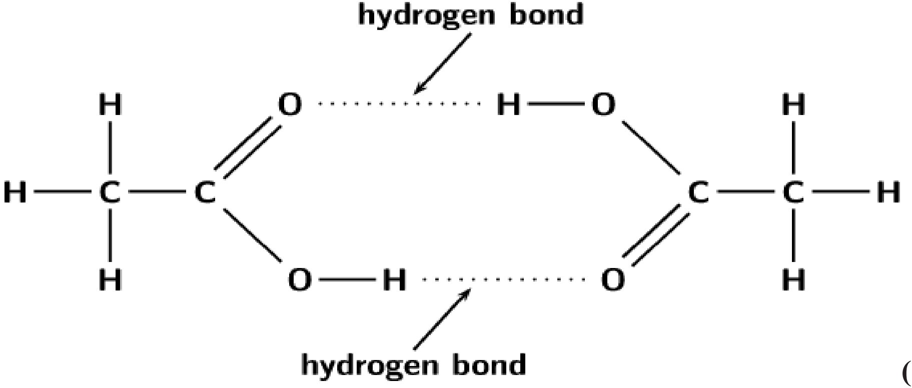
(i) Hydrogen bonding in ortho-nitrophenol is actually not intermolecular forces, it is intramolecular forces unlike in para-nitrophenol which is intermolecular hydrogen bonding. This makes ortho-nitrophenol to have weaker intermolecular forces and hence lower boiling point. **(1)**



P- Nitrophenol with inter molecular hydrogen bonding

(0.5)

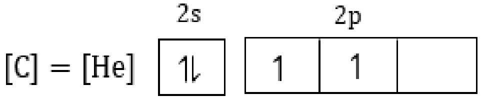
(ii) Acetic acid is capable of making very strong intermolecular hydrogen bonding especially in solvent with no hydrogen bonding like carbon tetrachloride. The high ability of forming strong hydrogen bonding enables the acid to dimerise to form the dimer with molar mass which is twice the expected molar mass **(1)**



(0.5)

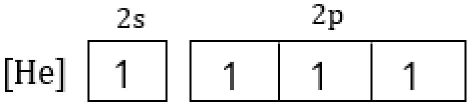
(c) For CH_4:

CH_4 is formed by sp^3 hybridisation as described below: (**0.5**)
At ground state carbon has the following electronic configuration:



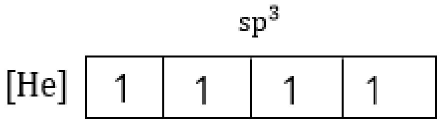
(0.25)

For carbon to four identical covalent bonds, one 2s-eectron must be excited to 2p-subenergy level and it must undergo sp^3 hybridisation as illustrated below (**0.25**)
[C] at excited state:



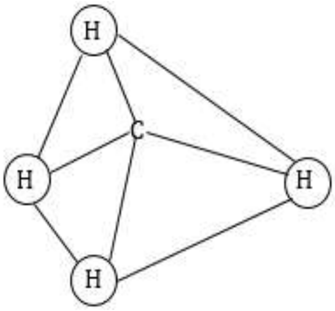
(0.25)

[C] after hybridisation:



(0.25)

To minimize repulsion the four hybrid orbitals are kept as far as possible in tetrahedral shape. (**0.5**)



(0.25)

For BF_3:

BF_3 is formed by sp^2 hybridisation as described below (**0.5**)

At ground state, boron has the following electronic configuration:

	2s	2p		
[B] = [He]	1l	1		

(**0.25**)

For boron, to form three identical covalent bonds, one 2s-electron must be excited to 2p-subenergy level and it must undergo sp^2 hybridisation. (**0.5**)

[B] at excited state:

	2s	2p		
[He]	1	1	1	

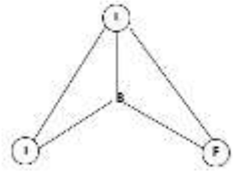
(**0.25**)

[B] after hybridisation

	SP^2			$2P_z$
[He]	1	1	1	

(**0.25**)

To minimize repulsion , the three hybrid orbitals are kept as far as possible in trigonal planar shape. (**0.25**)



(**0.25**)

For SCl_2:

SCl_2 is formed by sp hybridisation as described below

At ground state, S has the following electronic configuration:

	3s	3P		
[He]	1l	1l	1	1

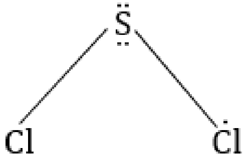
(**0.25**)

For S to form two identical covalent bonds and two lone pairs it must undergo SP^3 hybridisation at ground state. (**0.25**)

	SP^3			
[He]	1l	1l	1	1

(**0.25**)

To minimize repulsion lone pairs and bonded electron pairs, the bonded electron pairs are kept as for as possible from lone pairs in bent shape. (**0.25**)



(0.25)

(ii) BF_3 (**0.25**)

Question 3

(a)

(i) Disagree **(0.25)**

Explanation

Amount of pressure exerted by a gas does not directly depend on the mass of the gas; it depends on the number of gas molecules (particles). With equal mass of hydrogen and oxygen, hydrogen having smaller molar mass will possess greater number of gas molecules $\left(n = \frac{m}{M_r}\right)$ and hence greater pressure of hydrogen than that of oxygen despite the fact that the two have equal mass. **(1.25)**

(ii) Disagree **(0.25)**

Explanation

For the volume of the gas to double in accordance to Charles's law the temperature in Kelvin (absolute temperature) must double too. Although the given temperature seems in to double in Celsius scale but converting them to Kelvin gives 283K and 393K respectively which is clear that the latter is not twice of the former. **(1.25)**

(iii) Agree **(0.25)**

Explanation

Greater number of gas molecules means greater of both pressure deviation and volume deviation from their corresponding ideal results. This is because, with greater number of gas molecules the intermolecular forces will be higher with more gas molecules pulling the gas molecules backward before hitting the container's wall and hence more decrease in real pressure. Also greater number of gas molecules means greater volume occupied by gas molecules which in turn means less empty space is left compared to the volume of the container. **(1.25)**

(b) Using $n = \frac{m}{M_r}$

Number of moles of water $= \frac{11.2\text{g}}{18\text{g/mol}} = \frac{28}{45}$ mol (**0.5**)

Thus $\frac{1}{8}$mol of hydrated salt $\equiv \frac{28}{45}$ mol of water **(0.5)**

Then 1 mol of hydrated salt $\equiv \frac{28\times8}{45\times8}$ mol of water = 5 mol

Hence the number of molecules of water of crystallization in the salt is 5. (**0.5**)

(c) Actual molar volume of sodium atoms $= \frac{68.52}{100} \times 23.68\text{cm}^3 = 16.2255\text{cm}^3/\text{mol}$ (**1**)

Volume of one sodium atom $= \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.14 \times (1.86 \times 10^{-8}\text{cm})^3$

$= 2.6941 \times 10^{-23}\ \text{cm}^3/\text{atom}$ (**1**)

Then actual molar volume = Volume of one atom × Avogadro's constant, N_A

From which;

$N_A = \frac{\text{Actual molar volume}}{\text{Volume of onee atom}}$ **(1)**

$= \frac{16.2255\text{cm}^3/\text{mol}}{2.6941\times10^{-23}\ \text{cm}^3/\text{atom}} = 6.02 \times 10^{23}\text{atom/mol}$

Hence the Avogadro's constant is 6.02×10^{23} **(1)**

Question 4

(a)

(i) A solute in a solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature occupying the same volume. **(0.75)**

(ii) The depression of the freezing point of dilute solutions is proportional to the amount of the dissolved substance. **(0.75)**

(iv) The Van't Hoff's factor approaches the ideal value when the salt undergoes complete ionisation. $FeCl_3$ having higher degree of polarisation as result of greater polarising power of smaller sized and higher changed Al^{3+} than Na^+in NaCl, is more covalent in character and hence it has lower degree of ionisation than NaCl. **(1.5)**

(v) The Van't Hoff's factor is large when the degree of dissociation (or ionisation) is large too. When the solution is more concentrated, the degree of dissociation is lowered and therefore the Van't Hoff's factor becomes smaller. **(1.5)**

(vi) $\rho_{\text{soln}} = 1.071\text{gcm}^{-3} = 1071\text{gdm}^{-3}$

Thus; Mass of solution in 1dm^3 of the solution is 1071g

Then mass of the solute(NaCl)in $1\text{dm}^3 = \frac{1}{100} \times 1071\text{g} = 10.71\text{g}$

Using $\pi V = nRT$;

From which $\pi = \frac{nRT}{V} = \frac{mRT}{VM_r}$

Expected osmotic pressure, $\pi_{\text{ex}} = \frac{1071\text{g}\times0.082\text{atmdm}^3\text{mol}^{-1}\text{K}^{-1}\times298\text{K}}{1\text{dm}^3\times58.5\text{gmol}^{-1}} = 4.47\text{atm}$

Then Van't Hoff's factor,i $= \frac{\pi_{\text{ob}}}{\pi_{\text{ex}}} = \frac{7.83\text{atm}}{4.47\text{atm}} = 1.75$

NaCl ionises according to the following equation;

$$NaCl(aq) \rightleftharpoons Na^+(aq) + Cl^-(aq); N = 2$$

Then using; $\alpha = \frac{i-1}{N-1}$

Substituting $\alpha = \frac{1.75-1}{2-1} = 0.75$

The fraction of NaCl which exists as ion pair is 0.75 or 75%

Mass of NaCl in 100g of solution is 1g

Thus;

Mass of solute (NaCl)=1g

Mass of solvent (Water) = (100-1)g = 99g

Freezing point depression, $\Delta T = iK_fm = \frac{i\times K_f m_{su}}{m_{su}\times m_{sv}\text{in kg}}$

$$\Delta T = \frac{1.75 \times 1.86°\text{Ckgmol}^{-1} \times 1\text{g}}{58.5\text{gmol}^{-1} \times 0.099\text{kg}} = 0.562°\text{C}$$

Freezing point of the solution,$T_f = 0°\text{C} - \Delta T = 0°\text{C} - 0.562°\text{C} = -0.562°\text{C}$

The freezing point of the solution $-0.562°\text{C}$

Question 5

(a)

(i) $B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$ $(\mathbf{0.5})$

(ii) $Pb_3O_4 + 4HNO_3 \xrightarrow[Boil]{} 2Pb(NO_3)_2 + PbO_2 + 2H_2O$ $(\mathbf{0.5})$

(iii) $ZnO + 2NaOH(aq) \longrightarrow Na_2ZnO_2 + H_2O$ $(\mathbf{0.5})$

(iv) $CaO + SiO_2 \longrightarrow CaSiO_3$ $(\mathbf{0.5})$

(b)

(i) Are salts which are formed after replacing at least one hydrogen of carbonic acid by metallic ion. They are carbonates and bicarbonates.**(0.75)**

(ii)

1. Neutralisation method

Both carbonates and bicarbonates are commonly prepared by neutralisation reaction. This is done by passing carbon dioxide to alkaline solution. The formation of carbonate or bicarbonate depend on whether alkaline solution or carbon dioxide present in excess.**(1.25)**

- If the alkaline solution present in excess, carbonate is formed.

$$2OH^- + CO_2 \longrightarrow CO_3^{2-} + H_2O \ \mathbf{(0.25)}$$

- If the carbon dioxide solution present in excess, bicarbonate is formed.

$$OH^- + CO_2 \longrightarrow HCO_3^- \mathbf{(0.25)}$$

2. Precipitation method

Only insoluble carbonate may be prepared by **double decomposition precipitation reaction**. All bicarbonates are soluble (because bicarbonate ion may interact with water through hydrogen bonding), so they are not prepared by this method. Insoluble carbonates which can be prepared by this method are all carbonates except carbonates of alkali metals (except $LiCO_3$) and ammonium carbonate which are soluble. **(1.5)**
For example;

$$CaCl_2(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + 2NaCl(aq) \ \mathbf{(0.25)}$$

(iii)

1. As industrial bases **(0.25)**

Na_2CO_3(washing soda or soda ash) is mainly used for this purpose. For example, the carbonate can be used to increase the alkalinity in swimming pools, helping to ensure the proper pH balance of the water.**(1)**

2. As baking powder **(0.25)**

$NaHCO_3$ is mainly used for this purpose. $NaHCO_3$ (baking soda) is used as leavening agent to raise things like cookies, cakes because it decomposes to CO_2 and water upon heating. **(1)**

3. In fire extinguisher **(0.25)**

Bicarbonate are good fire extinguisher because they decompose to produce carbondioxide gas and the reaction is endothermic. $NaHCO_3$ is commonly used for this purpose.**(1)**

4. In production of quick lime **(0.25)**

Calcium carbonate undergoes thermolysis to give calcium oxide (quick lime) which is useful in the manufacture of cement for construction activities and slaked lime, $Ca(OH)_2$, for agricultural activities. **(1)**
Remarks:

1. Any three well explained daily life uses are acceptable.

2. The following uses are also acceptable:
- In softening hard water
- In making glass
- In soil liming

Question 6

(a)

(i) Is the heat evolved when one mole of an unsaturated compound is converted to the corresponding saturated compounds by the reaction with hydrogen under given conditions of temperature and pressure.

(ii) Is the heat change when one mole of a substance (solute) dissolves in a specified amount of solvent (water) to give a solution under given conditions of temperature and pressure.

(iii) Is the average energy (enthalpy) required to dissociate bonds of the same type in 1 mole of a given gaseous compound.

(iv) Is the energy evolved when one mole of the solid ionic crystal is formed from its corresponding gaseous ions under given conditions of temperature and pressure.

(b)

(i) Given:

$$\frac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{Cl(g)};\ \Delta H^{\theta} = +121\mathrm{kJ/mol} \ldots\ldots \text{(i)}$$

Reversing (i) gives;

$$\mathrm{Cl(g)} \rightarrow \frac{1}{2}\mathrm{Cl_2(g)};\ \Delta H^{\theta} = +121\mathrm{kJ/mol} \ldots\ldots \text{(ii)}\ \ (\mathbf{0.5})$$

Taking 2 × (ii) gives;

$$2\mathrm{Cl(g)} \rightarrow \mathrm{Cl_2(g)}\Delta H^{\theta} = 2 \times -121\mathrm{kJ/mol} = -242\mathrm{kJ/mol}$$

The standard enthalpy change for the given process is $-242\mathrm{kJ/mol}$ **(0.5)**

(ii) Given;

$$\mathrm{Na(s)} \rightarrow \mathrm{Na(g)};\ \Delta H^{\theta} = +108\mathrm{kJ/mol} \ldots\ldots \text{(i)}$$

$$\mathrm{Na(g)} \rightarrow \mathrm{Na^+(g)} + \mathrm{e};\ \Delta H^{\theta} = +496\mathrm{kJ/mol} \ldots\ldots \text{(ii)}$$

$$\frac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{Cl(g)};\ \Delta H^{\theta} = +121\mathrm{kJ/mol} \ldots\ldots \text{(iii)}$$

$$\mathrm{Cl(g)} + \mathrm{e} \rightarrow \mathrm{Cl^-(g)};\ \Delta H^{\theta} = -349\mathrm{kJ/mol} \ldots\ldots \text{(iv)}$$

Taking (i)+(ii)+(iii)+(iv) gives;

$$\mathrm{Na(s)} + \mathrm{Na(g)} + \frac{1}{2}\mathrm{Cl_2(g)} + \mathrm{Cl(g)} + \mathrm{e^-}$$
$$\rightarrow \mathrm{Na(g)} + \mathrm{Na^+(g)} + \mathrm{e} + \mathrm{Cl(g)} + \mathrm{Cl^-(g)}\Delta H^{\theta} = (108 + 496 + 121 - 349)\mathrm{kJ/mol}\ \mathbf{(1)}$$

Cancelling like terms which appear as both reactants and products gives;

$$\mathrm{Na(s)} + \frac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{Na^+(g)} + \mathrm{Cl^-(g)};\ \Delta H^{\theta} = +376\ \mathrm{kJ/mol}$$

The enthalpy change for the given process is $+376\ \mathrm{kJ/mol}$. **(0.5)**

Comparison:

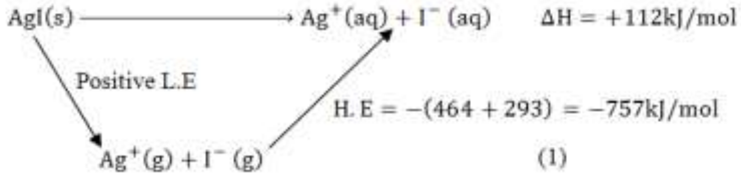
(iii) The enthalpy change of the process, $\mathrm{NaCl(s)} + \mathrm{H_2O(l)} \longrightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$ is **less endothermic** than that of the process $\mathrm{NaCl(s)} \rightarrow \mathrm{Na^+(g)} + \mathrm{Cl^-(g)}$ **(0.5)**

Comment:

The process, $NaCl(s) + H_2O(i) \rightarrow Na^+(aq) + Cl^-(aq)$ involves hydration of ions which is exothermic and hence the overall process becomes less endothermic with the hydration energy amounted to -783 kJ/mol ($4kJ/mol - 787kJ/mol$) accounting for the difference in enthalpy change of the two processes. **(1)**

(c)

(i)



By Hess's law:

$\Delta H = \text{Positive L.E} + \text{H.E}$ **(0.5)**

Substituting $+112\ kJ/mol = \text{Positive L.E} + (-757kJ/mol)$ **(0.5)**

From which positive L.E = $+757kJ/mol$

The lattice energy of silver iodide is $-757kJ/mol$ **(1)**

Remark: The negative sign must be included in the answer

Alternative solution:

Given that:

$AgI(s) \rightarrow Ag^+(aq) + I^-(aq);\ \Delta H = +112kJ/mol$ … … (i)

$Ag^+(g) \rightarrow Ag^+(aq);$ $\Delta H = -464kJ/mol$ … … (ii)

$I(g) \rightarrow I^-(aq)$ $\Delta H = -293kJ/mol$ … … (iii)

Reversing (i) gives;

$Ag^+(aq) + I^-(aq) \rightarrow AgI(s);\ \Delta H = -112kJ/mol$ … … (iv) **(1)**

Taking (ii)+(iii)+(iv) and cancelling like terms which appear as both reactants and products gives;

$Ag^+(aq) + I^-(g) \rightarrow AgI(s) \Delta H = -(464 + 293 + 112)kJ/mol$ **(1)**

Hence the lattice of silver iodide is $-869kJ/mol$ **(1)**

(ii) Having high degree of polarisation, AgI is highly covalent in character and therefore practically bonds are stronger than predicted. **(1)**

Question 7

(a)

(i) **First feature:**

Rate of forward reaction is equal to the rate of backward reaction. **(0.5)**

Second feature:

Concentration of reagents present in the system remain unchanged. **(0.5)**

(ii) Heating will force the system to resist the change by absorbing the heat and therefore favouring forward reaction which is endothermic and hence more NO_2 which appears in brown colouration will be formed. **(1)**

(iii) Increasing the pressure will force the system to resist the change by shifting the equilibrium position to the side with fewer gas molecules (N_2O_4 side) and hence the amount of NO_2 decreases. **(1)**

(b)

(i) It increases the rate of both forward and backward reaction by the same amount. **(1)**

(ii) A: To increase the production rate of ammonia. **(0.5)**

B: To reduce the production cost of ammonia. **(0.5)**

(c) Using $n = \frac{m}{M_r}$;

Initial number of moles of $CH_3COOH = \frac{24.4g}{60gmol^{-1}} = 0.4mol$ **(0.5)**

Initial number of moles of $CH_3CH_2OH = \frac{24.3g}{46gmol^{-1}} = 0.53mol$ **(0.5)**

CH_3COOH reacts with NaOH according to the following equation;

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ **(0.5)**

From which mole ratio of NaOH to CH_3COOH is 1:1

Thus $n_{NaOH} = n_{CH_3COOH} = \frac{26.5}{1000} \times 0.4mol = 0.0106mol$ **(0.5)**

Whence number of moles of CH_3COOH in $25cm^3$ of the solution is 0.0106mol.

Then number of moles of CH_3COOH in $250cm^3$ of the solution

$$= \frac{0.0106 \times 250}{25} mol = 0.106mol(\mathbf{0.5})$$

Hence number of moles of CH_3COOH at equilibrium was 0.106mol

$$\begin{array}{lcccc} & CH_3COOH(l) + & CH_3CH_2OH(l) \rightleftharpoons & CH_3COOCH_2CH_3(l) + & H_2O(l) \\ \text{Initially} & 0.4 & 0.53 & 0 & 0 \\ \text{At equilibrium} & 0.4 - x & 0.53 - x & x & x \ \mathbf{(0.5)} \end{array}$$

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]} (\mathbf{0.5})$$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.4-x}{V}\right)\left(\frac{0.53-x}{V}\right)} = \frac{x^2}{(0.4-x)(0.53-x)} (\mathbf{0.5})$$

But $0.4 - x = 0.106$; $x = 0.294(\mathbf{0.5})$

Substituting;

$$K_c = \frac{0.294^2}{(0.4-0.294)(0.53-0.294)} = 3.46$$

Hence the equilibrium constant is 3.46 **(0.5)**

Question 8

(a)

(i) Is the rule which predict the formation of major product when unsymmetrical molecule is added to unsymmetrical alkene via electrophilic additional reaction mechanism and it states that: When unsymmetrical molecule is added to unsymmetrical alkene, an electrophile tends to add to the carbon with greater number of hydrogen atoms. (**1**)

(ii) Is the rule which predict the formation of major product in elimination reactions of compounds (commonly secondary and tertiary haloalkane and alcohol) with possibility of giving more than one elimination product (alkene). It states that: Alkene with greater number of alkyl groups at double bond is more stable. (**1**)

Remark: An examinee should not only state the rule, must also provide relevant extra information about the rule. (The question asked, 'what do you understand' and not to 'state' the rule).

(b) Ethane<ethene<ethyne **(0.5)**

Reason:

Carbon in ethyne being sp hybridised has greatest percentage of s-character while in ethane where the carbon is sp^3 hybridised has the least percentage. Higher percentage of s-character means higher electronegativity which in turn means hydrogen bonded to the carbon is more positively polarised and hence more acidic. **(1.5)**

(c)

(i) Initiation step:

$Cl_2 \rightarrow 2Cl^{\bullet}$ **(0.5)**
First propagation step:
$CH_2Cl_2 + Cl^{\bullet} \rightarrow HCl_2C^{\bullet} + HCl$ **(0.5)**
Second propagation step:
$HCl_2C^{\bullet} + Cl_2 \rightarrow CHCl_3 + Cl^{\bullet}$ **(0.5)**

(ii) Essential condition : Ultra-violet light **(0.5)**

Type of mechanism: Free radical substitution mechanism **(0.5)**

(d)

(i) C_nH_{2n}
(ii) Structure: $CH_3CH_2CH = CH_2$

IUPAC name: but-1-ene/1-butene

(iii) A. $C_{15}H_{32} \rightarrow 2CH_3CH = CHCH_3 + C_7H_{16}$
C. Name of the process: Thermal cracking
D. Reason: To produce smaller hydrocarbons which have higher demand.

C: In order to break $C - C$ and $C - H$ bonds which are very stable.
(iv) Equation: $C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$

Effect: Products are greenhouse gases so they can cause global warming.

(e)

(i) H_2, Ni(or Pt or Pd)
(ii) It is used as fuel.
(iii) $2C_4H_{10}(g) + 5O_2(g) \rightarrow 8C(s) + 10H_2O(i)$
(iv) Lungs damage leading to breathing problems.

Question 9

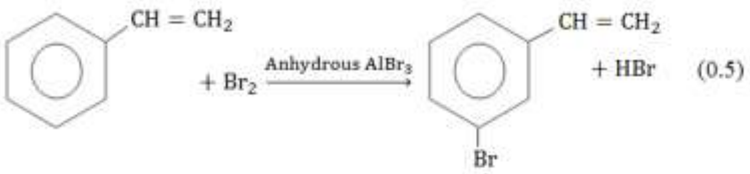
(a)

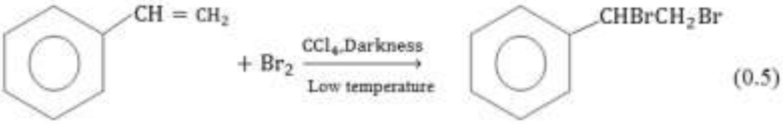
(i) Benzene + concentrated nitric acid $\xrightarrow{\text{conc}H_2SO_4,50°C}$ nitrobenzene + water **(1)**
(ii) Benzene + ozone $\xrightarrow{Zn,H_2O}$ ethanedial + zinc oxide **(1)**
(iii) Benzene+2-chloropropane $\xrightarrow{\text{Anhydrous } AlCl_3}$ isopropylbenzene+hydrogen chloride **(1)**
(iv) Toluene + chloromethyl
$\xrightarrow{\text{Anhydrous } AlCl_3}$ 2 − methyltoluene + 4 − methyltoluene + hydrogen chloride(**1**)
(v) Toluene + Mild oxidising agent → benzaldehyde (or phenylmethanal) **(1)**

(b) $CH_3CH_2Br > CH_3CH_2CH_2CH_2Br > CH_3CH_2CH(CH_3)Br > (CH_3)_3Br$ **(2)**

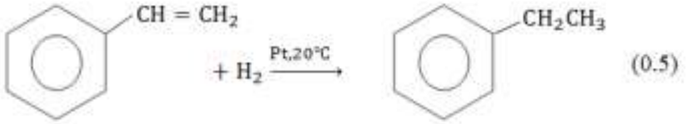
(c)

(i) Both side chain and aromatic ring. **(0.5)**

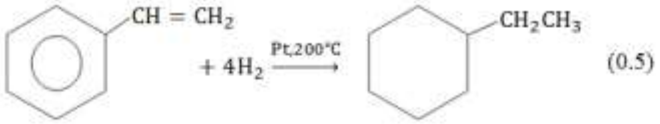




(ii) Side chain. **(0.5)**



(iii) Both side chain and aromatic ring. **(0.5)**



(i) Silver nitrate solution test: With solution of sodium hydroxide followed by addition of silver nitrate solution at room temperature, benzyl chloride gives **white precipitate** of AgCl while phenylchloride does not. **(1)**

(ii) Silver nitrate solution test: With solution of sodium hydroxide followed by addition of silver nitrate solution, bromoethane gives light **yellow (creamy) precipitate** of AgBr while chloroethane gives **white precipitate** of AgCl **(1)**

(iii) Carbylamine test: With ethylamine (primary amine) under presence of KOH solution, chloroform gives offensive smell of carbylamine while carbon tetrachloride does not. **(1)**

(iv) Potassium permanganate test: Toluene decolourise purple colouration of potassium permanganate while benzene does not. **(1)**

(v) Potassium permanganate test: n-butylbenzene decolourises purple coloration of potassium permanganate while benzene does not. **(1)**

Question 10

(a)

(i) Is the reaction of soil solution which represents the degree of acidity or basicity caused by the relative concentration of hydronium ions, H_3O^+, (acidity) or hydroxide ions, OH^-, (basicity) present in the soil. **(1)**

(ii) Is the fraction of exchangeable cations that are base cations expressed as percentage. **(1)**

(b) Promotes highly fertility of soil to affect an optimized agricultural production.

In good soil; earthworms, insects, bacteria and fungi are present which feed on the plant and animal remains. These microorganism break down the organic matter releasing its nutrients usually in the form of water-soluble inorganic compounds which can be taken in by plants. **(1.5)**

(c)

Microbial activity

Microbial activity lowers soil pH as they catalyze decomposition of organic matter and nitrification of ammonium ions leading to formation of acidic soil.**(0.75)**

$$CH_2O + O_2 \xrightarrow{\text{microbes}} CO_2 + H_2O$$ **(0.25)**

Then $$CO_2 + H_2O \rightarrow H_2CO_3$$ **(0.25)**

And $$NH_4^+ + 2O_2 \xrightarrow{\text{Bacteria(microbes)}} H_2O + NO_3^- + 2H^+$$ **(0.25)**

Fertility

Fertile soil always has large content of organic matter accompanied with large amount of microbes. These microbes catalyse the decomposition of the organic matter leading to formation of CO_2 and H_2O which in turn react together to give carbonic acid thus lowering soil pH. **(1)**

$$\underset{\downarrow}{CH_2O} + 2O_2 \xrightarrow{\text{Microbes(present in fertile soil)}} CO_2 + H_2O$$ **(0.25)**

Dominant in fertile soil

Then $$CO_2 + H_2O \rightarrow \underset{\downarrow}{H_2CO_3}$$ **(0.25)**

Account for lowering in soil pH

Leaching

As water from rainfall or irrigation activities passes through the soil, basic cations such as Ca^{2+} , Mg^{2+} and K^+ are leached. These basic cations are replaced by acidic cations such as Al^{3+} and H^+ and hence the soil become acidic with low pH. **(1.5)**

(d)

(i) Is the waste treatment systems which employs high temperature. **(0.5)**

(ii) Thermal incineration is a process that uses high temperature thermal oxidation to convert a waste to a less bulky, less toxic or less noxious material. **(0.5)**

It is a volume – reduction process in that many of the component elements of organic materials including the most common ones (C, H and O) are converted wholly or partially to gaseous form leaving only the non-combustible inorganic volume. **(0.5)**

$$\text{Organic waste} + O_2 \underset{\Delta}{\rightarrow} CO_2 + H_2O$$

$$\text{Incombustible inorganic waste} + O_2 \underset{\Delta}{\rightarrow} \text{No reaction}$$

(iii)

1. It reduces bulkiness of waste **(0.25)**

   Through incineration both weight of the waste and the waste volume are reduced much.**(1)**

2. It saves landfill**(0.25)**

   Minimum of land is needed compared to the dimensions of waste disposal sites. This is because; through incineration waste volume is reduced much (to almost 10% of the initial value). **(1)**

3. It is energy retrieval**(0.25)**

   Being highly exothermic, the incineration of waste provides two possibilities of using the produced energy in heating and generating electricity by means of steam turbines. **(1)**

4. It help disposes of non – biodegradable waste**(0.25)**

   Through incineration, non-biodegradable waste like plastics are decomposed (destroyed).**(1)**

5. It gives non smelly products**(0.25)**

   The produced residues, ash and slag as well as the developed flue gases, are odour-free compared to the partly offensive smells caused by dumps. **(1)**
   Remark: Any four well outlined advantages are enough to award maximum score of 5 marks.

(iv)
1. May produce toxic gases like dioxin if the temperature is not properly managed (when temperature is low) **(0.5)**
2. Waste of fossil resources **(0.5)**
3. Precludes recycling of paper or plastics **(0.5)**
4. Produces CO_2 gas which causes global warming **(0.5)**

   Remark: Any three disadvantages are enough to award maximum score of 1.5 marks.

Solutions Examination Sixteen
CHEMISTRY 2H

Question 1

(a)

(i) Liquid ethanol contains an extensive hydrogen bonding network, and cyclohexane is non-polar with Van-der-Waals dispersion forces. Because the cyclohexane molecules cannot interact favorably with the polar ethanol molecules, they will disrupt the hydrogen bonding. As a result, the intermolecular interactions in the solution will be weaker than those intermolecular interactions in pure ethanol and pure cyclohexane leading to a higher vapour pressure than predicted by Raoult's law and hence the solution will be non-ideal with positive deviation. **(2)**

(ii) Methanol contains an extensive hydrogen bonding network. With the polar acetone molecules, it create intermolecular interactions in the solution which are stronger than the intermolecular interactions in pure components. This makes the real vapour of solution to be lower than that predicted by Raoult's law and hence the solution will be non-ideal with negative deviation. **(2)**

(iii) Hexane and isooctane are both non-polar molecules. Thus the predominant intermolecular forces in both liquids are London dispersion forces. So in the solution the intermolecular interactions will be similar to those intermolecular forces in the pure liquids. As result, the real vapour pressure of the solution will be almost the same as that predicted by Raoult's law and hence the solution will be approximately ideal. **(2)**

(b)

P_x at 95°C $= 760\text{mmHg} - P_w = (760 - 635)\text{ mmHg} = 125\text{mmHg}$ $(\mathbf{0.5})$

Using $\frac{m_x}{m_w} = \frac{P_x M_x}{P_w M_w}$ $(\mathbf{0.5})$

Substituting given values:

$\frac{m_x}{m_w} = \frac{125\times160}{635\times18} = \frac{2000}{1143}$ **(1)** or $m_x : m_w = 2000 : 1143$

If $m_x = 40g$ then $\frac{40g}{m_w} = \frac{2000}{1143}$

$m_w = \frac{1143\times40}{2000}g = 22.86g(\mathbf{1})$

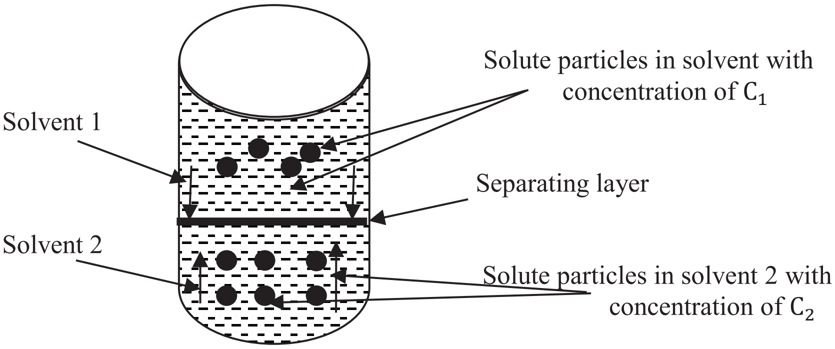
So mass of water in the distillate is 22.86g

And mass of X in the distillate is 40g (Given)

Hence the mass of the distillate is $(40 + 22)g = 62g$ **(1)**

(c) Consider the following diagram:

(i)



(1)

The rate of diffusion of solute particles from one solvent to another in directly proportional to the concentration of the solute in the solvent

So if;

R_1 is the rate of diffusion of the solute from the solvent 1 to solvent 2

R_2 is the rate of diffusion of the solute from the solvent 2 to solvent 1

Then $R_1 \propto C_1$ or $R_1 = K_1C_1 \dots\dots$ (i) (K_1 is the constant for proportionality) **(0.5)**

And $R_2 \propto C_2$ or $R_2 = K_2C_2 \dots\dots\dots$ (ii)(K_2 is the constant for proportionality) **(0.5)**

After certain time of diffusion, the equilibrium will be established where; $R_1 = R_2$

Thus at equilibrium: $K_1C_1 = K_2C_2$ or $\frac{K_2}{K_1} = \frac{C_1}{C_2}$ **(0.5)**

But $\frac{K_2}{K_1}$ gives another constant which is known as the partition coefficient, K_d

Hence $K_d = \frac{\text{Concentration of solute in the solvent 1}}{\text{Concentration of solute in the solvent 2}}$ **(0.5)**

(ii)

1. Solvent extraction **(0.5)**
2. Partition chromatography **(0.5)**
3. Release of drug from dosage form **(0.5)**
4. Passage of drug through membranes **(0.5)**
5. Preservation of emulsions and creams **(0.5)**
6. Formation of solubilized system **(0.5)**

Remark: Any four applications are enough to get maximum score of 2 marks.

Question 2

(a) For HNO_3 to dissolve Au, the following reaction must occur:

$NO_3^- + Au + 4H^+ \rightarrow Au^{3+} + NO + 2H_2O$ (**1**)

The cell diagram corresponding to the above reaction is as follows:

$Au \mid Au^{3+}(aq) \parallel NO_3^- \mid NO$ (**0.5**)

From which: $E^{\emptyset}_{Cell} = E^{\emptyset}_{R} - E^{\emptyset}_{L} = E^{\emptyset}_{NO_3^-/NO} - E^{\emptyset}_{Au^{3+}/Au}$ **(0.5)**

$= (0.96 - 1.5)V = -0.54V$ (**0.5**)

Since $E^{\emptyset}_{Cell}$ is negative, the reaction is not spontaneous and hence the given nitric acid will not dissolve the gold. (**1**)

(b)

(i) This is because, unlike $K_2Cr_2O_7$:

- $KmnO_4$ cannot be obtained pure enough. **(0.5)**
- $KmnO_4$ readily reacts with traces of organic material or other reducing substances in water. **(0.5)**
- $KmnO_4$ decomposes in sunlight. **(0.5)**

(ii) Potassium permanganate ($KMnO_4$) is so strong oxidizing agent that can oxidise Cl^- from HCl thus interfering the measurement of volume of $KMnO_4$ which was exactly used to oxidise Fe^{2+} in the titration. (**1**)

$$2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O \ \textbf{(0.5)}$$

(iii) This is due to oxidation of Cl^- (reducing agent) in NaCl to Cl_2 by potassium dichromate (VI), $K_2Cr_2O_7$ (oxidizing agent) while itself becomes reduced to Cr^{3+}which is detected by its green colouration. (**1**)

$$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O \ \textbf{(0.5)}$$

(c) From simplified Arrhenius equation:

$\log\left(\frac{k_1}{k_2}\right) = \frac{E_a}{2.303R}\left(\frac{T_1 - T_2}{T_1T_2}\right)$ (**0.5**)

Where:

$R = 8.314 Jmol^{-1}K^{-1}$

$T_1 = (27 + 273)K = 300K$

$T_2 = (37 + 273)K = 310K$

$E_a = 83.14\ kJmol^{-1} = 83.14 \times 10^3 J/mol$ **(0.5)**

Then substituting:

$\log\left(\frac{k_1}{k_2}\right) = \frac{83.14 \times 10^3 J/mol}{2.303 \times 8.314 Jmol^{-1}K^{-1}}\left(\frac{300 - 310}{300 \times 310}\right)$ **(0.5)**

$\log\left(\frac{k_1}{k_2}\right) = -0.467$

From which $\frac{k_1}{k_2} = \log^{-1}(-0.467) = 0.34$

Hence the approximate ratio is 0.34 (**1**)

From c(i);

$\log\left(\frac{k_1}{k_2}\right) = -0.467$

If E_a changed from $83.14\ kJmol^{-1}$ to $53.59\ kJmol^{-1}$;

New $\log\left(\frac{k_1}{k_2}\right) = -\frac{0.467}{83.14} \times 53.59$

Thus new $\log\left(\frac{k_1}{k_2}\right) = -0.301$**(1)**

And new $\frac{k_1}{k_2} = \log^{-1}(-0.301) = 0.5$

Hence the ratio will be 0.5. (1)

(d) The rate would decrease as time passes due to decrease in concentration of reactants as the reaction proceed. (**1**)

Remark: The response: *the reaction rate would* ***change*** *instead of would* ***decrease*** is not allowed.

Assuming the reaction takes place in the single step

$R = k[H_2][I_2] = 9 \times 10^{-8} Msec^{-1}$ (**0.5**)

Since pressure varies directly proportional to the concentration of gases (Boyle's law), doubling pressure will double concentration of each reactant too. **(1)**

New $R = k \times 2[H_2] \times 2[I_2]$ (**0.5**)

$= k[H_2][I_2] \times 4 = 9 \times 10^{-8} \times 4\text{Msec}^{-1} = 3.6 \times 10^{-7}\text{Msec}^{-1}$
Hence the initial rate would be $3.6 \times 10^{-7}\text{Msec}^{-1}$(**1**)

(e) For first order reaction:

$\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$ (**0.5**)
Or $-\log\left(\frac{a}{a-x}\right) = -\frac{kt}{2.303}$ (**0.5**)
$\log\left(\frac{a}{a-x}\right)^{-1} = \log\left(\frac{a-x}{a}\right) = -\frac{kt}{2.303}$ (**0.5**)
Where $\left(\frac{a-x}{a}\right) \times 100\% =$ Percentage of reactants reamined after any time t (**0.5**)
But the percentage of reactants reacted after 45 seconds = 35% (reaction was 35% complete).
It follows that; $\left(\frac{a-x}{a}\right) \times 100 = (100 - 35) = 65$ (**0.5**)
Substituting $\log 0.65 = -\frac{k \times 65s}{2.303}$
From which $k = 6.63 \times 10^{-3}s^{-1}$ (**0.5**)
Half-life of first order reaction is given by $t_{1/2} = \frac{0.693}{k}$ (**0.5**)
Substituting $t_{\frac{1}{2}} = \frac{0.693}{6.63 \times 10^{-3}s^{-1}}$ (**0.5**)
$= 104.5s$
Hence the half-life is 104.5seconds (**0.5**)

Question 3

(a)

(i) Is the ability of a certain solute to be dissolved in a given solvent which is given as the amount of the solute dissolved in one litre of saturated solution.(**0.5**)

(ii) Is an equilibrium constant which is given as the product of concentration of ions in a saturated solution of sparingly soluble electrolyte, each raised to power of their stoichiometric coefficients in the balanced chemical equation.**0.5**)

(iii) Is the relative ability of buffer solution to resist pH change on addition of acid or base.(**0.5**)

(iv) Is a technique that separates ions from solution based on their different solubility and hence different solubility products, K_{sp}.

(b) Let the molar solubility of $PbCl_2$ in water be x

$$PbCl_2(s) \rightleftharpoons \underset{x}{Pb^{2+}(aq)} + \underset{2x}{2Cl^-(aq)} \quad (\mathbf{0.5})$$

$K_{sp} = [Pb^{2+}][Cl^-]^2$ (**0.5**)
$K_{sp} = x(2x)^2 = 4x^3$
From which $x = \sqrt[3]{\frac{K_{sp}}{4}}$
Substituting $x = \sqrt[3]{\frac{1.6 \times 10^{-5}}{4}} = 0.015874\ \text{moldm}^{-3}$ (**0.5**)
Using;
mass solubility = Molar solubility × molar mass
Mass solubility $= 0.015874 \times 278\text{gdm}^{-3}$(**0.5**)

$= 4.413\ \text{gdm}^{-3}$

Hence the solubility of $PbCl_2$ in water is $4.413\ \text{gdm}^{-3}$ (0.5)

$Pb(NO_3)_2$ being strong electrolyte ionises according to the following equation:

$Pb(NO_3)_2(aq) \rightarrow Pb^{2+}(aq) + 2NO_3^-(aq)$

0.1M 0.1M

Let the solubility of $PbCl_2$ in $Pb(NO_3)_2$ solution be y

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

$y + 0.1 \quad 2y$ **(0.5)**

Since $PbCl_2$ is sparingly soluble electrolyte, $[Pb^{2+}]$ from $PbCl_2$ is very small compared to $[Pb^{2+}]$ that comes from $Pb(NO_3)_2$ which is strong electrolyte.

Thus $y + 0.1 \approx 0.1$

Thence $[Pb^{2+}] = 0.1M$

And $[Cl^-] = 2y$

Then $K_{sp} = [Pb^{2+}][Cl^-]^2 = 0.1 \times (2y)^2$ **(0.5)**

From which $y = \sqrt{\frac{K_{sp}}{0.4}} = \sqrt{\frac{1.6\times10^{-5}}{0.4}}$

$= 6.32246 \times 10^{-3}\text{moldm}^{-3}$ **(0.5)**

mass solubility = Molar solubility × molar mass

$= 6.32246 \times 10^{-3} \times 278\text{gdm}^{-3} = 1.76\ \text{gdm}^{-3}$ **(0.5)**

Hence the solubility of $Pb(NO_3)_2$ solution is $1.76\ \text{gdm}^{-3}$. (0.5)

Remark: To get full score, an examinee must show clearly each step of calculation and give the answer in gdm^{-3}. **Deduct 1 mark** if the answer is in moldm^{-3} instead of gdm^{-3}(or g/L).

(c) Reaction equation: $NaOH + HCl \rightarrow NaCl + H_2O$ **(0.5)**

From which mole ratio of NaOH to HCl is 1: 1 **(0.5)**

Using n = MV;

$n_{NaOH} = 0.1M \times 1 \times 10^{-3}\text{dm}^3 = 1 \times 10^{-4}\text{mol}$ **(0.5)**

$n_{HCl} = 0.001M \times 100 \times 10^{-3}\text{dm}^3 = 10^{-4}\ \text{mol}$ **(0.5)**

Thus the given amount of NaOH and HCl satisfy the given mole ratio and therefore nothing present in excess and thus all given NaOH and HCl will react. **(1)**

(d) Using $\text{pH} = \text{pKa} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$ **(0.5)**

From which;

$\text{pH} = \text{pKa} + \log\frac{\text{Number of moles of salt}}{\text{Number of moles of acid}}$ **(0.5)**

Also using; n = [ ]V

Number of moles of acid $= 0.12\ \text{moldm}^{-3} \times \frac{500}{100}\text{dm}^3 = 0.06\ \text{mol}$ **(0.5)**

Then

$4.6 = -\log(1.8 \times 10^{-5}) + \log\frac{\text{Number of moles of salt}}{0.06}$ **(0.5)**

From which $\log\frac{\text{Number of moles of salt}}{0.06} = -0.14$ **(0.5)**

Or number of moles of salt $= 006 \times \log^{-1}(-0.14)$

$= 0.04347\text{mol}$ **(1)**

Then using $m = nM_r$

Mass of salt $= 0.04347 \times 82$ **(0.5)**

$= 3.56\text{g}$

Hence the mass of sodium acetate added is 3.56g (**1**)

(e) The formula of calcium bicarbonate $(Ca(HCO_3)_2)$ suggests that one mole of $Ca(HCO_3)_2$ contain two moles of HCO_3^-

Thus if $[Ca(HCO_3)_2]$ is 0.01M, $[HCO_3^-]$ will be 0.02M. (**1**)
Then using $[H^+] = \alpha C$ (**0.5**)
Where $C = [HCO_3^-] = 0.02M$ and α is the degree of dissociation.

But from Ostwald dilution law $\alpha = \sqrt{\frac{K_a}{C}}$ (**1**)

Then $[H^+] = C\sqrt{\frac{K_a}{C}} = \sqrt{CK_a}$ and

$pH = -\log[H^+] = -\log\sqrt{CK_a}$ (**0.5**)
Substituting $pH = -\log\sqrt{0.02 \times 4.8 \times 10^{-12}}$ (**1**)
$= 6.5$
Hence pH of 0.01M calcium bicarbonate solution is 6.5.(**1**)

Question 4

(a)

(i) Dobereiner's law of triads

Advantages

1. Atomic mass (which is fundamental property of an atom) was considered as basis of classification. **(0.5)**
2. It made chemists to look at elements in terms of groups of elements with similar physical and chemical properties which eventually led to discovery of modern periodic table. **(0.5)**

Disadvantages

1. Not all known elements can be arranged in the form of triads. **(0.5)**
2. Some elements with dissimilar properties were grouped as triads. **(0.5)**

(ii) Newlands law of octaves

Advantages

1. It introduced the idea of periodicity (the core idea in which the modern periodic table is based). **(0.5)**
2. Dobereiner's triads occurred in the octaves of Newlands. **(0.5)**

Disadvantages

1. It was not valid for elements beyond calcium. **(0.5)**
2. When new elements like noble gases were discovered, Newland's table had no place for them. **(0.5)**

(iii) Long form of periodic table

Advantages

1. The modern periodic table is based on atomic number which is more fundamental property of an atom than atomic mass (weight). **(0.5)**
2. The table shows why elements in the same group display similar properties. **(0.5)**

Disadvantages

1. No clear position for hydrogen. **(0.5)**

2. Lanthanides and actinides are not accommodated in the main body of the periodic table. **(0.5)**

   Remark: Accept any two correct advantages and disadvantages in each case.

(b)

1. Both have an oxidation state of -1 **(1)**
2. Both have a high affinity to metals forming salts with them. **(1)**
3. Both act as ligand in complex formation. **(1)**
4. CN^-form HCN when its salt react with strong acid like halides which gives hydrogen halides with strong acids. **(1)**
5. CN^- undergo oxidation similar to halide ions. **(1)**
6. CN^- forms $(CN)_2$ which undergo disproportionation in alkaline medium like the halogens (formed after oxidation of halide ions. **(1)**
7. The CN^- forms precipitates with $Ag^+(aq)$and $Pb^{2+}(aq)$ like the halide ions **(1)**
8. Their hydride are acidic, i.e. both HCN and HX are acidic. **(1)**

   Remark: Any five correct advantages with maximum score of 5 marks.

(c)

(i) Mg being metal there is metallic bond existing between its atoms which is stronger than Van der Waals dispersion forces existing between phosphorous molecules which is non-metal. Stronger intermolecular forces means higher melting point for magnesium. **(1.5)**

(ii) Potassium has greater number of protons so there is a greater nuclear attractive force per electron in K^+ than in Cl^-; leading to more contraction of shells and hence smaller size for potassium ion.**(1.5)**

(iii) Due to its very small atomic size, it was expected fluorine to have greatest attraction to the added electron and hence greatest electron affinity. However the size of fluorine is so small that there is very large repulsion between its electrons (the small atomic size makes electrons to be very close to each other). This weakens the ability of fluorine to attract electrons and hence fluorine has unexpectedly lower electron affinity. **(1.5)**

(iv) The ionisation energy of K^+ to K^{2+} (in KCl_2) is too high to be compensated by either lattice energy in the solid KCl_2 or hydration energy in aqueous KCl_2 and hence the compound does not exist unlike KCl which has no such problem.

(v) With electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$, the element has very stable electronic configuration of exactly full filled electronic structure. The stability leads to difficulty of removing an electron from an atom of the element.**(1.5)**

(vi) Aluminium itself is so strong reducing that its ore which is composed of aluminium oxide cannot be reduced by common reductants like carbon. It requires stronger reduction method like electrolysis to get aluminium from its ore. **(1.5)**

Question 5

(a)

(i) Is the element whose atom or at least one of its ions have partially filled d-orbitals. (**0.5**)

(ii) Is an addition product which does not lose its identity in solution and behaves as one entity that consists of the central metal atom (or ion) and several ligands bonded to it by dative bond. **(0.5)**

(iii) Is the complex part of the complex compound that consists of central metal atom (or iron) and several ligands bonded to it by dative bond enclosed in large square brackets. **(0.5)**

(iv) Is the number of dative bonds the central metal atom makes with ligands during complex formation. **(0.5)**

(b)

(i) Hexaaquacobalt(III) ion **(1)**
(ii) Triamminediaquasulphatocopper (II) **(1)**
(iii) Tetraaquadicyanoiron (III) chloride **(1)**

(c)

(i) The white precipitate is due to the formation of insoluble silver chloride which dissolves in the aqueous ammonia due to the formation of soluble complex. (**1**)

$$\underset{}{AgNO_3(aq) + HCl(aq) \rightarrow} \underset{\text{Insoluble}}{AgCl(s)} + HNO_3(aq)$$

$$\text{Then } AgCl(s) + 2NH_3(aq) \rightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl} \quad (\mathbf{0.5})$$

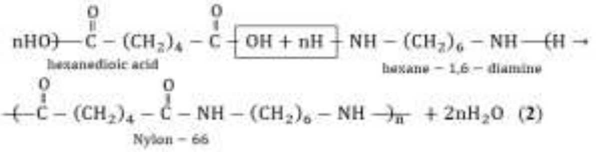
(ii) Dilute HCl depress the ionisation of H_2S by common ion effect thus lowering the concentration of S^{2-} in the solution and hence no precipitate of ZnS will be formed. (**1**)

That is:
$H_2S \rightleftharpoons 2H^+ + S^{2-}$ ……………… (i)
$HCl \rightarrow H^+ + Cl^-$ ……………….. (ii)
Thus adding $HCl(aq)$ is equivalent to increase of $[H^+]$ in (i) therefore shifting the position of equilibrium to the H_2S side. (**0.5**)

(d)

(i) Is a reaction in which two or more molecules of the same or different compounds combine to form new compound with or without elimination of small molecules (like H_2O and HCl). (**0.5**)
(ii) Nylon-66 is formed by **condensation polymerisation** of hexanedioic acid and hexane-1,6-diamine monomers. (**0.5**)

The two monomers link to form nylon-66 by eliminating water molecules as shown below:



$$nHO\!\!-\!\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\boxed{-OH + nH-}NH-(CH_2)_6-NH-H \rightarrow$$

$$\left(\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\right)_n + 2nH_2O \quad (2)$$

It is called nylon-66 because each of its constituent monomers contain six carbon atoms. (**1**)

(e) Firstly a solution of sucrose to which yeast is added, is heated. An enzymes, invertase, which present in yeast is added and this act as a catalyst to convert the sucrose into glucose and fructose. (**2**)

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \quad (\mathbf{1})$$

The glucose, $C_6H_{12}O_6$, and fructose, $C_6H_{12}O_6$, are then converted into ethanol and carbon dioxide by another enzymes, zymase, which is also present in yeast. (**2**)

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2 \quad (\mathbf{1})$$

The fermentation process is carried out at temperature between 250°C and 300°C. The ethanol is finally obtained by fractional distillation. (**2**)

Question 6

(a)

(i) $CH_3CH_2CH_2Br + NH_3(Excess) \xrightarrow{\text{Alcohol},\Delta} CH_3CH_2CH_2NH_2 + HBr$ **(1)**

(ii) First step:

$CH_3CH_2Br + KCN \xrightarrow{\text{Alcohol,reflux}} CH_3CH_2CN + KBr$ **(1)**

Second step;

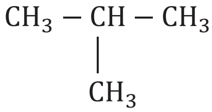
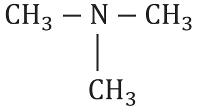
$CH_3CH_2CN + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$ **(1)**

(iii) Propyl group in the propylamine exerts positive inductive effect and therefore making easier for the amine to donate its lone pair and stabilizing the positive charge that is formed after the lone pair donation and hence propylamine becomes stronger base than ammonia. **(1.5)**

(iv) Strong acid like hydrochloric acid. **(0.5)**

Remark: $CH_3CH_2CH_2NH_3Cl$ (or any strong salt containing $CH_3CH_2CH_2NH_3^+$ is acceptable).

(v)

1. $CH_3CH_2CH_2NH_2$ **(0.75)**
2.  $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ **(0.75)**
3. $CH_3NHCH_2CH_3$ **(0.75)**
4.  $CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$ **(0.75)**

(b)

(i) The pain in the ant's bite is due to the release of methanoic (formic) acid in the ant's sting. So rubbing with the baking soda ($NaHCO_3$) which is the base will neutralise the acid in acid – base reaction and hence pain are eliminated. **(1.5)**

$\underset{\text{Baking soda}}{NaHCO_3} + \underset{\text{Ant's sting}}{HCOOH} \rightarrow HCOONa + CO_2 + H_2O$ **(0.5)**

(ii) Fishy odour is the result of presence of amine which is basic. Vinegar being acidic in neutralises amine present in the fish in acid-base neutralisation reaction and therefore reducing the smell. **(1.5)**

$(CH_3)_2NH(\text{or } (CH_3)_3N) + CH_3COOH$
$\longrightarrow (CH_3)_2NH_2COOCH_3\ (\text{or}(CH_3)_3NHCOOCH_3\ )$

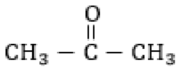
Fish odour Vinegar **(0.5)**

(iii) Ethanal is very strong reducing agent that is capable of reducing Tollen's reagent into silver metal and hence it becomes suitable in silvering of mirror.

$$RCHO + 2[Ag(NH_3)_2]NO_3 + H_2O \rightarrow RCOONH_4 + 2Ag + 3NH_3 + 2HNO_3$$

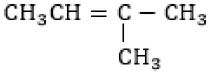
(c) Product obtained on ozonolysis of B, suggest that D is carbonyl compound with three carbons and the only carbonyl compound, with three carbons which gives positive iodoform test is propanone (**1**)

Thus structure of D is



$CH_3-\overset{\overset{O}{||}}{C}-CH_3$

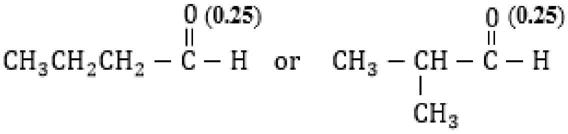
So ozonolysis of B gives ethanal and propanone and hence B is alkene with the following structure: (**0.5**)



$CH_3CH=\underset{\underset{CH_3}{|}}{C}-CH_3$

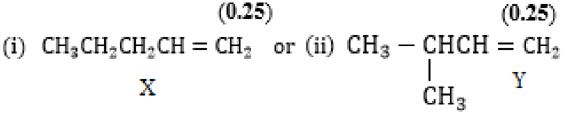
Products obtained on ozonolysis of C suggest that E is the carbonyl compound with four carbons and the carbonyl compound which gives positive Benedict's solution test is aldehyde. (**0.5**)

Thus structure of E is either:



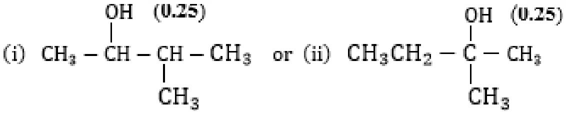
$CH_3CH_2CH_2-\overset{\overset{O}{||}}{C}-H$ (0.25) or $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-H$ (0.25)

And the structure of C may be either:
(Labelled X and Y)



(i) $\underset{X}{CH_3CH_2CH_2CH=CH_2}$ (0.25) or (ii) $\underset{Y}{CH_3-\underset{\underset{CH_3}{|}}{CH}CH=CH_2}$ (0.25)

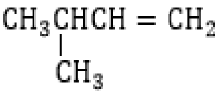
The alcohol which gives B upon dehydration has one of the following structure:



(i) $CH_3-\overset{\overset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ (0.25) or (ii) $CH_3CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$ (0.25)

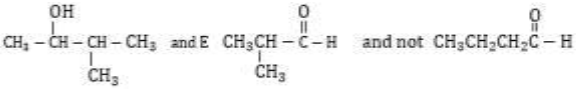
Since neither of the above two alcohols may give X upon dehydration, C cannot be X, it must be Y (**0.5**)

Thus the structure of C is



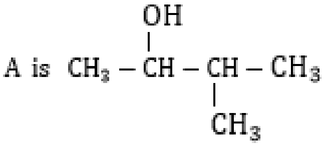
$CH_3\underset{\underset{CH_3}{|}}{C}HCH=CH_2$

Also from above two alcohol, the only alcohol which may give C is (i) and not (ii);$^{(0.5)}$ thus the structure of A must be



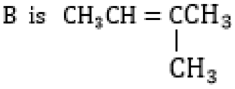
$CH_3-\overset{\overset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ and E $CH_3\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-H$ and not $CH_3CH_2CH_2\overset{\overset{O}{||}}{C}-H$

Hence structure of each compound is as follows:



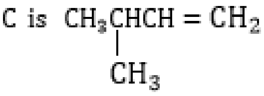
A is $CH_3-\overset{\overset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(**0.25**)



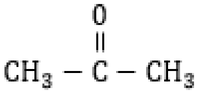
B is $CH_3CH=\underset{\underset{CH_3}{|}}{C}CH_3$

(**0.25**)

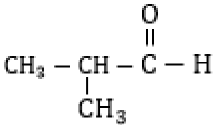


C is $CH_3\underset{\underset{CH_3}{|}}{C}HCH=CH_2$

(**0.25**)

D is 

$CH_3 - \overset{\overset{\large O}{||}}{C} - CH_3$ **(0.25)**

E is 

$CH_3 - \underset{\underset{\large CH_3}{|}}{CH} - \overset{\overset{\large O}{||}}{C} - H$ **(0.25)**

Solutions Examination Seventeen

CHEMISTRY 1I

Question 1

(a)

(i) In the ground state, electrons tend to occupy the orbital with minimum energy.**(0.5)**

(ii) No two electrons in the same atom can have the same all four quantum numbers.**(0.5)**

(iii) Electrons are not allowed to pair up unless the empty degenerate orbitals are singly occupied with parallel spins electrons. **(0.5)**

(iv) For d and f orbitals the full or half full configurations in the sub –shells are very stable configuration with minimum energy content. **(0.5)**

(b) From the Heisenberg's equation;

$$\Delta x \times m\Delta v \approx \frac{h}{4\pi}$$

Rearranging the above equation gives;

$$\Delta x \approx \frac{h}{4\pi \times m\Delta v}\mathbf{(0.5)}$$

From which it can be deduced that the uncertainty in determining position (Δx) of an object of mass, m, varies inversely proportional to the uncertainty in the determination of velocity (Δv) of the object. **(0.75)**

That means if the velocity of the object is determined with more accuracy then its position will determined with less accuracy as suggested in Heisenberg uncertainty principle. **(0.75)**

(c) Using; $Z = A - \text{Number of neutrons}$

Atomic number of $x = 35 - 18 = 17 = \text{Atomic number}$
For neutral atom; atomic number = number of electrons
Thus **number of electrons in Y is 17 (0.75)**
Using Number of neutrons = A – Z
Number of neutrons in Y = 37 – 17 = 20
Thus **number of neutrons in Y is 20 (0.75)**

(d) Energy of one photon is given by the following Planck's equation; $E = hf = \frac{hc}{\lambda}$

Substituting $E = \frac{6.63\times10^{-34}\text{J}\times3\times10^{8}\text{m/s}}{987\times10^{-9}\text{m}} = 2.0152\times10^{-19}\text{J/photon}$

But total energy emitted in $32\text{sec} = 0.52\text{J}$

And the total energy=Energy per photon×Number of photons

Thus Number of photons emitted (in 32s)

$$= \frac{\text{Total energy}}{\text{Energy per photon}} = \frac{0.52\text{J}}{2.0152\times10^{-19}\text{J/photon}} = 2.58\times10^{18}\text{ photons}$$

And number of photons emitted per second

$$= \frac{\text{Total number of photons emitted}}{\text{Time taken}} = \frac{2.58\times10^{18}\text{ photons}}{32\text{sec}}$$

$$= 8.0625\times10^{16}\text{photon/sec}$$

Hence 8.0625×10^{16} photons were emitted in one second.

(e)

(i) Disagree **(0.5)**

Reason:

Due to isotopy, it is possible for atoms of the same element to have different number of neutrons. **(01)**

(ii) Agree **(0.5)**

Reason:
Atoms of the same element may have different number of neutrons and hence different atomic masses. **(1)**
Remark: The reason must base on isotopy.

Question 2

(a)

(i) Is the special type of intermolecular forces between the partially positively charged hydrogen atom in a polar bond and lone pair (non-bonding electron) on a nearby small electronegative ion or atom.

Remark: Definition which gives the idea that hydrogen bond is the force of attraction between partial positive and **partial negative** is **not** acceptable.

(ii)

1. It increases boiling point of compounds **(0.5)**
2. It increases solubility of compounds in water **(0.5)**

(b)

(i) Van-der-Waals dispersion forces and hydrogen bond **(0.75)**
(ii) Van-der-Waals dispersion forces **(0.5)**
(iii) Van-der-Waals dispersion forces and permanent dipole-dipole forces **(0.75)**
(c) If the molecule is symmetrical, there is cancellation of dipole moments leading to zero resultant of dipole moment, the molecule will be non-polar even if it contains polar bond. **(1)**

Example: Carbondioxide molecule (CO_2) **(0.5)**

(d)

(i) Electronic configuration of P= $[Ne]3s^1$ **(0.5)**

Electronic configuration of Q= $[Ne]3s^2 3P^3$ **(0.5)**
Electronic configuration of R= $[Ne]3s^2 3P^5$ **(0.5)**
Electronic configuration of S= $[Ar]3d^{10}4s^1$ **(1)**

(ii) P and R: Ionic (or electrovalent) bonding **(0.5)**

Q and R: Covalent bonding **(0.5)**
P and S: No bonding **(0.5)**
Atoms of R: Covalent bonding **(0.5)**
Atoms of P: Metallic bonding **(0.5)**

Question 3

(a)

(i) Is the gas which obeys ideal gas equation (PV=nRT) in all conditions of temperature and pressure. **(0.5)**
(ii) Ideal gas equation can be derived by combining Boyle's law, Charles's law and Avogadro's law as shown below:

From Boyle's law: $V \propto \frac{1}{P}$; constants: n and T**(0.25)**
From Charles's law: $V \propto T$; constants: n and P **(0.25)**

Avogadro’s law: $V \propto n$; constants: P and T **(0.25)**
Combining the three laws: $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$ **(0.25)**
Where R is the proportionality constant which is known as universal molar gas constant. Hence $PV = nRT$ and the result is known as ideal gas equation. **(0.5)**

(b)
(i) At low temperature, kinetic energy is not enough to break intermolecular forces and therefore making the molecular attraction high. **(1)**
(ii) Ammonia having intermolecular hydrogen bonding which is stronger than the Van-der-Waals dispersion forces present in the nitrogen, has stronger intermolecular forces and hence larger value of ‘a’ for ammonia. But larger molecular mass of nitrogen implies that nitrogen molecule has larger molecular volume and hence larger value of ‘b’ for nitrogen. **(2)**
(c) Molar mass of CaF_2 is 78 g/mol. Thus mass of F in 78g of $CaF_2 = 38$ g

And mass of F in 0.2631g of $CaF_2 = \frac{38 \times 0.2631g}{78} = 0.1282g$ **(0.5)**
If P_xF_y represent the molecular formula of the compound (of phosphorous and fluorine).
Then 0.1282 g will also be the mass of F in 0.2324 g of P_xF_y
And mass of P in 0.2324 of P_xF_y will be $(0.2324 - 0.1282)g = 0.1042$ g **(0.5)**
Using $n = \frac{PV}{RT}$ (From $PV = nRT$)
Number of moles of $P_xF_y = \frac{97.3 \times 378 \times 10^{-3}}{760 \times 0.082 \times 350}$ moles $= 1.6862 \times 10^{-3}$ mol **(0.5)**
Then using $n = \frac{m}{M_r}$;
Number of moles of P atoms in 1.6862×10^{-3} mol of P_xF_y

$$= \frac{0.1042g}{31g/mol} = 3.3613 \times 10^{-3} \text{mol} \ \textbf{(0.5)}$$

Thus number of moles of P atoms in 1 mole of P_xF_y

$$= \frac{3.3613 \times 10^{-3}}{1.6862 \times 10^{-3}} \text{mol} = 2 \text{ mol of P atoms } \textbf{(0.5)}$$

Whence x = 2 (x is the number of moles of P atoms in 1 mol of P_xF_y). **(0.5)**
Also number of moles of F atoms in 1.6862×10^{-3} mol of P_xF_y

$$= \frac{0.1282g}{19g/mol} = 6.7474 \times 10^{-3} \text{mol} \quad \textbf{(0.5)}$$

Thus number of moles of F atoms in 1 mol of P_xF_y

$$= \frac{6.7474 \times 10^{-3}}{1.6862 \times 10^{-3}} \text{mol} = 4 \text{ mol of F atoms } \textbf{(0.5)}$$

Whence y = 4 **(0.5)**
Hence the molecular formula of the formula compound is P_2F_4 **(0.5)**

Question 4

(a)
(i) Van’t Hoff theory of dilute solutions **(0.75)**
(ii)

First law:
For dilute solution of a given solute, at constant temperature, the osmotic pressure of the solution is directly proportional to its mass concentration. **(0.75)**
Second law:

The osmotic pressure of given concentration of solution is directly proportional to its absolute temperature. **(0.75)**

Third law:

Osmotic pressure and temperature being the same, equal volumes of solution contains equal number of moles (or molecules) of the solute. **(0.75)**

(b) As a solution freezes, the solvent molecules are removed from the solution which causes an increase in the concentration. This causes further freezing temperature depression. **(1)**

(c) Using $\Delta T = K_f m = \frac{K_f \times m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$ $\mathbf{(0.5)}$

Where $\Delta T = (25.5 - 24.59)°C = 0.91°C$

$M_{su} = 18\text{gmol}^{-1}$

$m_{sv} = 10\text{g} = 0.01\text{kg}$

Substituting $0.91 = \frac{9.1 \times m_{su}}{18 \times 0.01}$ $\mathbf{(1)}$

From which; $m_{su} = 0.018\text{g}$

The mass of water in the sample is 0.018g **(0.5)**

(d)

Constituent elements	C	O	N	H
%age of each	19.93	26.7	46.7	6.67
Mass of each in 100g of the compound	19.93g	26.7g	46.7g	6.67g
Number of moles of each, $n = \frac{m}{M_r}$	$\frac{19.93}{12\text{gmol}^{-1}}$ $= 1.66\text{mol}$	$\frac{26.7\text{g}}{16\text{gmol}^{-1}}$ $= 1.67\text{mol}$	$\frac{46.7\text{g}}{14\text{gmol}^{-1}}$ $= 3.336\text{mol}$	$\frac{6.67\text{g}}{1\text{gmol}^{-1}}$ $= 6.67\text{mol}$
Dividing by smallest to get simpler ratio	$\frac{1.66\text{mol}}{1.66\text{mol}}$ $= 1$	$\frac{1.67\text{mol}}{1.66\text{mol}} =$ 1=1	$\frac{3.336\text{mol}}{1.66\text{mol}}$ $= 2$	$\frac{6.67\text{mol}}{1.66\text{mol}}$ $= 4$

The empirical formula is CON_2H_4

Using $\Delta T = K_b m = \frac{K_b \times m_{su}}{M_{su} \times m_{sv} \text{in kg}}$

From which:

$$M_{su} = \frac{K_b \times m_{su}}{\Delta T \times m_{sv} \text{in kg}}$$

Where:

$\Delta T = (82.3 - 80.2)°C = 21°C$

$m_{su} = 5\text{g}$

$m_{sv} = 100\text{g} = 0.1\text{kg}$

Substituting:

$$m_{su} = \frac{2.53 \times 5}{2.1 \times 0.1}\text{gmol}^{-1} = 60\text{gmol}^{-1}$$

Let the molecular formula be $(CON_2H_4)_n$

Then $12n + 16n + 28n + 4n = M_r = 60$

$60n = 60; n = 1$

The molecular formula is CON_2H_4

Question 5

(a)

(i) Sodium carbonate (washing soda) **(0.5)**

(ii) Sodium bicarbonate **(0.5)**

(iii) Sodium carbonate/calcium carbonate **(0.5)**

(iv) Sodium carbonate (washing soda or soda ash) **(0.5)**

(v) Calcium carbonate **(0.5)**

(b)

(i) Because during the reaction metals displace (reduce) hydrogen from dilute H_2SO_4 to form their respective sulphates. **(0.75)**

(ii) Examples: Magnesium sulphate and zinc sulphate **(0.5)**

Remark: Any sulphate out of sulphate of magnesium, aluminium, zinc, iron or tin is **not** acceptable.

Equations:

$Zn(s) + H_2SO_4(dil) \rightarrow ZnSO_4(aq) + H_2(g)$**(0.25)**

$Zn(s) + H_2SO_4(dil) \rightarrow ZnSO_4(aq) + H_2(g)$ **(0.25)**

(iii)

1. The metal must be stronger reducing agent than hydrogen **(0.5)**
   Metals which meet this condition are found above hydrogen in the electrochemical series. Metals below hydrogen in the electrochemical series are not strong reducing agent enough to reduce in dilute acids and therefore these metals will not get oxidised to their sulphate.**(0.75)**
2. The sulphate of the metal must be soluble **(0.5)**
   Even reactive metals (which are stronger reducing agent than hydrogen) may not react with dilute H_2SO_4 if they form insoluble sulphate which prevents further reaction. **(0.75)**
3. The metal must be moderately reactive **(0.5)**

   The metal may meet above two conditions but still its sulphate cannot be prepared by displacement method if the metal is so reactive that its reaction with dilute H_2SO_4 cause an explosion thus making unsafe to conduct the experiment in the laboratory. **(0.75)**

(iv) No. **(0.25)**

Explanation

Copper being weaker reducing agent than hydrogen, does not react with dilute H_2SO_4 and hence the displacement method is not suitable for preparation of $CuSO_4$.**(0.75)**

That is: $Cu(s) + H_2SO_4(dil) \rightarrow$ No reaction

(v) **Alternative method:** Neutralisation method **(0.5)**

Equation: $CuO(s) + H_2SO_4(dil) \rightarrow CuSO_4(aq) + H_2O(l)$ **(0.5)**

Remark: Allow the reaction between copper and concentrated sulphuric acid.

$$Cu(s) + 2H_2SO_4(conc.) \rightarrow CuSO_4 + SO_2 + 2H_2O$$

Question 6

(a)

(i) Is the energy required to break one mole of molecules to their corresponding gaseous atoms under given conditions of temperature and pressure. **(0.5)**

(ii) Is the heat required to convert an element in its normal state into one mole of its corresponding gaseous atoms under standard conditions of temperature and pressure. **(0.5)**

(iii) Is the energy required to remove completely the most loosely bound electron each from one mole of gaseous atom or ion at given conditions of temperature and pressure. **(0.5)**

(iv) Is the energy change when electrons are added to one mole of gaseous atom or ion at given conditions of temperature pressure. **(0.5)**

(v) Is the heat change when one mole of a substance (solute) dissolves in a specified amount of solvent (water) to give a solution under given conditions of temperature and pressure. **(0.5)**

(vi) Is the heat change when one mole of substance is added to so much water that further addition of water produces no further heat change under given conditions of temperature and pressure. **(0.5)**

(b)

(i) Enthalpy of solution **(0.5)**

(ii) Atomisation energy **(0.5)**

(iii) First electron affinity **(0.5)**

(iv) Enthalpy of neutralisation **(0.5)**

(c) Using m = nM_r;

Mass of trichloromethane, $m_t = 0.05\text{mol} \times 119\text{gmol}^{-1} = 5.975\text{g}$ **(0.5)**

Mass of ethoxyethane, $m_e = 0.3\text{mol} \times 74\text{gmol}^{-1} = 22.2\text{g}$ **(0.5)**

Since the temperature increased, the heat change is negative (The process is exothermic)

Thus $\Delta H = -(m_t C_t \Delta T + m_e C_e \Delta T)$ **(0.5)**

Substituting; $\Delta H = -\big((5.975 \times 0.98 \times 5.4) + (22.2 \times 2.28 \times 5.4)\big)\text{J}$ **(0.5)**

$$= -304.95\text{J}$$

The heat change in the experiment is the experiment is -304.95J (1)

The molar enthalpy change = $\frac{\text{Heat change}}{\text{Number of moles of CHCl}_3}$

$$= \frac{-304.95\text{J}}{0.05\text{mol}}\ (\mathbf{0.5})$$

$$= -6099\text{Jmol}^{-1} = -6.099\text{kJmol}^{-1}$$ **(0.5)**

The enthalpy change of mixing one mole of trichloromethane with excess ethoxyethane is -6.099kJ (1)

Question 7

(a)

In terms of Le-Chatelier's principle: To decrease the applied high pressure the equilibrium position will shift to the side with fewer gas particles (ammonia side) by producing more ammonia and hence high pressure has an advantage of increasing the ammonia yield in the Haber process. **(1.5)**

In terms of behaviour of particles: High pressure makes gases to be more compressed into smaller volume and therefore more concentrated leading to greater collision frequency and hence higher reaction rate. So high pressure has another advantage of increasing the rate of ammonia production in the Haber process. **(1.5)**

(b) Catalyst affects chemical equilibrium by enabling the equilibrium to be reached earlier. It has no effect on the **position** of chemical equilibrium (not chemical equilibrium in general). **(2)**

(c)

(i) $K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]}$ **(0.5)**

(ii) At equilibrium:

$n_{Acid} = 1 - x;\ \ n_{Ethanol} = 2 - x$
$n_{Ester} = x;\ \ n_{Water} = 5 + x$
But $n_{Ester} = x = 0.54mol;$
Thus $n_{Water} = 5 + x = (5 + 0.54) = 5.54mol$
The number of moles of water is 5.54mol **(1)**

(iii)

$$K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]} = \frac{\left(\frac{x}{V}\right)\left(\frac{5+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{2-x}{V}\right)} = \frac{x^2 + 5x}{x^2 - 3x + 2}\ (\mathbf{0.5})$$

Substituting;

$$K_c = \frac{0.54^2 + 5(0.54)}{0.54^2 - 3(0.54) + 2}\ (\mathbf{0.5}) = 4.45$$

The value for K_c is 4.45 **(1)**
The K_c value has no units because there is an equal number of molecules in either side (reactants side and products side) of the reaction equation.

(iv) A: The amount will decrease. **(0.5)**
B: The time will decrease. **(0.5)**
C: The value will decrease. **(0.5)**

Question 8

(a)

(i) Is the atom or bond(s) which determine characteristic chemical reaction of organic compound. Example, carboxylic group (-COOH)for carboxylic acid.**(0.5)**

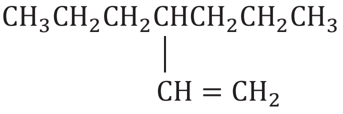
(ii) Is the hydrocarbon that is formed after removing only one hydrogen atom from alkane. Example, ethyl group (C_2H_5) **(0.5)**

(b)

(i) Missed structure:

$CH_3CH(CH_3)CH_2CH = CH_2$ **(0.5)**
Correct name: 4-methylpent-1-ene **(0.5)**

(ii) Missed structure;

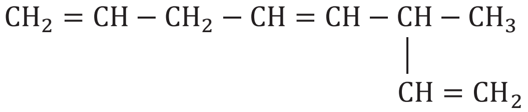


$$\underset{\displaystyle CH=CH_2}{CH_3CH_2CH_2\overset{}{C}HCH_2CH_2CH_3}$$

(0.5)

Correct name 3-propylhex-1-ene **(0.5)**

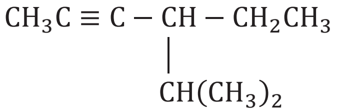
(iii) Missed structure:



$CH_2 = CH - CH_2 - CH = CH - \underset{\underset{CH = CH_2}{|}}{CH} - CH_3$ **(0.5)**

Correct name: 3-methylocta-1,4,7-triene **(0.5)**

(iv) Missed structure:



$CH_3C \equiv C - \underset{\underset{CH(CH_3)_2}{|}}{CH} - CH_2CH_3$ **(0.5)**

Correct name: 4-ethyl-5-methylhex-2-yne

(v) Missed structure:

$CH_2 = CH - C \equiv CH$ **(0.5)**

Correct name: 1-buten-3-yne **(0.5)**

(c)

(i) $CH_3CH_2OH + H_2SO_4(conc) \xrightarrow[170°C]{} CH_2 = CH_2 + H_2O$ **(1)**

(ii) $CH_3C \equiv CH + H_2 \xrightarrow{pd,BaSO_4/25°C} CH_3CH = CH_2$ **(1)**

(iii) $CH_3CH_2CH_2CH_2Br + 2[H] \xrightarrow{Zn|HCl(aq)} CH_3CH_2CH_2CH_3 + HBr$ **(1)**

(iv) $CH_3CHO + 4[H] \xrightarrow{Zn-Hg,HCl(conc)} CH_3CH_3 + H_2O$ **(1)**

(v) $CH_3CH_2Cl + HC \equiv CAg \rightarrow CH_3CH_2C \equiv CH + AgCl$ **(1)**

(d) $C_5H_{10} + O_3 \xrightarrow{Zn,H_2O} HCHO + CH_3 - CH(CH_3) - CHO$ **(0.5)**

R S

Thus R is alkene with the following structure:

$CH_3CH(CH_3)CH = CH_2$ **(0.75)**

And S is aldehyde with the following structure:

$CH_3CH(CH_3)CHO$ **(0.5)**

$C_5H_{12}O \xrightarrow{H_2SO_4(Conc),170°C} CH_3CH(CH_3)CH = CH_2$ **(0.5)**

Q R

Thus Q is primary alcohol with the following structure:

$CH_3CH(CH_3)CH_2CH_2OH$ **(0.5)**

$C_5H_{11}Br + NaOH(aq) \rightarrow CH_3CH(CH_3)CH_2CH_2OH + NaBr$ **(0.5)**

P

Thus P is bromoalkanes with the following structure:

$CH_3CH(CH_3)CH_2CH_2Br$ **(0.5)**

Question 9

(a)

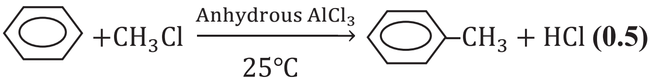
(i) Is an organic reaction whereby atoms (or groups of atoms) are removed from organic compound. **(0.5)**

Example:

$CH_3CH_2OH + H_2SO_4(conc) \xrightarrow[170°C]{} CH_2 = CH_2 + H_2O$ **(0.5)**

(ii) Is an organic reaction whereby atom or group of atoms is replaced by electrophile from the organic compound. **(0.5)**

Example:



(0.5)

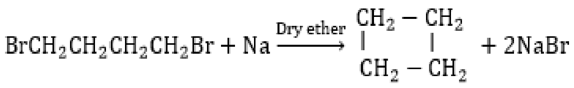
(iii) This is an organic reaction whereby atom (or group of atoms) is replaced by nucleophile from the organic compound. **(0.5)**

Example:

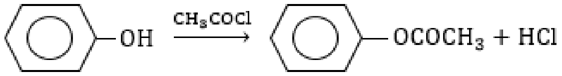
$CH_3CH_2Cl + NaOH(aq) \xrightarrow[25℃]{} CH_3CH_2OH + NaCl$ **(0.5)**

(b)

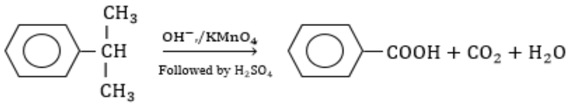
(i)



(ii)



(iii)

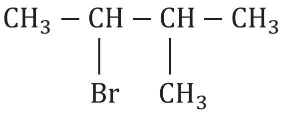


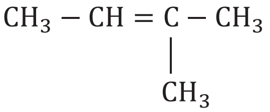
(c) The hypothetical cyclohexa-1,3,5-triene is expected to have enthalpy of hydrogenation of 3× (−120kJ/mol) which is − 360kJ/mol.

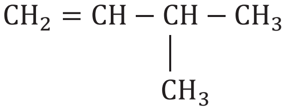
Benzene having enthalpy of hydrogenation of −208kJ whose magnitude is smaller than −360kJ/mol is more stable than the triene due to stabilization of its pie bonds by mesomerism and the difference of the two enthalpies amounted to 152kJ/mol which is known as resonance energy reflects the extra stability the benzene possess over the stability of cyclohexa-1,3,5-triene. **(3)**

(d)

(i) Elimination **(0.5)**

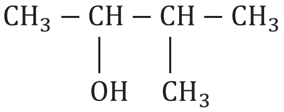
(ii)

$CH_3 - \underset{Br}{\underset{|}{CH}} - \underset{CH_3}{\underset{|}{CH}} - CH_3$ **(0.5)**

(iii)

$CH_3 - CH = \underset{CH_3}{\underset{|}{C}} - CH_3$ **(1)**

(iv)

$CH_2 = CH - \underset{CH_3}{\underset{|}{CH}} - CH_3$ **(0.5)**

(v) Position isomerism **(0.5)**

(e)

(i)  (1)

$CH_3-CH(OH)-CH(CH_3)-CH_3$

(ii)

1. Potassium hydroxide should be **diluted (0.5)**
2. The solution mixture should be **cooled (0.5)**
3. The ethanol solvent medium should be replaced by **aqueous medium (0.5)**

(iii) Nucleophilic substitution **(0.5)**

Question 10

(a)

(i) Sulphur dioxide

Sources:

1. Metal smelter **(0.5)**
2. Oil refining **(0.5)**
3. Paper and pulp manufacturing **(0.5)**
4. Burning coal **(0.5)**

Effects:

1. Lungs disease **(0.5)**
2. Plant problems **(0.5)**
3. Corrosion problems **(0.5)**
4. Damage of buildings **(0.5)**

(ii) Ground level ozone

Sources:

1. Electrical discharge **(0.5)**
2. Photodissociation of NO_2 **(0.5)**

Effects:

1. Eye irritation **(0.5)**
2. Compromised lung functions **(0.5)**
3. Aggravation of respiratory conditions like asthma **(0.5)**
4. Increased susceptibility to infection **(0.5)**
5. Photochemical smog formation **(0.5)**

(iii) Particulate matter

Sources:

1. Combustion of pyrite **(0.5)**
2. Mining and processing of uranium ore **(0.5)**
3. The fly ash **(0.5)**
4. Nuclear weapon testing **(0.5)**

Effects:

1. Heart disease **(0.5)**
2. Lung disease **(0.5)**

(iv) Lead

Sources:

1. Gasoline in piston engine aircraft **(0.5)**
2. Paints **(0.5)**
3. Storage batteries and battery manufacturing **(0.5)**
4. Pipes
5. Smelters (metal refineries). **(0.5)**

Effects:

1. Renal system **(0.5)**
2. Cardiovascular system **(0.5)**
3. Reproductive system **(0.5)**
4. Nervous system **(0.5)**

(b) Mass of Ca in 20g of soil sample is 0.0015g

So mass of Ca in 100g of soil sample will be $\frac{100\times 0.0015}{20} = 0.0075\text{g}$ **(0.5)**

Number of moles of calcium $= \frac{0.0075}{40} = 0.0001875\text{mol}$ (using $n = \frac{m}{M_r}$) **(0.5)**

But 1 mol = 1000mmol (millimoles)

Thus, there are 0.0001875×1000 mmol or 0.1875mmol of Ca in 100g of the soil **(0.5)**

Using, number of milliequivalents

= number of millimoles × amount of ionic charge

But ionic form of calcium is Ca^{2+} whose amount of ionic charge is 2.

Then number of meq of calcium in 100g of the soil

$$= 0.1875\times 2\text{meq} = 0.375\text{meq}$$

Hence the concentration of the calcium is 0.375 meq/100g soil **(0.5)**

(c)

(i) Are very small organic and inorganic particles present in the soil which are responsible for potential fertility of the soil. **(0.5)**

(ii) As soil is formed during the weathering processes, some minerals and organic matter are broken down to extremely small particles. Chemical changes further reduce these particles until they cannot be seen with the naked eye. The very smallest particles are known as soil colloids. **(1)**

(iii)

1. Layer silicate clays **(0.5)**
2. Iron and aluminium oxide clays (sesquioxide clays) **(0.5)**
3. Allophane and associated amorphous clays **(0.5)**
4. Humus (Organic colloid) **(0.5)**

(iv) Soil colloids facilitate plant nutrition by affecting intake of nutrients by plants. Being negative charged accompanied with large surface area, they adsorb nutrient cations and they allow them (nutrients cations) to be taken by plants through cation exchange reaction. **(1.5)**

Solutions Examination Eighteen
CHEMISTRY 2I

Question 1

(a)

(i) Ideal solution **(0.5)**

(ii) Non-ideal solution with negative deviation **(0.5)**

(iii) Non-ideal solution with positive deviation **(0.5)**

(iv) Non-ideal solution with negative deviation **(0.5)**

(b)

An alcohol-water solution has a higher vapour pressure than that of pure water because alcohol is a volatile solute and therefore contributes significantly to the vapour of the solution. This high vapour pressure accounts for the lower boiling point in alcohol-water solution. **(1)**

On another hand, a salt-water solution has a lower vapour pressure than that of pure water because salt is a non-volatile solute and solute-solvent interaction decrease the vapour of the solution. This low vapour pressure accounts for the higher boiling point in salt-water solution. **(1)**

(c)

(i) Partition coefficient **(0.5)**

(ii) Given that: $\frac{\text{Concentration of phenylamine in water}}{\text{Concentration of phenylamine in ethoxyethane}} = 0.2(\mathbf{0.5})$

Let mass of phenylamine extracted in ethoxyethane layer be x

Then $\frac{20-x/_{100}}{x/_{100}} = 0.2, (\mathbf{1})$ $\frac{20-x}{x} = 0.2 \text{ or } x = 16.67\text{g per dm}^3$**(1)**

But exact volume used was 100cm^3

So exact mass extracted was $\frac{100}{1000} \times 16.67\text{g} = 1.667\text{g}$ **(0.5)**

Hence 1.667g of phenyl amine was extracted in phenylamine layer **(1)**

(iii) By dividing the total volume of the extractive solvent (ethoxyethane) into as many smaller portions as possible rather than using the whole volume at once. **(1.5)**

(d)

(i) Let mass of each component be m (the two components weighs equal).

Then nnumber of moles of benzene, $n_b = \frac{m}{78}$

And number of moles of toluene, $n_t = \frac{m}{92}$

So in the liquid mixture: $X_b = \frac{n_b}{n_b + n_t} = \frac{\frac{m}{78}}{\frac{m}{78}+\frac{m}{92}} = \frac{46}{85}$ **(1)**

And $X_t = 1 - X_b = 1 - \frac{46}{85} = \frac{39}{85}$ **(0.5)**

By Raoult's law: $P_t = P_t^o X_t = \frac{290\times39}{45}\text{torr} = 133\text{torr}$

And $P_b = P_b^o X_t = \frac{753\times46}{85}\text{ torr} = 407.5\text{torr}$

Hence:

Partial pressure of toluene is 133torr **(0.5)**

Partial pressure of benzene is 407.5torr **(0.5)**

(ii) The solution will boil when the vapour pressure of the solution (P_{soln}) is equal to the atmospheric pressure. **(0.5)**

- But by Dalton's law of partial pressure: $P_{soln} = P_t + P_b = (133 + 407.5)\text{torr} = 540.5\text{torr}$

  Hence the atmospheric pressure required to boil the solution is 540.5torr **(1)**

(iii) Mole fraction of toluene in the vapour phase; $X_t^v = \frac{P_t}{P_{soln}} = \frac{133\ \text{torr}}{540.5\ \text{torr}} = 0.246(\mathbf{0.5})$

And $X_b^v = 1 - X_t^v = 1 - 0.246 = 0.754$**(0.5)**

When the vapour is condensed, the composition the condensed liquid does not change compared to the composition of the vapour. **(0.5)**

That is; liquid composition = composition of vapour which has been condensed to get the liquid

Hence the composition of the distillate (condensed liquid) will be 0.246 and 0.754 for toluene and benzene respectively by the mole fraction. **(0.5)**

Question 2

(a)

(i) Is the unstable chemical specie that results from successful collision between reacting particles that has partially formed and broken bonds.(**0.5**)

Remark: An alternative definition: It is an intermediate product that is formed when collided reactants have just attained activation energy.

(ii) Is the differential equation that describe the mathematical relationship between rate of reaction and concentration of reactants. (**0.5**)

Remark: An examinee is not supposed to state the law (rate law) as the question asked to give the **meaning** and not to **state** the law. (**Award zero score** if the examinee stated the law instead of giving the meaning).

(iii) Is the total number of reactant molecules which takes part in a particular **elementary** reaction. (**0.5**)

Remark: The keyword 'elementary/step of reaction mechanism' must appear in the definition. (Molecularity is for elementary reaction only and not for the overall reaction unless the reaction takes place through one step only).

(iv) Are powers (exponents) of concentration of reactants in the rate law. **(0.5)**

(b)

(i) p is a probability factor (or steric factor or orientation factor). It is the probability that the collision will have good orientation. **(0.75)**

z is a total number of binary collisions per unit time. It is the total number of collisions whether they have proper orientation or not or whether they have activation energy or not. **(0.75)**

(ii) Name: Arrhenius constant. **(0.5)**

Significance: It gives total number of binary collisions with proper orientation per unit time. **(1)**

(iii) **First way:** By decreasing the value of E_a**(0.5)**

Explanation

Catalyst provides alternative route of reaction with smaller activation energy (E_a). From the given equation, smaller value of E_a means larger value of k. **(1)**

Second way: By increasing the value of p **(0.5)**

Explanation

Catalyst improves orientation of reacting particles. By doing this it increases the value of p. From the given equation, large value of p means large value of k. **(1)**

(c) From the given balanced reaction equation:

$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$ **(0.5)**

But $-\frac{d[N_2O_5]}{dt} = 4.2 \times 10^{-7} \text{molsec}^{-1}$

Then substituting:

$\frac{1}{2} \times 4.2 \times 10^{-7} \text{molsec}^{-1} = \frac{1}{4}\frac{d[NO_2]}{dt}$**(0.5)**

From which: $\frac{d[NO_2]}{dt} = 8.4 \times 10^{-7} \text{molsec}^{-1}$

Hence the rate of appearance of NO_2 is $8.4 \times 10^{-7} \text{molsec}^{-1}$ (0.5)

Remark: It is **not** correct to use $\frac{\Delta[\ ]}{\Delta t}$ instead of $\frac{d[\ ]}{dt}$ (Here we are dealing with **instantaneous rate** (refers the words; 'at particular **instant**' in the question) and the 'Δ'is used for the **average rate**).

$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt}$ **(0.5)**

Substituting $\frac{1}{2} \times 4.2 \times 10^{-7} \text{molsec}^{-1} = \frac{d[O_2]}{dt}$**(0.5)**

From which; $\frac{d[O_2]}{dt} = 2.1 \times 10^{-7} \text{ molsec}^{-1}$

Hence the rate of appearance of O_2 is $2.1 \times 10^{-7} \text{molsec}^{-1}$ (0.5)

(d) $KMnO_4$ was used to oxidise the undecomposed H_2O_2 **(0.5)**

So the volume of $KMnO_4$ used in the titration varies directly proportional to the concentration of the undecomposed H_2O_2 (Greater amount of H_2O_2 needs larger volume of $KMnO_4$ for its oxidation) **(0.5)**

Thus if a and V_o are respectively representing the original concentration of H_2O_2 and the original volume of $KMnO_4$ used for the titration (to oxidise the H_2O_2) **(0.5)**

And $a - x$ and V_t are respectively representing concentration of H_2O_2 and volume of $KMnO_4$ used to oxidise the H_2O_2 after any time, t, of its (H_2O_2) decomposition' **(0.5)**

Then $a \propto V_o$ or $a = kV_o$

And $a - x \propto V_t$ or $a = kV_t$

Thence $\frac{a}{a-x} = \frac{kV_o}{kV_t} = \frac{V_o}{V_t}$ **(0.5)**

But from the differential rate equation of first order

$\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$ **(0.5)**

But $\frac{a}{a-x} = \frac{V_o}{V_t}$ (As shown above)

Thus $\log\left(\frac{V_o}{V_t}\right) = \frac{kt}{2.303}$

From which $k = \frac{2.303}{t}\log\left(\frac{V_o}{V_t}\right)$ **(0.5)**

Where $V_o = 70 \text{ cm}^3$

When $t = 6 \text{ min}, V_t = 47 \text{ cm}^3$

Then $K_1 = \frac{2.303}{6}\log\left(\frac{70}{47}\right) = 0.0664 \text{ min}^{-1}$ **(1)**

When $t = 9 \text{ min}, V_t = 30 \text{ cm}^3$

Then $K_2 = \frac{2.303}{9}\log\left(\frac{70}{30}\right) = 0.0942 \text{ min}^{-1}$ **(1)**

When $t = 20\ \text{min}, V_t = 13\ \text{cm}^3$

Then $K_3 = \frac{2.303}{20}\log\left(\frac{70}{7.2}\right) = 0.0842\ \text{min}^{-1}$ (**1**)

When $t = 29\ \text{min}, V_t = 7.2\ \text{cm}^3$

Then $K_4 = \frac{2.303}{29}\log\left(\frac{70}{7.22}\right) = 0.0784\ \text{min}^{-1}$ (**1**)

Since the rate constants do not differ much, the given data obey differential rate equation of first order and hence the reaction is of the first order. (**1.5**)

Rate constant, $k = \frac{k_1+k_2+k_3+k_4}{4}$ (**0.75**)

$= \frac{(0.0664+0.0942+0.0842+0.0784)min^{-1}}{4}$ (**0.75**)

$= 0.0808\ \text{min}^{-1}$

The rate constant is $\mathbf{0.0808\ min^{-1}}$ (0.5)

Question 3

(a) $PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

$\qquad\qquad\qquad x \qquad\qquad x$ (**0.5**)

$K_{sp} = [Pb^{2+}][SO_4^{2-}] = x^2$ (**0.5**)

Where x = molar solubility of $PbSO_4 = \frac{\text{Mass slubility of } PbSO_4}{\text{Molar mass of } PbSO_4}$

Where the mass solubility $= \frac{4.25\times10^{-3}g}{0.1dm^3} = 4.25 \times 10^{-2}gdm^{-3}$ (**0.5**)

And the molar mass = $303\ g/mol$

Thus $x = \frac{4.25\times10^{-2}}{303}\ moldm^{-3} = 1.40264 \times 10^{-4}\ moldm^{-3}$ (**0.5**)

Then $K_{sp} = (1.40264 \times 10^{-4}\ moldm^{-3})^2$ (**0.5**)

$= 1.9674 \times 10^{-8}mol^2dm^{-6}$

The solubility product of $PbSO_4$ is $1.9674 \times 10^{-8}mol^2dm^{-6}$ (**0.5**)

(b)

(i) Is the negative of common logarithm of hydronium ion (H_3O^+) **concentration** in very **dilute solution.** (**0.5**)

Remark: The definition; *is a negative of common logarithm of hydronium ion*, is incorrect. We cannot find logarithm of just hydronium ion, it is non-sense! (hydronium ion is not physical quantity).

(ii) Yes (It is possible). (**0.5**)

Explanation:

For the solution to be neutral, $[H_3O^+]$ must just be equal to $[OH^-]$. Only at 25°C, the equality occurs when $[H_3O^+] = 10^{-7}M$ which inturn gives the value of pH of 7, because at 25°C, $K_W = 10^{-14}M^2$. However the K_W being an equilibrium constant, it is temperature dependent whose value increases with an increase in temperature. So at higher temperature than 25°C, the K_W value will be greater than 10^{-14} therefore making pH of neutral solution to be less than 7 (for example if $K_W = 10^{-12}M^2$, pH of the neutral solution will be 6).(**2**)

$$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$$

$$\qquad\qquad\qquad\qquad \alpha c \qquad \alpha c$$

$pOH = -\log[OH^-]$ (**0.5**)

But $[OH^-] = \alpha c$ (**0.5**)

$pOH = -\log(4.37 \times 10^{-5} \times 0.005) = 5.66$ (**0.5**)

Then $\mathrm{pH} = 14 - \mathrm{pOH}\ (\mathrm{pH} + \mathrm{pOH} = 14)$ (**0.5**)
$= 14 - 5.66 = 8.34$
The pH is 8.34

(c) In aqueous solution, NaF undergoes anionic salt hydrolysis according to the following equation: $\mathrm{NaF} + \mathrm{H_2O} \rightleftharpoons \mathrm{HF} + \mathrm{NaOH}$

The above equation can be written ionically as follows:
$\mathrm{F^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HF} + \mathrm{OH^-}$ (**1**)
From which $\mathrm{K} = \frac{[\mathrm{HF}][\mathrm{OH^-}]}{[\mathrm{F^-}]}$ (**0.5**)
Where K stands for dissociation constant.
But $[\mathrm{HF}] = [\mathrm{OH^-}]$
Then $\mathrm{K} = \frac{[\mathrm{OH^-}]^2}{[\mathrm{F^-}]}$
$[\mathrm{OH^-}] = \sqrt{\mathrm{K}[\mathrm{F^-}]}$ (**0.5**)
Then $\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log\sqrt{\mathrm{K}[\mathrm{F^-}]}$
Where $[\mathrm{F^-}] = [\mathrm{NaF}] = 0.25\mathrm{M}$(Since K is very small) (**0.5**)
$\mathrm{pOH} = -\log\sqrt{1.5 \times 10^{-11} \times 0.25} = 5.7$ (**0.5**)
Using $\mathrm{pH} = 14 - \mathrm{pOH}\ (\mathrm{pH} + \mathrm{pOH} = 14)$
$= 14 - 5.7 = 8.3$
Hence the pH of 0.25M NaF is 8.3 (**0.5**)
In solution, $\mathrm{NH_3}$ ionises according to the following equation:
$\mathrm{NH_3} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_4^+} + \mathrm{OH^-}$
$\alpha c \quad \alpha c$ (**0.5**)
Where $[\mathrm{OH^-}] = \alpha c$
And $\mathrm{pOH} = -\log[\mathrm{OH^-}]$ (**0.5**)
But from Ostwald's dilution law; $\alpha = \sqrt{\frac{\mathrm{K_b}}{c}}$
Then $[\mathrm{OH^-}] = \mathrm{C}\sqrt{\frac{\mathrm{K_b}}{c}} = \sqrt{\mathrm{CK_b}}$ (**0.5**)
$\mathrm{pOH} = -\log\sqrt{\mathrm{CK_b}}$
where $\mathrm{K_b} = 1.77 \times 10^{-5}$ and $\mathrm{C} = 0.01\mathrm{M}$
Substituting $\mathrm{pOH} = -\log\sqrt{0.01 \times 1.77 \times 10^{-5}}$
$= 3.34$ (**0.5**)
Then $\mathrm{pH} = 14 - \mathrm{pOH}\ (\mathrm{pH} + \mathrm{pOH} = 14)$
$= 14 - 3.38 = 10.62$
Hence the pH of $\mathbf{0.01M\ NH_3(aq)}$ is 10.62 (**0.5**)

(d) Ethanoic acid/sodium ethanoate mixture is acidic buffer solution whose pH is given by the following equation: $\mathrm{pH} = \mathrm{pKa} + \log\left(\frac{[\mathrm{Salt}]}{[\mathrm{Acid}]}\right)$ (**0.5**)

Where $[\mathrm{Acid}] = [\mathrm{CH_3COOH}] = 1\mathrm{M}$
And $[\mathrm{Salt}] = [\mathrm{CH_3COONa}]$
Substituting;
$4.742 = -\log(1.8 \times 10^{-5}) + \log\frac{[\mathrm{Salt}]}{1}$ (**0.5**)
From which $[\mathrm{Salt}] = 0.99\mathrm{M}$
Hence concentration of sodium ethanoate is 0.99M (**0.5**)

HCl being strong electrolyte ionises according to the following equation:

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

0.01 mol 0.01mol (**0.5**)

Thus the addition of $HCl(aq)$ is equivalent to the addition of H^+.

The added H^+ will disturb the ionisation of CH_3COOH in the buffer solution thus shift the position of equilibrium to the left hand side as shown below: (**0.5**)

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Before addition of HCl	1 mol	0.99mol	(n = MV)
After addition of HCl	(1 + 0.01)mol	(0.99 − 0.01) mol	(0.5)

Thus at new equilibrium:

$[CH_3COOH] = \frac{(1+0.01)mol}{1dm^3} = 1.01M = [Acid]$ (**0.25**)

$[CH_3COO^-] = \frac{(0.99-0.01)mol}{1dm^3} = 0.98M$ (**0.25**)

Then new $pH = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.98}{1.01}\right) = 4.732$

Hence the pH after the addition of acid is 4.732 (0.5)

NaOH being strong base, ionises completely according to the following equation:

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

0.01 mol 0.01 mol **(0.5)**

Introduction of OH^-, shifts the position of chemical equilibrium of the buffer solution to the right hand side as shown below: (**0.5**)

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Before addition of NaOH	1 mol	0.99mol	(n = MV)
After addition of NaOH	(1 − 0.01)mol	(0.99 + 0.01) mol	(0.5)

Thus at new equilibrium;

$[CH_3COOH] = \frac{(1-0.01)mol}{1dm^3} = 0.99M = [Acid]$ (**0.25**)

$[CH_3COO^-] = \frac{(0.99+0.01)mol}{1dm^3} = 1M = [Salt]$ (**0.25**)

Then new $pH = -\log(1.8 \times 10^{-5}) + \log\left(\frac{1}{0.99}\right) = 4.749$

Hence the pH after the addition of acid is 4.749 (0.5)

When NaOH is added to pure water, it ionises completely (because it is strong base) according to the following equation:

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

0.01 mol 0.01 mol (**0.5**)

Thus by using [ ] = $[NaOH] = \frac{0.01\ mol}{1dm^3} = 0.01M$ (**0.5**)

Then $pOH = -\log[OH^-] = -\log 0.01 = 2$ (**0.5**)

It follows that:

$pH = 14 - pOH$ (From $pH + pOH = 14$)

$= 14 - 2 = 12$

Hence the pH of the $NaOH(aq)$ is 12 (0.5)

Question 4

(a)

(i) Choking smell of ammonia is observed. (**0.5**)

$Mg_3N_2(s) + 6H_2O(l) \longrightarrow 2NH_3(g) + 3Mg(OH)_2(s)$ (**0.5**)

(ii) Reddish brown colouration of bromine is observed. (**0.5**)

$Cl_2 + 2NaBr \longrightarrow 2NaCl + Br_2$ (**0.5**)
(Or ionically: $Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$)

(iii) Firstly dense white fumes of gaseous mixture of ammonia and hydrogen chloride will be observed and on recombining the white sublimate of ammonium chloride is formed. (**0.5**)

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ (**0.5**)

(iv) Effervescence of colourless gas which turns lime water milky, that is CO_2 is observed. (**0.5**)

$\underset{\text{Egg shell}}{CaCO_3(s)} + 2HCl(aq) \longrightarrow CaCl_2 + CO_2 + H_2O$ (**0.5**)

(v) Brown fumes of NO_2 will be observed. (**0.5**)
$2Ca(NO_3)_2 \underset{\Delta}{\rightarrow} 2CaO + 4NO_2 + O_2$(**0.5**)

(vi) Firstly white precipitate of $CaCO_3$ will be observed. Thereafter the precipitate dissolves into clear solution of $Ca(HCO_3)_2$ (calcium bicarbonate) when carbon dioxide is added in excess. (**0.5**)

That is $Ca(OH)_2 + CO_2 \rightarrow \underset{\text{(white precipitate)}}{CaCO_3} + H_2O$ (**0.25**)
Then: $CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$ (**0.25**)
(Or $Ca(OH)_2 + 2CO_2 \rightarrow Ca(HCO_3)_2$)

(b) Br_2 being stronger oxidising agent than I_2, exerts stronger oxidation whereby it oxidises the sulphur from an oxidation number of $+2$ in $S_2O_3^{2-}$ to $+6$ in SO_4^{2-} in which the change in oxidation number is $+4$. **(1)**

On another hand, the weaker oxidising agent, I_2, oxidises the sulphur from $+2$ in $S_2O_3^{2-}$ to just $+2.5$ in $S_4O_6^{2-}$ in which the change in the oxidation number is only $+0.5$. **(1)**

(c)

(i) Concentrated sulphuric acid being good oxidising agent oxidises H_2S which is good reducing agent to sulphur and itself become reduced to SO_2 instead of removing water (drying) the gas. **(1.5)**

That is; H_2SO_4 (conc) + $H_2S \rightarrow SO_2 + S + H_2O$**(0.5)**

(ii) Binary compound of Aluminium and carbon is aluminium carbide which consists of highly distorted carbide ion (C^{4-}) ion brought about by very large polarising power of a small in size and high charged Al^{3+}. This makes the carbide to form methane, CH_4 on hydrolysis instead of ethyne, C_2H_2 which would be formed if the normal carbide ion, C_2^{2-} would be undistorted. **(1.5)**

That is; $Al_4C_3 + H_2O \underset{\Delta}{\rightarrow} Al_2O_3 + CH_4$**(0.5)**

(iii) In sea water, magnesium exists in the form of magnesium chloride ($MgCl_2$) which is soluble. Thus introducing liming material like calcium hydroxide precipitate the insoluble magnesium hydroxide which in turn on addition of hydrochloric acid to the precipitate, $MgCl_2$ is formed again from which pure magnesium is obtained by electrolysis. **(1.5)**

That is; $MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$ **(0.25)**
Then $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$ **(0.25)**
And finally; at the cathode: $Mg^{2+}(aq) + 2e \rightarrow Mg(s)$

(iv) With solution of sodium hydroxide, carbon dioxide does not give any observable changes as it gives soluble sodium carbonate. **(1.5)**

That is; $CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O$ **(0.5)**

(v) Hard water contains soluble Ca^{2+} and Mg^{2+}, so introducing washing soda in the water precipitates out insoluble $CaCO_3$ and $MgCO_3$ thus treating hard water.**(1.5)**

That is; $Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$
Or $Mg^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow MgCO_3(s)$ **(0.5)**

(vi) With water, SO_2 form sulphurous acid (H_2SO_3) which is weaker reducing agent than H_2S, so the sulphurous acid oxidises the sulphide to sulphur which appears as a yellow solid. **(1.5)**

That is; $2H_2S(g) + SO_2(aq) \longrightarrow 2H_2O(l) + 3S(s)$ **(0.5)**

Question 5

(a)
(i) Coordinate bond is the covalent bond whereby all shared electrons come from single atom. (**0.5**)
(ii) Coordination number is the total number of dative bonds the central metal atom makes with ligands. (**0.5**)
(b)
(i) $[CoBr(NH_3)_5]SO_4$ yields $[CoBr(NH_3)_5]^{2+}$ and SO_4^{2-} (**0.5**)
$[Co(SO_4)_4(NH_3)_5]Br$ yields $[Co(SO_4)_4(NH_3)_5]^{+}$ and Br^{-} (**0.5**)
(ii) 6 (**0.5**)

Remark: Sign must **not** be included in coordination number. The coordination number has no sign. **Award zero score,** if there is either positive sign or negative sign in the number.

(iii) **First test:**

With solution of $BaCl_2$ (or $Ba(NO_3)_2$), $[CoBr(NH_3)_5]SO_4$ gives **white precipitate** while $[Co(SO_4)(NH_3)_5]Br$ does not. (1.**25**)
Second test:
With solution of $AgNO_3$, $[CO(SO_4)(NH_3)_5]Br$ gives **light yellow precipitate** while $[COBr(NH_3)_5]SO_4$ does not. (**1.25**)

(c)
(i) Let the oxidation state of cobalt be x

Then $x + (6 \times 0) + (3 \times -1) = 0$ or $x = 3$
Thus the oxidation state of cobalt is $+3$ (**1**)

(ii) Chloride ions are not directly bonded to central metal atom by dative bond in coordination sphere; they are ionically bonded to complex cation in the ionisation sphere (**2**)
(iii) $[Co(NH_3)_6]^{3+}$ (**1**)
(iv) $[CoCl_2(NH_3)_4]Cl$ (**1**)
(d) Since A gives white precipitate with mixture of H_2S and HCl (aq), it may be a compound with one of the following cations: $Cu^{2+}, Cd^{2+}, Sn^{2+}, Sn^{4+}$ Sb^{3+} or Hg^{2+} (**2**)
- Since the precipitate (sulphide) dissolves in the solution of KCN, A must contain either Cu^{2+} or Cd^{2+} cations (**1.5**)
$Cu^{2+} + 4CN^{-} \rightarrow [Cu(CN)_4]^{2-}$

$Cd^{2+} + 4CN^- \rightarrow [Cd(CN)_4]^{2-}$
Other cations do not form complex with CN^-

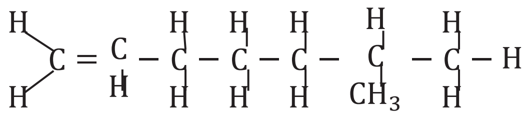
- Since the precipitate does not dissolve in excess $NH_3(aq)$, A cannot contain Cu^{2+} which forms soluble complex with $NH_3(aq)$, it must contain Cd^{2+} (**1**)
- Since A gives white precipitate with $BaCl_2(aq)$, it must contain one of the following anions: SO_4^{2-}, SO_3^{2-}, CO_3^{2-} or $C_2O_4^{2-}$ (**2**)
- Since the precipitate dissolve in HCl(aq), without evolvement of any gas, the anion must be $C_2O_4^{2-}$(**1.5**)

$Ba_2C_2O_4 + 2HCl \rightarrow BaCl_2 + H_2C_2O_4$

Hence:
Cation in A is Cd^{2+} (**1**)
Anion A is $C_2O_4^{2-}$ (**1**)

Question 6

(a)
(i) $\text{Propan} - 2 - \text{ol}$ (**0.5**)
(ii)


(**0.5**)

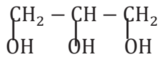
(iii) Amide **(0.5)**
(iv) Function isomer of A is $CH_3CH_2 - CO - O - CH_3$**(0.75)**

Hence the name of the isomer is methyl propanoate **(0.75)**

(v) Amines are base while lemon juice is an acid. Therefore the acid-base neutralisation reaction takes place to eliminate the smell. **(1)**

(b) Sodium salt of long chain carboxylic acid. **(0.5)**

By product



$\underset{OH}{CH_2} - \underset{OH}{CH} - \underset{OH}{CH_2}$ **(0.5)**

(c) $CH_3COCH_3 < CH_3CHO < HCHO$ **(1)**
(d)

(i) Equation: $C_6H_5CH_2Br + NH_3 \underset{\Delta}{\rightarrow} C_6H_5CH_2NH_2 + HBr$ **(0.5)**
(Or $C_6H_5CH_2Br + 2NH_3 \underset{\Delta}{\rightarrow} C_6H_5CH_2NH_2 + NH_4Br$
Type of reaction: nucleophilic substitution reaction. **(0.5)**
Explanation:
Further substitution occurs to give a mixture of primary, secondary and tertiary amine and quaternary ammonium compounds. **(1)**

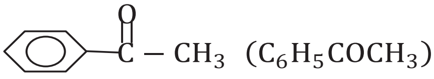
(ii) **Type of reaction:** Reduction **(0.5)**
Equation: $C_6H_5CN + 4[H] \rightarrow C_6H_5CH_2NH_2$ **(0.5)**
Reagent: $LiAlH_4$, dry ether **(0.5)**
Explanation: The reaction gives only one product (No further substitution). **(1)**

(iii) Phenylamine is weaker base. **(0.5)**

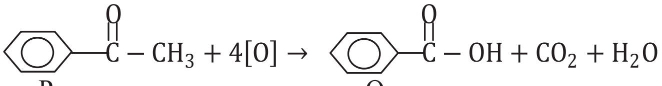
Explanation:
Lone pairs on nitrogen of phenylamine are less available as they delocalized in the mesomerism. **(1)**

(e) The molecule formula C_8H_8O confirm the general molecular formula of $C_nH_{2n-8}O(\mathbf{0.5})$

- Thus with 8 carbon , P may be aromatic aldehyde or ketone **(0.5)**
  Since P give iodoform reaction there is terminal methyl group bonded to carbonyl group in P. (P contains $-CO-CH_3$ group). **(0.5)**
- Therefore P must be aromatic ketene with the following structure;


$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$ $(C_6H_5COCH_3)$
P

P undergo vigorous oxidation as per equation


$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3+4[O]\rightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-OH+CO_2+H_2O$
P Q

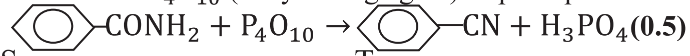
Formation of buff coloured when Q is treated with $FeCl_3$ confirm that Q is carboxylic acid as indicated above. **(0.5)**
Q reacts with PCl_5 as per equation


$C_6H_5-COOH+PCl_5\rightarrow C_6H_5-COCl+POCl_3+HCl$**(0.5)**
Q R

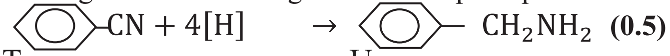
R reacts with concentrated aqueous ammonia as per equation:


$C_6H_5-COCl+NH_3\rightarrow C_6H_5-CONH_2+HCl$ **(0.5)**
R S

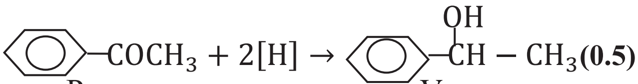
S reacts with P_4O_{10} (dehydrating agent) as per equation


$C_6H_5-CONH_2+P_4O_{10}\rightarrow C_6H_5-CN+H_3PO_4$**(0.5)**
S T

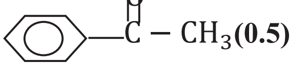
T undergoes reduction to give amine as per equation


$C_6H_5-CN+4[H]\rightarrow C_6H_5-CH_2NH_2$ **(0.5)**
T U

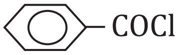
P may also undergo reduction as per equation

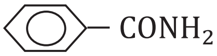

$C_6H_5-COCH_3+2[H]\rightarrow C_6H_5-\overset{OH}{\overset{|}{C}}H-CH_3$**(0.5)**
P V

Where [H] stand for nascent hydrogen from mixture of concentrated HCl and sodium amalgam

P is 
$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$**(0.5)**

Q is 
C_6H_5-COOH **(0.5)**

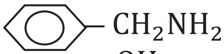
R is 
C_6H_5-COCl **(0.5)**

S is 

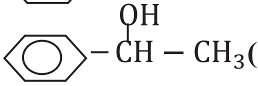
(0.5)

T is 

(0.5)

U is 

(0.5)

V is 

(0.5)

Solutions Examination Nineteen
CHEMISTRY 1J

Question 1

(a)

(i) Is the total number of protons and neutrons present in the nucleus of an atom.**(0.5)**

(ii) Is the weighted average of the mass of the isotopes of the element relative to the $\frac{1}{12}$th mass of the $\mathrm{C}-12$ isotope whose mass is taken as $12\ \mathrm{a.m.u}$ exactly. **(0.5)**

(b)

1. Any radiation is associated with energy. **(0.5)**
2. Radiant energy is emitted or absorbed in small packets as quanta. **(0.5)**
3. The energy associated with a quantum is proportional to the frequency. **(0.5)**

   $E \propto f$ or $E = hf$; where h is constant of proportionality which is known as Planck constant. **(0.5)**

4. The energy is absorbed or emitted in whole number of quanta. **(0.5)**

   That is: $E = nhf$ where $n = 1, 2, 3, 4, 5$ etc. **(0.5)**

(c)

(i) Heat energy from electrically heated metal coil and kinetic energy from fast moving electrons. **(0.5)**

Remark: Electron bombardment by electron gun or a beam of fast moving electrons with high kinetic energy is also **acceptable**.

(ii) $\mathrm{I(g)} + \mathrm{Heat} \rightarrow \mathrm{I^+(g)} + \mathrm{e^-}$ **(0.5)**

Then $\mathrm{I(g)} + \mathrm{e^-} \rightarrow \mathrm{I^+(g)} + 2\mathrm{e^-}$ **(0.5)**

Remarks:

- The state symbols are not for the electron but if they are they must be (g)
- It is not necessary to show charge on electron
- If the electron bombardment is used, **only** the equation $\mathrm{I(g)} + \mathrm{e^-} \rightarrow \mathrm{I^+(g)} + 2\mathrm{e^-}$ is required with a score of **1 mark.**

(iii) To prevent further ionisation of the indium so that ions with higher charge are not formed. **(0.5)**

Remark: To ensure that only one electron is knocked off is also acceptable.

(iv)

1. To enable **acceleration** of ions in the acceleration chamber of the mass spectrometer. **(0.5)**
2. To enable **deflection** of ions in the deflection chamber of the mass spectrometer. **(0.5)**
3. To enable **detection** of ions (isotopes) in the detector of the mass spectrometer. **(0.5)**

Remark: Any **two** correct reasons are enough to get maximum score of **1 mark**.

(v) **Name:** Detector (or detection plate) **(0.5)**

Explanation:
The amount (concentration) of ions of particular isotope hitting the detector determine the amount of electric current established and hence the isotopic abundance of the isotope. If the current generated is high, means that the amount of ions that hit the detector was high too and hence high abundance for the isotope. **(1)**

(vi) Using $A_r = \frac{m_1P_1+m_2P_2}{100}$; where $P_2 = 100 - P_1$ **(0.5)**

Substituting $114.5 = \frac{113P_1+115(100-P_1)}{100}$ **(0.5)**

From which $P_1 = 25$ and therefore $P_2 = 100 - 25 = 75$

The percentage abundance for $I - 113$ and $I - 115$ are 25% and 75% respectively. **(0.5)**

Question 2

(a)

(i) Is the covalent bond whose bonded atoms have partial charges. **(0.5)**

(ii) Is the product of distance between two charges and magnitude of the charges. **(0.5)**

(iii) Is the molecule of covalent compound which partially behave as ionic compound. **(0.5)**

(b)

(i) For a covalent bond to possess dipole moment, the bond must be polar covalent bond and for a molecule to be a polar covalent molecule, the molecule must possess non-zero resultant of dipole moment. This means that the formation of the polar covalent bond leads to the formation of dipole moment and the formation of dipole moment in the molecule leads to the formation of polar covalent molecule. **(1.5)**

(ii) Phosphorous. **(0.5)**

Reason: If **X** would be boron all electron domains would be bonded electron pairs making the molecule symmetrical and therefore leading to the cancellation of dipole moments and hence the molecule becomes non-polar. But with X as phosphorous there is one lone pair in P making the molecule non-symmetrical.**(1)**

(c) $-85°C$ **(0.5)**

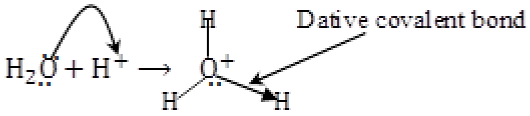
Reason:

There is intermolecular hydrogen bonding existing between molecules of H_2O which is stronger intermolecular forces than Van-der-Waals dispersion forces existing between molecules of H_2S. **(1)**

(d)

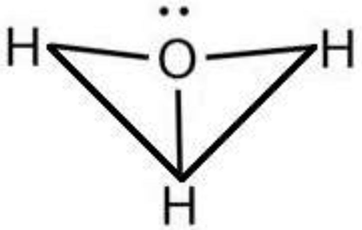
(i) Dative covalent bond. **(0.5)**

(ii) Due to presence of (two) **lone pairs** in O of H_2O and **empty orbital** in H^+, it is possible for one atomic orbital of the oxygen from H_2O with the lone pair to be fused together with the empty atomic orbital of H^+, thus forming the molecular orbital containing two shared electrons between O and H and hence forming H_3O^+ through the dative bond formation with all shared electron coming from O. **(1)**



(0.5)

(iii)



(0.5)

Name of the shape: Trigonal pyramid. **(0.5)**
Remarks:

- Distorted pyramid or triangular pyramid or pyramid is **acceptable.**
- The positive (+) sign is not necessary for getting maximum score.

(iv) $107°$ **(0.5)**

Remark: Any value in the range of $106° - 108°$ is allowable.

(v) Ammonia (NH_3) **(0.5)**

Question 3

(a)

(i) Pressure of given mass of a gas varies directly proportional to its absolute temperature provided that the volume of the gas is constant. **(0.5)**

Mathematical equation: $P \propto T$ or $P = kT$ or $\frac{P}{T} = k$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ **(0.25)**

(ii) Volume of fixed mass of a gas varies directly proportional to its absolute temperature and inversely proportional to its pressure. **(0.5)**

Mathematical equation: $V \propto \frac{T}{P}$ or $\frac{PV}{T} = k$ or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ **(0.25)**

(iii) Volume of all gases varies inversely proportional to their pressure and directly proportional to their number of moles and absolute temperature. **(0.5)**

Mathematical equation: $V \propto \frac{nT}{P}$ or $V = \frac{nRT}{P}$ or $PV = nRT$**(0.25)**

(iv) Volume of all gases varies directly proportional to their number of moles at constant temperature and pressure. **(0.5)**

Mathematical equation: $V \propto n$, or $V = kn$ or $\frac{V}{n} = k$ or $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ **(0.25)**

(b)

(i) **Assumption 1:** Intermolecular forces of attraction are negligible in the motion of gas molecules. **(0.5)**

This assumption needs modification because there is intermolecular forces of attraction between molecules of real gas. **(0.25)**
Assumption 2: Volume of a gas molecule (particle) is negligible compared to the volume of the whole gas or the volume of the container. **(0.5)**
This assumption needs modification because molecules of real gases have size and therefore they occupy volume. **(0.25)**

(ii) Using $c = \sqrt{\frac{3RT}{M_r}}$ **(0.5)**

Where $R = 8.314\text{Jmol}^{-1}\text{K}^{-1}$, $T = (25 + 273)\text{K} = 298\text{K}, M_r = 4\text{g/mol} = 0.004\text{kgmol}^{-1}$ **(0.5)**

Substituting $c = \sqrt{\frac{3 \times 8.314\text{J}\cancel{\text{mol}^{-1}}\cancel{\text{K}^{-1}} \times 298\cancel{\text{K}}}{0.004\text{kg}\cancel{\text{mol}^{-1}}}}$; where $\text{J} = \text{kgm}^2\text{s}^{-2}$**(0.5)**

It follows that $c = \sqrt{1858179\frac{\cancel{\text{kg}}\text{m}^2\text{s}^{-2}}{\cancel{\text{kg}}}} = 1363\text{ms}^{-1}$

The root mean square speed is 1363m/s **(0.5)**

(c) If P_1 and P_2 represents partial pressure in each of the given bulb.

Then by Dalton's law of partial pressure;
$P_1 + P_2 = P_T = 760$ mmHg (At s.t.p, pressure $= 1$ atm $= 760$ mmHg) (**0.5**)
But since temperature is constant and the two bulbs have equal volume;
$P_1 = P_2 = P$.
Thus $P + P = 2P = 760$ mmHg
From which $P = 380$ mmHg (**0.5**)
Thence pressure exerted by the gas at each of the two bulbs at 273K is 380 mmHg.
When one of the bulb is lowered into the melting ice and another into hot water, the partial pressure of the gas in the melting ice (273K) will remain 380 mmHg while that in hot water will rise in accordance to P-T law.
$P_T = 380 +$ pressure of the gas in the hot bulb $(P_2) = 877.6$mmHg (**0.5**)
From which $P_2 = 497.6$ mmHg (**0.5**)
Then by using P-T law; $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ or $T_2 = \left(\frac{P_2}{P_1}\right)T_1$ (**0.5**)
Where $P_1 = 380$ mmHg $T_1 = 273$K, $P_2 = 497.6$ mmHg $T_2 =?$
Substituting $\frac{497.6\text{mmHg}}{380\text{mmHg}} \times 273\text{K}(\mathbf{0.5}) = 357.5\text{K}$
Hence the temperature of hot water is 357.5K or 84.5°C. (**0.5**)

Question 4

(a)

(i) Is the solution which does not produce vapour at the boiling point of the solution. **(0.5)** It is the solute with low vapour pressure and high boiling point; for example, table salt. **(0.5)**

Remarks:

- To get full score the examinee must add some relevant fact about the solute apart from defining it as the question is asked 'what' and not simply to 'define'.
- The meaning must include the correct idea relating to the solution/solvent as the question asked about 'non-volatile **solute**' and not simply 'non-volatile'.

(ii) Solute with large molar mass like protein, exerts very small colligative properties. While very small osmotic pressure is measurable, very small boiling point elevation and freezing point depression are not measurable and hence the osmotic becomes more reliable for the determination. **(1)**

(b) From $n = \frac{m}{M_r}$;

$n_{glucose} = \frac{50\text{g}}{180\text{gmol}^{-1}} = 0.2778\text{mol}$ **(0.25)**
$n_{water} = \frac{60\text{g}}{18\text{gmol}^{-1}} = 33.3333\text{mol}$ **(0.25**
$X_{water} = \frac{n_{water}}{n_{total}} = \frac{33.3333\cancel{\text{mol}}}{0.2778\cancel{\text{mol}}} = 0.9917$ **(0.5)**
From Raoult's law and Dalton's law of partial pressure;

$$P_{soln} = X_{water}P^o_{water} + X_{glucose}P^o_{glucose}$$

Since glucose is non-volatile solute; $P^o_{glucose} = 0$
Thus $P_{soln} = X_{water}P^o_{water} = 0.9917 \times 23.8\text{torr}\ (\mathbf{0.5}) = 23.6\text{torr}$
The vapour pressure of the solution is 23.6torr. **(0.5)**

(c)

(i)

Solution	Van't Hoff factor,i	Effective molality of solute, m
$0.010\text{m}Na_3PO_4$	4**(0.5)**	0.04m **(0.5)**
$0.020\text{m}CaBr_2$	3**(0.5)**	0.06m **(0.5)**
0.020mKCl	2**(0.5)**	0.04m **(0.5)**
0.020mHF	$1 < i < 2$ or slightly greater than 1**(0.5)**	$0.02\text{m} < \text{m} < 0.04\text{m}$slightly greater than 0.02m. **(0.5)**

(ii) $0.010\text{m}Na_3PO_4$ and 0.020mKCl **(0.5)** (Both have effective molality of 0.04m).
(iii) $0.020\text{m}CaBr_2$ **(0.5)** (It has largest effective molality and therefore largest freezing point depression).
(iv) 0.020mHF **(0.5)** (It has smallest effective molality and therefore smallest lowering in vapour pressure).
(v) 0.020mHF **(0.5)** (It has effective molality which is closer to 0.02m).

Question 5

(a)
(i) Neutral oxide is the oxide which show neither acidic nor basic properties. **(0.5)**

Example: NO **(0.5)**
Remark: Other allowable examples are: CO, N_2O and F_2O
Compound oxide is the metallic oxide which behave as if it is made up of two oxides, lower and higher oxide of the same metal. **(0.5)**
Example: Red lead oxide (Pb_3O_4) **(0.5)**
Remark: Another example is Ferro-ferric oxide (Fe_3O_4).

(ii) Oxoacid is the hydroxide of non-metal and metalloid whose acidic character is explained by presence of OH group. **(0.5)**

Example: H_2SO_4 **(0.5)**

(b) **First way:**

By reaction of oxygen with a compound at high temperature. **(0.5)**
For example:
$2PbS + 3O_2 \underset{\Delta}{\rightarrow} 2PbO + 2SO_2$ **(0.5)**
Second way:
By thermal decomposition of certain compounds like hydroxides, carbonates and nitrates. **(0.5)**
Example: $MgCO_3 \underset{\Delta}{\rightarrow} MgO + CO_2$ **(0.5)**
Third way:
By oxidation of some elements with nitric acid. **(0.5)**
Example: $2Cu + 8HNO_3 \underset{\Delta}{\rightarrow} 2CuO + 8NO_2 + 4H_2O + O_2$ **(0.5)**

(c)
(i) **Condition for the carbonate formation:** The alkaline solution should be present in excess. **(0.5)**

$$2OH^- + CO_2 \longrightarrow CO_3^{2-} + H_2O(\mathbf{0.5})$$

Condition for the bicarbonate formation: The carbon dioxide should be present in excess. **(0.5)**

$$OH^- + CO_2 \longrightarrow HCO_3^- (\mathbf{0.5})$$

(ii) **Alternative method:** Precipitation method **(0.5)**

(iii) No. **(0.5)**

Explanation:
Only insoluble carbonate may be prepared by the precipitation method. All bicarbonates are soluble as bicarbonate ion may interact with water through hydrogen bonding and hence they are not prepared by this method. **(1.5)**

Question 6

(a)

(i) Practically it is impossible to prevent dissolving of the crystals in water thus the obtained enthalpy change will always accompany enthalpy of solution of the dissolved part of the crystals. **(1)**

(ii) Consider the formation of $Mg^{2+}(aq)$ and $Cl^-(aq)$ from anhydrous $MgCl_2(s)$ and H_2O by the following possible routes:

Route 1: Direct route.
$MgCl_2(s) + H_2O\ (excess) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq) \quad \Delta H = -155kJ/mol$ **(0.5)**
Route 2: Indirect route under the following steps:
Step 1: $MgCl_2(s) + 4H_2O(l) \longrightarrow MgCl_2.4H_2O(s) \quad \Delta H = \Delta H_1$ **(0.5)**
Step 2: $MgCl_2.4H_2O(s) + H_2O\ (excess) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)\ \Delta H_2 = -39kJ/mol$**(0.5)**
Then from Hess's law:
Enthalpy change in route 1 = Enthalpy change in route 2
$\Delta H = \Delta H_1 + \Delta H_2$**(0.5)**
Substituting $-155kJ/mol = \Delta H_1 + -39kJ/mol;$ $(\mathbf{0.5})$ $\quad \Delta H_1 = -116kJ/mol$
The enthalpy change is $-116kJ/mol$ **(0.5)**

(b)

(i) Methane undergoes combustion according to the following equation:

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta H_c^\theta = -890kJ/mol$ **(0.5)**
From which; $\Delta H_c^\theta = 2\Delta H_f^\theta(H_2O) + \Delta H_f^\theta(CO_2) - 2\Delta H_f^\theta(O_2) - \Delta H_f^\theta(CH_4)$ **(0.5)**
But $\Delta H_f^\theta(O_2) = 0, \Delta H_f^\theta(CO_2) = \Delta H_c^\theta(C) = -394kJ/mol, \quad \Delta H_f^\theta(H_2O) = \Delta H_c^\theta(H_2) = -286kJ/mol$
Then $-890kJ/mol = (2 \times -286kJ/mol) + (-394kJ/mol) - \Delta H_f^\theta(CH_4)$
From which $\Delta H_f^\theta(CH_4) = -76kJ/mol$**(0.5)**

(ii) Ethene undergoes combustion according to the following equation:

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l);\ \Delta H_c^\theta = -1390kJ/mol$ **(0.5)**
From which; $\Delta H_c^\theta = 2\Delta H_f^\theta(H_2O) + 2\Delta H_f^\theta(CO_2) - 3\Delta H_f^\theta(O_2) - \Delta H_f^\theta(C_2H_4)$**(0.5)**
But $\Delta H_f^\theta(O_2) = 0, \Delta H_f^\theta(CO_2) = \Delta H_c^\theta(C) = -394kJ/mol, \quad \Delta H_f^\theta(H_2O) = \Delta H_c^\theta(H_2) = -286kJ/mol$
Then $-1390kJ/mol = (2 \times -286kJ/mol) + (2 \times -394kJ/mol) - \Delta H_f^\theta(C_2H_4)$
From which $\Delta H_f^\theta(C_2H_4) = +30kJ/mol$ **(0.5)**

(iii) $\Delta H_r^\theta = \Delta H_f^\theta(CH_3CH_2OH) - \Delta H_f^\theta(H_2O) - \Delta H_f^\theta(C_2H_4)$**(0.5)**
$= -276kJ/mol - (-286kJ/mol) - 30kJ/mol = -20kJ/mol$**(0.5)**

(iv) From ideal gas equation; $n = \frac{PV}{RT}$; Where $P = 1atm$ and $T = 298K$ (standard conditions) **(0.5)**

$$n_{ethene} = \frac{1\cancel{atm}\times 4.48\cancel{dm^3}}{0.082\cancel{atmdm^3}mol^{-1}\cancel{K^{-1}}\times 298\cancel{K}} = 0.183mol\mathbf{(0.5)}$$

Then $\Delta H = n_{ethene} \times \Delta H_c^\theta(ethene) = 0.183\cancel{mol} \times (-1390kJ/\cancel{mol})(\mathbf{0.5})$

$= -254.37kJ$

Hence the heat change is approximately $-254kJ$**(0.5)**

Question 7

(a)

(i) *Is the condition which occurs in the reversible reaction when the rate of forward reaction is equal to the rate of reverse reaction.* In this case the equilibrium occurs when the rate of consumption of 3-menthlybutanoic acid and ethanol is equal to the rate of producing ester and water at which concentration of all reagents (acid, ethanol, ester and water) remain unchanged. **(1)**

(ii) In order to increase the yield of ester. This is because, according to Le-Chatelier's principle; using high concentration of ethanol shifts equilibrium position to ester side (side with lower concentration) and therefore forming more ester. **(1.5)**

(iii) Catalyst enable the equilibrium to be reached in shorter time. However it has no effect in equilibrium position because it increases the rate of both forward and reverse reaction by equal amount. **(1.5)**

(b) $$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Number of moles (At = 0) $\quad 3 \quad 1 \quad 0 \quad 0$

Number of moles (at equilibrium) $\quad 3-x \quad 1-x \quad x \quad x\ (\mathbf{0.5})$

$$K_p = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})} = \frac{(X_{CO_2}P_T)(X_{H_2}P_T)}{(X_{CO}P_T)(X_{H_2O}P_T)}(\mathbf{0.5})$$

$$K_p = \frac{(X_{CO_2})(X_{H_2})}{(X_{CO})(X_{H_2O})} = \frac{\left(\frac{n_{CO_2}}{n_T}\right)\left(\frac{n_{H_2}}{n_T}\right)}{\left(\frac{n_{CO}}{n_T}\right)\left(\frac{n_{H_2O}}{n_T}\right)} = \frac{n_{CO_2} \times n_{H_2}}{n_{CO} \times n_{H_2O}}(\mathbf{1})$$

$$K_p = 0.65 = \frac{(x)(x)}{(3-x)(1-x)} = \frac{x^2}{x^2-4x+3}$$

From which $0.37x^2 + 2.52x - 1.89x = 0(\mathbf{0.5})$

Solving above equation gives practical value of x which is 0.68

(i) Hence the number of moles of H_2 is 0.68mol **(1)**

(ii) $n_T = (3-x) + (1-x) + x + x = 4mol$

$$P_{CO} = X_{CO}P_T = \left(\frac{n_{CO}}{n_T}\right)P_T = \left(\frac{3-x}{4}\right)P_T(\mathbf{0.5})$$

Substituting;

$$P_{CO} = \left(\frac{3-0.68}{4}\right)2atm = 1.16atm$$

Similarly;

$$P_{H_2O} = \left(\frac{n_{H_2O}}{n_T}\right)P_T = \left(\frac{1-X}{4}\right)P_T = \frac{(1-0.68)}{4} \times 2atm = 0.16atm$$

$$P_{H_2} = P_{CO_2} = \left(\frac{X}{4}\right)P_T = \left(\frac{0.68}{4}\right) \times 2atm = 0.34atm$$

Hence:

Partial pressure of CO = 1.16atm **(0.5)**
Partial pressure of H_2O = 0.16atm **(0.5)**
Partial pressure of H_2 = 0.34atm **(0.5)**
Partial pressure of CO_2 = 0.34atm**(0.5)**

Question 8

(a)

(i) It the family of organic compounds which contain characteristic group and have similar properties. Example alkane **(0.5)**

(ii) It an organic molecule which contain positively charged carbon in trivalent state. Example H_3C^+ **(0.5)**

(iii) Is an organic reactant which single unpaired electron. Example $C_2H_5^{\bullet}$ **(0.5)**

(iv) Is an organic compound which consists of carbon and hydrogen only. Example, ethane.

(b)

(i) Crude oil **(0.5)**

(ii) Fractional distillation**(0.5)**

(iii) Skeletal (or chain or nuclear) isomerism**(0.5)**

Examples: $CH_3CH_2CH_2CH_2CH_2CH_3$ and $CH_3CH(CH_3)CH_2CH_2CH_3$ **(1)**

(iv) $X \xrightarrow{\text{Cracking}} C_6H_{14} + 2C_3H_6$

The molecular formula of X is $C_{12}H_{26}$ **(1)**

(v) Type of cracking; Thermal cracking **(0.5)**

Conditions: 400°C – 900°C, 70atm **(0.5)**

(vi)

A. Free radical substitution reaction **(0.5)**

B. Corrosive **(0.5)**

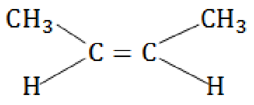
C. High temperature which is above 500°C **(0.5)**

(c)

(i) The reaction type is elimination reaction which may be defined as; an organic reaction whereby atoms (or groups of atoms) are removed from organic compound.**(1)**

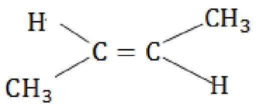
(ii) $CH_3CH_2CH = CH_2$ **(0.5)**

Name: but – 1 – ene **(0.5)**



(0.5)

Name: cis-but-2-ene **(0.5)**



(0.5)

Name: trans-but-2-ene **(0.5)**

(d)

(i) Structure: $CH_3COCH_2CH_3$**(0.5)**

Name: butanone **(0.5)**

(ii) Carbonyl compound. **(0.5)**

(iii) Acts as an oxidising agent. **(0.75)**

(iv) Fractional distillation **(0.75)**

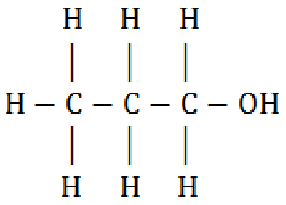
Question 9

(a)

(i) 4-chlorophenol> Benzene > 4 − nitrotoluene **(0.75)**
(ii) Chlorobenzene> 4 − chloronitrobenzene > 2,4 − dinitrobenzene **(0.75)**
(iii) Isopropylbenzene> chlorobenzene > carboxybenzene **(0.75)**
(iv) Methylbenzene> 4 − nitromethylbenzene > 2,4 − dinitromethylbenzene**(0.75)**

(b)

(i)



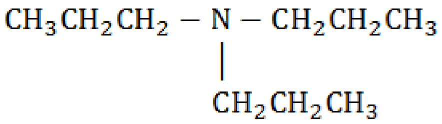
$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-OH$$

(0.5)

(ii) Name: Nucleophilic substitution **(0.5)**

Conditions:
First condition: Ammonia should be in excess to prevent more substitution which would give mixture of products like secondary amine, tertiary amine and even quaternary ammonium salt. **(0.75)**
Second condition: The solvent medium must be non-aqueous (commonly alcoholic medium is used) to prevent formation of alcohol because NH_3 would give OH^- with water which in turn would give alcohol with the given bromopropane. **(0.75)**

(iii) Structure



$$CH_3CH_2CH_2-\underset{\underset{CH_2CH_2CH_3}{|}}{N}-CH_2CH_2CH_3$$

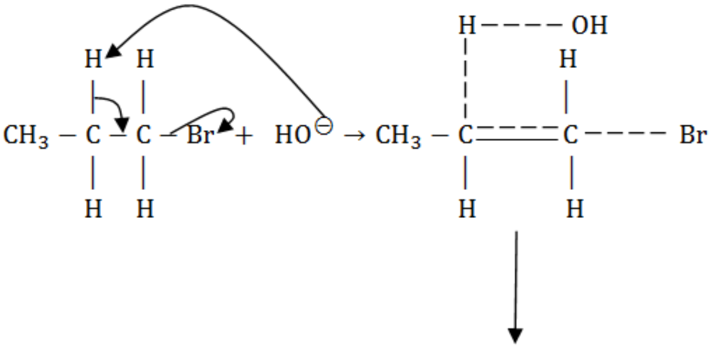
(0.5)

Functional group with its classification; Tertiary amine **(0.5)**

(iv) Reagents: Concentrated KOH, ethanol (alcohol) **(0.5)**

Condition: High temperature **(0.5)**
Reagents: Base induced β- elimination reaction **(0.5)**

(v)



$CH_3CH = CH_2 + Br^- + H_2O$ (1)

(c)

(i) Due to presence of $C-Cl$ bond in alkyl chloride, in which Cl is more electronegative, the carbon is positively polarised and therefore it has high affinity to nucleophile. **(1.5)**

(ii) Nitration in benzene ring is done under presence of concentrated nitric acid. The acid is capable of reacting with amino group(NH_2) in aminobenzene to form an intermediate positively changed side group ($-NH_3^+$) which is strong deactivator and hence it act as meta director accounting for the formation of meta product. **(1.5)**

(iii) In hexene pie bonds are localised while in benzene pie bonds have been delocalised in mesomerism making them more stable and hence it become more difficult for benzene to undergo addition reactions like hydrogenation.**(1.5)**

(iv) With water in the solution, sodium carbonate produce OH^- which is responsible of the alcohol formation when react with bromoethane.

That is $CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$

Then $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$ **(1.5)**

Question 10

(a)

(i) Is the negative logarithm of concentration of hydronium ions in the soil solution.**(0.5)**

(ii) Prolonged use of ammonium sulphate fertilizer makes the soil solution more acidic thus lowering soil pH. **(1)**

This is due to:

Nitrification of NH_4^+ ions by bacteria

$$NH_4^+(aq) + O_2(g) \xrightarrow{\text{bacteria}} 2H^+(aq) + H_2O(l) + NO_3^-(aq)(\mathbf{0.5})$$

$\downarrow$

From $(\mathbf{NH_4})_2\mathbf{SO_4}$

Cationic hydrolysis of $(\mathbf{NH_4})_2\mathbf{SO_4}$

$$NH_4^+(aq) + H_2O(l) \rightarrow NH_4OH(aq) + H^+(aq)(\mathbf{0.5})$$

(iii)

1. Decomposition of organic matter **(0.5)**

   Organic matter in the soil undergoes catalytic oxidation to CO_2 and H_2O. The produced CO_2 reacts with H_2O producing carbonic acid, H_2CO_3, which lowers soil pH

   $CH_2O\ (s) + O_2\ (g) \xrightarrow{\text{microbes}} H_2O(l) + CO_2(g)$

   Then $H_2O(l) + CO_2(g) \rightarrow H_2CO_3(aq)$

   So while soil with high organic matter content have low soil pH, soils with low organic matter content are expected to have high soil pH. **(1)**

2. Presence of soluble Al^{3+} and Fe^{3+} **(0.5)**

   In soil water solution $\mathbf{Al^{3+}}$ and $\mathbf{Fe^{3+}}$ tend to form hexaaqua complexes which undergo hydrolysis in ligand substitution reaction forming acidic solution and hence soil pH is lowered

   $$[Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(H_2O)_5OH]^{2+} + H_3^+O$$

   $\downarrow$

   From Al^{3+}(aq)

   $$[Fe(H_2O)_6]^{3+} + H_2O \rightarrow [Fe(H_2O)_5OH]^{2+} + H_3^+O$$

Thus , while soils with high concentration of Al^{3+} and Fe^{3+} are expected to have low pH , soils with low concentration of Al^{3+} and Fe^{3+} will have high pH. **(1)**

3. Excessive leaching due to irrigation or rainfall **(0.5)**

   As water from rainfall or irrigation activities passes through the soil, basic cations such as Ca^{2+} , Mg^{2+} and K^+ are leached. These basic cations are replaced by acidic cations such as Al^{3+} and H^+ and hence the soil becomes acidic with low pH. Thus, soils in areas with excessive leaching have low pH while soils in dry areas where there is no leaching have high pH. **(1)**

4. Industrial fertilizers **(0.5)**

   Acidic mineral fertilizers like ammonium sulphate make the soil acidic with low soil pH due to hydrolysis and nitrification.

   Hydrolysis: $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$

   Nitrification: $NH_4^+ + 2O_2 \xrightarrow{\text{bacteria}} 2H^+ + NO_3^- + H_2O$ **(1)**

5. Plant uptake **(0.5)**

   Plants take up more nutrient cations than anions. In order to compensate for the extra positive charge, they release H^+ from root and hence the soil becomes acidic with low soil pH. Also some plants exude organic acid to help solubilize metal nutrients thus lowering the soil pH. **(1)**

(b)

(i) Hot water: Causes water pollution. **(1)**
(ii) CFCs: Cause ozone depletion and global warming. **(1)**
(iii) Sulphur dioxide: Causes air pollution (acid rain). **(1)**
(iv) Lead: Causes land pollution and water pollution. **(1)**
(v) DDT: Causes water pollution (biomagnification). **(1)**

Solutions Examination Twenty
CHEMISTRY 2I

Question 1

(a)

(i) Polar liquid may form partially miscible mixture which are normally behaving as non-ideal solution with positive deviation. For example, ethanol and water are both polar liquid but the ethanol-water mixture is non-ideal solution with positive deviation. Also some polar liquids like sulphuric acid ionises in the polar solvent, water, resulting to ion-ion interactions in the solution and hence the soltion becomes non-ideal with negative deviation. **(1.5)**

(ii) The given statement does not hold for any solution. Non-ideal solution with positive deviation has the boiling point which lower than either of the pure component while non-ideal solution with negative deviation has boiling point which is higher than either of the pure component. **(1.5)**

(iii) Simple fractional distillation cannot be used to get pure water and pure ethanol from the mixture due to the formation of azeotropic mixture as the ethanol-water mixture is non-ideal solution. **(1.5)**

(b) **Zero heat change:** This occurs when strength of intermolecular forces in pure liquid is equal to that in solution such that the energy absorbed in breaking intermolecular forces in pure liquid is equal to the energy evolved in forming intermolecular forces in the solution. As result, solution under this category are ideal solution. **(1.5)**

Positive heat change: This occurs when strength of intermolecular forces in solution are smaller than those in pure liquid such that the energy absorbed in breaking intermolecular forces in pure liquid is greater than the energy evolved in forming intermolecular forces in the solution. As result, solution under this category are non-ideal solution with positive deviation**.** **(1.5)**

Negative heat change: This occurs when strength of intermolecular forces in solution are higher than those in pure liquid such that the energy absorbed in breaking intermolecular forces in pure liquid is smaller than the energy evolved in forming intermolecular forces in the solution. As result, solutions under this category are non-ideal solution with negative deviation. **(1.5)**

(c) $K_d = \frac{\text{Concentration of } \mathbf{X} \text{ in } \mathbf{Y}\text{(extractive solvent)}}{\text{Concentration of } \mathbf{X} \text{ in water}} (\mathbf{0.5})$

But 18g of **X** distribute itself such that mass of X in water is 2g.

If follows that mass of **X** in **Y** is $(18 - 2)\text{g} = 16\text{g}(\mathbf{0.5})$

Then $K_d = \frac{16\text{g}/1\text{dm}^3}{2\text{g}/1\text{dm}^3} = 8$

So partition coefficient between **Y** and water is 8. $(\mathbf{1})$

Let mass of **X** extracted from 1g of **X** in water be m.

Then $K_d = \frac{m/1}{1-m/1} = \frac{m}{1-m} (\mathbf{0.5})$

From which $m = 8/9\ \text{g}(\mathbf{1})$

Mass of X left in water $= 1 - 8/9 = 1/9\text{g}(\mathbf{0.5})$

So the percentage of X left in water $1/9 \times 100\% = 11\%$ to nearest integer

Hence the percentage of X left in water is 11% $(\mathbf{1})$

(d)

(i) Using $\frac{n_c}{n_w} = \frac{P_c}{P_w}$ (For immiscible liquids) **(0.5)**

Where n_c and n_w is the number of moles of Chlorobenzene and water respectively in the distillate

P_c and P_w is the vapour pressure of Chlorobenzene and water respectively at 91℃

$\frac{n_c}{n_w} = \frac{760-540}{540} = \frac{11}{27}$ or $n_c : n_w = 11:27$ **(0.5)**

$\%n_c \left(\frac{11}{11+27}\right) \times 100\% = 28.9\%$

$\%n_w = (100 - 28.9)\% = 71.1\%$

Hence the mole composition of distillate is 28.9% Chlorobenzene and 71.1%water **(1)**

(ii) Using $\frac{m_c}{m_w} = \frac{P_cM_c}{P_wM_w}$ **(0.5)**

Where M_c and M_w are molar masses of Chlorobenzene and water respectively

m_c and m_w are masses of Chlorobenzene and water respectively in the distillate.

Then $\frac{m_c}{m_w} = \frac{(760-540)\times 112.5}{540\times 18} = \frac{275}{108}$ **(0.5)**

$m_c : m_w = 275:108$

$\% m_c = \left(\frac{275}{275+108}\right) \times 100\% = 71.8\%$

$\% m_w = (100 - 71.8)\% = 28.2\%$

Hence the mass composition of the distillate is 71.8% Chlorobenzene and 28.2% water.**(1)**

(iii) If 90% of chlorobenzene has been steam distilled:

Mass of chlorobenzene in the distillate = $\frac{90}{100}\times 20g = 18g$ **(0.5)**

If m_T is the total mass of the distillate

If follows that $\frac{71.8m_T}{100} = 18g$ or $m_T = \frac{100\times 18g}{71.8} = 25g$ **(0.5)**

Using $V = \frac{m}{\rho}$

Total volume of distillate = $\frac{25}{1.1}cm^3 = 22.72cm^3$

Hence total volume of distillate obtained is 22.72 cm^3 **(1)**

Question 2

(a)

(i) It states that: The molar conductivity of an electrolyte at infinite dilution is the sum of molar conductivities of individual constituent ions present in the solution. (**0.75**)

(ii)

1. Electronic conductors, conduct electricity by using moving electrons (delocalised valence electrons) while electrolytic conductors conduct electricity by using moving ions. (**0.75**)
2. Electronic conductors, conduct electricity in solid state while electrolytic conductors, conduct electricity in liquid state. (**0.75**)
3. Electronic conductors are elements while electrolytic conductors are compounds. (**0.75**)

(b) Cell constant = $\frac{l}{A}$ **(0.5)**

Substituting: Cell constant = $\frac{1cm}{2cm^2} = 0.5\ cm^{-1}$ **(0.5)**

The cell constant is $0.5\ cm^{-1}$ **(0.5)**

Conductivity = Conductance × Cell constant (**0.5**)

But Conductance = $\frac{1}{\text{Resistance}}$ **(0.5)**

The conductivity = $\frac{\text{Cell constant}}{\text{Resistance}}$ **(0.5)**

$= \frac{0.5\ cm^{-1}}{7.25\ \Omega}$ **(0.5)**

$= 0.069\ \Omega^{-1}\text{cm}^{-1}$

The conductivity is $\mathbf{0.069\ \Omega^{-1}cm^{-1}}$(0.5)

Resistance, $R = \rho \times$ Cell constant (**0.5**)

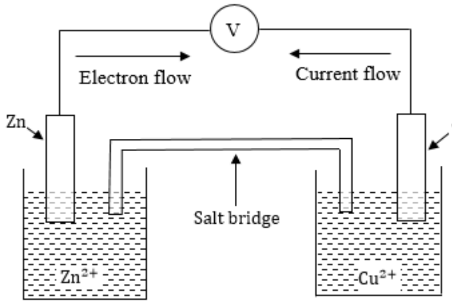
Where $\rho = 361\Omega\text{cm}$

And cell constant $= 0.5\ \text{cm}^{-1}$ (It is constant for given cell)

Then $\mathbf{R = 361\Omega cm \times 0.5\ cm^{-1} = 180.5\ \Omega}$ (**0.5**)

(c)

(i)



(**2**)

Remark: Since zinc has smaller electrode potential, zinc electrode must be in anode half cell (at left hand side) while copper electrode must be in cathode half cell (right hand side). **Award zero score** if copper half-cell is at left hand side while zinc half-cell is at right hand side. (Zinc is anode, so it must be at LHS while copper being cathode must be at RHS).

(ii) Cell reaction:

$\text{Zn(s)} + \text{Cu}^{2+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{Cu(s)}$ (**1**)

$E^{\emptyset}_{\text{Cell}} = E^{\emptyset}_{\text{cathode}} - E^{\emptyset}_{\text{anode}} = E^{\emptyset}_{\text{Cu}^{2+}/\text{Cu}} - E^{\emptyset}_{\text{Zn}^{2+}/\text{Zn}}$ (**0.5**)

$= +0.34\text{V} - (-0.76\text{V}) = 1.1\text{V}$

The e.m.f is 1.1V (**0.5**)

(iii) From the Nernst equation

$E_{\text{cell}} = E^{\emptyset}_{\text{Cell}} - \frac{0.0591}{n}\log R_Q$ (**0.5**)

But at equilibrium: $E_{\text{cell}} = 0$ and $R_Q = K_c$

Thus $0 = E^{\emptyset}_{\text{Cell}} - \frac{0.0591}{n}\log K_c$

An therefore $E^{\emptyset}_{\text{Cell}} = \frac{0.0591}{n}\log K_c$ (**0.5**)

Where $E^{\emptyset}_{\text{Cell}} = 1.1\text{V}$ and $n = 2$

Substituting $1.1 = \frac{0.0591}{n}\log K_c$ (**0.5**)

From which $K_C = 1.68 \times 10^{37}$

Hence the equilibrium constant is 1.68×10^{37} (**0.5**)

(d) Using $n = MV$;

Number of moles of $KMnO_4$ used $= \frac{20}{1000} \times 0.02\ \text{mol} = 4 \times 10^{-4}\ \text{mol}$ (**0.5**)

$= \text{number of moles of } MnO_4^-$

But from the given balanced reaction equation; mole ratio of MnO_4^- to $C_2H_4O_4 \bullet xH_2O$ is $2:5$

Thus number of moles of $C_2H_4O_4 \bullet xH_2O$ is $\frac{5}{2} \times 4 \times 10^{-4}$ mol $= 1 \times 10^{-3}$ mol (**0.75**)

Using $M_r = \frac{m}{n}\left(\text{From } n = \frac{m}{M_r}\right)$

Where $m = 0.126g$ (given)

$M_r(C_2H_4O_4 \bullet xH_2O) = \frac{0.126g}{1\times10^{-3}\text{ mol}} = 126g/mol$ (**0.75**)

Thus:

$(2 \times 12) + (4 \times 1) + (4 \times 16) + 18x = 126$ (**0.5**)

From which $x = 2$

Hence the value of x is 2 (**0.5**)

Question 3

(a)

(i) In the solution, HSO_3^- ionises to give hydrogen proton (H^+) and thus HSO_3^- acts as hydrogen proton donor, donating the H^+ to water in the solution to give hydronium ion (H_3O^+) (**1.25**)

That is $HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq)$ … (i)

Then $H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq)$………... (ii)

Overall reaction equation: (i) + (ii)

$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_3^{2-}(aq)$ (**0.75**)

(ii) Conjugate base: SO_3^{2-} (**0.5**)

(iii) HSO_3^- can accept hydrogen proton (H^+) from strong acid like HCl thus acting as base.(**0.75**)

$HSO_3^- + HCl \rightleftharpoons H_2SO_3 + Cl^-$ (**0.75**)

Base Acid

(b)

(i) The product of concentration of Pb^{2+} and Cl^- raised to the powers of their stoichiometric coefficients in the balanced ionisation equation of $PbCl_2$ in its saturated solution at 298K is $1.6 \times 10^{-5} mol^3 dm^{-9}$.

That is $1.6 \times 10^{-5} = [Pb^{2+}][Cl^-]^2$ (**1.5**)

Remark: General meaning of solubility product is not acceptable (The meaning must be specific to $PbCl_2$).

(ii) $K_{sp} = [Pb^{2+}][Cl^-]^2$ (**0.5**)

$= x(2x)^2 = 4x^3$

$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.6\times10^{-5}}{4}} = 0.015874 moldm^{-3}$ (**1**)

Then solubility = Molar solubility × $M_r(PbCl_2)$

$0.015874 \times 278\ gdm^{-3} = 4.413 gdm^{-3}$ (**1**)

Hence the solubility is $4.413 gdm^{-3}$.

(iii) Again let the molar solubility of $PbCl_2$ in $Pb(NO_3)_2$ be x

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

$x + 0.1 \approx 0.1M \quad 2x$

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$K_{sp} = 0.1 \times (2x)^2 = 0.4x^2$ (**0.5**)

$x = \sqrt{\frac{K_{sp}}{0.4}} = \sqrt{\frac{1.6\times10^{-5}}{0.4}}$

$x = 6.32 \times 10^{-3}$ moldm^{-3} (**0.5**)

Using solubility = Molar solubility × M_r

$= 6.32 \times 10^{-3} \times 278$ g/dm^3 = 1.757 g/dm^3

Hence the solubility in 0.1M$Pb(NO_3)_2$ is 1.757 g/dm^3(**1**)

(c) Using $pH = -\log[H^+]$

From which $[H^+] = \log^{-1}(pH)$ (**0.5**)$= \log^{-1}(-2.69) = 2.042 \times 10^{-3}M$

Hence $[H^+]$ is $2.042 \times 10^{-3}M$ (**1**)

The equation to show ionisation of HX in solution:

$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$

From which $K_a = \frac{[H^+][X^-]}{[HX]}$ (**0.5**)

But $[H^+] = [X^-]$

Thus $K_a = \frac{[H^+]^2}{[HX]}$ (**0.5**)

Substituting $K_a = \frac{(2.042\times10^{-3}M)^2}{0.15M} = 2.78 \times 10^{-5}M$ (**0.5**)

Hence the value of K_a is $2.78 \times 10^{-5}M$ (**0.5**)

HX reacts with NaOH according to the following equation:

$HX + NaOH \rightarrow NaX + H_2O$ (**0.5**)

Since only half of HX has neutralized, after the reaction there are following compounds; HX (unreacted) and NaX (produced) in water (solution) (**0.5**)

Since HX is weak acid, the mixture of HX and NaX (NaX is strong salt containing conjugate base of the weak acid, HX) forms acidic buffer solution whose pH value is given by the following equation: (**1**)

$pH = pK_a + \log\frac{[X^-]}{[HX]}$ (**1**)

Where $[X^-] = [NaX] = [Salt]$

And $[HX] = [Acid]$ but $[X^-] = [HX]$

Thence $pH = pK_a = \log(2.78 \times 10^{-5})$(**1**)

$= 4.56$

Hence the pH of the solution is 4.56 (**0.5**)

Question 4

(a)

(i) Position of isotope

Presence of isotopes makes difficult to arrange some atoms of elements in the periodic table according to Mendeleeff's law. This is because isotopes have different atomic masses despite the fact that they come from the same element. So according to Mendeleeff periodic law, isotopes should be kept in different position despite the fact that they have the same chemical properties while keeping them in the same position is against the Mendeleeff's law. **(1.5)**

(ii) Position of isobars

Presence of isobars makes difficult to arrange some atoms of elements in the periodic table according to the Mendeleeff's law. This is because isotopes have the same atomic mass despite the fact that they come from different element. Strictly following Mendeleeff's periodic law, isobars should take the same position despite the fact that they have different properties while keeping isobars in different position (as they have different properties) is against the Mendeleeff's periodic law. **(1.5)**

(iii) Anomalous pairs

Some elements with lower atomic weight were kept after those of higher atomic weight and Mendeleeff was unable to give convincing reasons for doing such reverse. For example, Tellurium which has greater atomic weight (its relative atomic mass is 127.5) than iodine (which has relative atomic mass of 126.9) was kept before the iodine. **(1.5)**

(iv) Position of lanthanides and actinides

Arrangement of these elements as per the basic law of the table produced an undue side-wards projection, which was not explainable to Mendeleeff because their position cannot be justified on the basis of atomic masses. **(1.5)**

(v) Superfluous relationship

Some elements like copper (Cu) and gold (Au) were placed in the same group in spite of their dissimilar properties and some other elements like palladium and nickel were arranged in different groups without concerning their similar properties. **(1.5)**

(b) NaI being stronger reducing agent than NaBr, exerts stronger reduction whereby it reduces the sulphur from an oxidation number of $+6$ in H_2SO_4 to -2 in H_2S in which the change in oxidation number is -8. **(1)**

On another hand, the weaker reducing agent, NaBr, reduces the sulphur from $+6$ in H_2SO_4 to just $+4$ in SO_2 in which the change in the oxidation number is only -2. **(1)**

(c)

(i) $AlCl_3$ has greater degree of covalent characters brought about by its greater degree of polarisation caused by smaller sized and higher charged Al^{3+} and hence in molten state it has no enough concentration of ions which can conduct electricity like in molten NaCl. **(2)**

(ii) Fluorine does not disproportionate in water like other halogens due to absence of empty d-orbitals so as to accommodate a lone pair of oxygen from water. But fluorine being on the top of halogen group, it has greatest oxidising power thus oxidising water to oxygen (and itself becoming reduced to HF). **(1.5)**

That is $2F_2 + 2H_2O \longrightarrow 4HF + O_2$ $(\mathbf{0.5})$
While $X_2 + H_2O \longrightarrow HOX + HX$ where X is Cl or Br $(\mathbf{0.5})$

(iii) Alkali metals have low atomisation energy (due to their weak metallic bond) accompanied with low ionisation energy. The two factors make the activation energy of oxidation reaction, $\mathbf{M(s) \rightarrow M^+(aq)}$, very low. In other words, alkali metals undergo oxidation readily and hence they become good reducing agent. **(2)**

(iv) Under the presence of heat (warm sodium nitrite), ammonium nitrite which would be formed by double decomposition reaction between ammonium chloride and sodium nitrite, undergo thermal decomposition yielding nitrogen gas which appears as effervescence of colourless gas. **(1.5)**

That is $NaNO_2(aq) + NH_4Cl(aq) \longrightarrow NaCl(aq) + NH_4NO_2(aq)$ $(\mathbf{0.25})$
Then $NH_4NO_2(aq) \longrightarrow 2H_2O(l) + N_2(g)$ $(\mathbf{0.25})$

(v) In aqueous solution PCl_3 hydrolyse yielding enough concentration of H^+ and Cl^-ions which are responsible for electrolytic conduction. **(1.5)**

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3H^+(aq) + 3Cl^-(aq)(\mathbf{0.5})$$

Question 5

(a)

(i) Is the oxidation state whose value **does not change** easily **through** oxidation, reduction or **disproportionation reaction. (0.5)**

(ii) Oxidation state of +7: $KMnO_4$ (**0.5**)

Oxidation state of +6: MnO_3 (**0.5**)
Oxidation state of +4: H_2MnO_3 (**0.5**)

(b)

(i) In aqueous solution, Cu^{2+} coordinate with H_2O ligands to form complex, $[Cu(H_2O)_4]^{2-}$ which is responsible for blue colour formation. Cl^- (In hydrochloric acid) substitute H_2O in the complex through ligand substitution reaction leading to the formation of $[CuCl_4]^{2-}$. Cl^- being weaker ligand than H_2O leads to the formation of colour with smaller energy and hence the colour change from blue to green. (**1**)

That is:
$[Cu(H_2O)_4]^{2-} + 4Cl^- \rightarrow [CuCl_4]^{2-}$ (**0.5**)
Blue Green

(ii) In aqueous solution, iron (III) ions, form acidic hexaaqua complex. This hexaaqua complex donate hydrogen proton (in acid-base reaction) to aqueous alkali resulting to the formation of neutral complex which is therefore insoluble and it appears as the precipitate with gelatinous reddish brown colour (**1**)

$[Fe(H_2O)_6]^{3+} + 3OH^- \rightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$ (**0.5**)

(iii) In aqueous solution, nickel form hexaaqua complex which is acidic. So in small amount of aqueous NH_3 which is basic, the complex donate hydrogen proton to the NH_3 in acid-base reaction resulting to the formation of neutral complex which is insoluble. (**0.5**)

$[Ni(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Ni(OH)_2(H_2O)_4] + 2NH_4^+$ (**0.25**)

(iv) However when aqueous NH_3 present in the excess, the hexaaqua complex undergoes ligand substitution reaction resulting to the formation of cationic complex which is soluble (**0.5**)

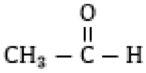
$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6] + 6H_2O$ (**0.25**

(v) With concentrated HNO_3, iron form very thin insoluble layer of Fe_2O_3 over surface of the metal. The impervious protective oxide layer prevents further oxidation of the iron by the acid. (**1**)

$4Fe + 12HNO_3(conc) \rightarrow 2Fe_2O_3 + 12NO_2 + 6H_2O$ (**0.5**)

(c) B is haloalkane with the following structure: CH_3CH_2Cl (**1**)

C is Griginard reagent with the following structure: CH_3CH_2MgCl (**1**)
D is alcohol with the following structure: $CH_3CH_2CH_2OH$ (**1**)
E is alcohol with the following structure: CH_3CH_2OH (**1**)
F is aldehyde with the following structure:



$$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H$$ **(1)**

(d) The molecular formula $C_6H_{14}O$ confirms the general molecular formula of $C_nH_{2n+2}O$. **(0.5)**

Thus Cis an alcohol with the following possible structure:

$$CH_3CH_2CH_2CH_2CH_2CH_2OH$$ **(0.5)**

The molecular formula $C_6H_{12}O_2$ confirms the general molecular formula of $C_nH_{2n}O_2$ Thus D may be carboxylic acid or ester. But because D was formed from the oxidation of alcohol(C), it cannot be ester, it must be carboxylic acid with the following possible structure: **(0.5)**

$$CH_3CH_2CH_2CH_2CH_2COOH$$ **(0.5)**

Since C was formed by decarboxylation reaction of by using soda lime, there is sodium carboxylate group in B and hence B has the following possible structure: **(0.5)**

$$NaOCOCH_2CH_2CH_2CH_2CH_2CH_2OH$$ **(0.5)**

That is

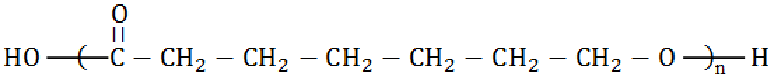
$$NaOCOCH_2CH_2CH_2CH_2CH_2CH_2OH + NaOH \xrightarrow{CaO} CH_3CH_2CH_2CH_2CH_2CH_2OH + Na_2CO_3$$ **(0.5)**

Formation of sodium carboxylate group after A reacting with NaOH(aq) indicates that there is carboxylic group in A. **(0.5)**

Also presence of hydroxyl (OH) group in B which could not react with the NaOH(aq), indicates that there is OH group in A too. **(0.5)**

Thus A is homopolymer formed from condensation reaction of monomers having both carboxylic group and hydroxyl group in the same compound. **(0.5)**

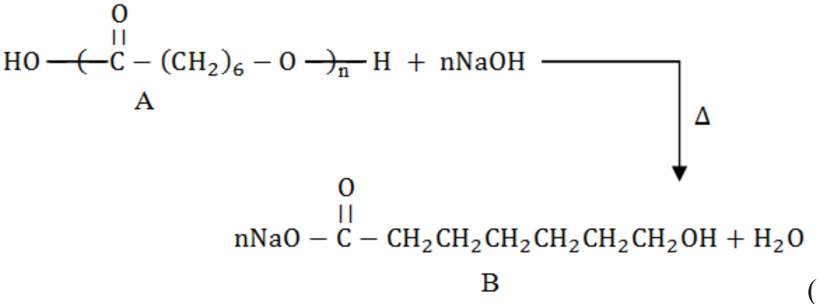
Hence A has the following possible structure:



$$HO-\!\!\left(\overset{\overset{\displaystyle O}{||}}{C}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-O\right)_n\!\!-H$$ **(1)**

Equations:

Formation of B from A:



$$\underset{A}{HO-\!\!\left(\overset{\overset{\displaystyle O}{||}}{C}-(CH_2)_6-O\right)_n\!\!-H} + nNaOH \xrightarrow{\Delta} \underset{B}{nNaO-\overset{\overset{\displaystyle O}{||}}{C}-CH_2CH_2CH_2CH_2CH_2CH_2OH} + H_2O$$ **(0.5)**

Formation of D from C

$$\underset{C}{CH_3CH_2CH_2CH_2CH_2CH_2OH} \xrightarrow[\Delta]{KmnO_4,H^+} \underset{D}{CH_3CH_2CH_2CH_2CH_2COOH}$$ **(0.5)**

Question 6

(a)

(i) Propyl methanoate **(0.5)**

(ii) C belongs to **ester** family and D belongs to **carboxylic acid** family. **(1)**

(iii) Reagent: $NaHCO_3$**(0.5)**

Observation: With$NaHCO_3$, D gives effervescence of colourless gas (CO_2) while C does not indicating no reaction. **(1)**

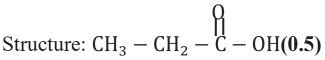
Remark: Other tests:

1. Reagent: Acidified $K_2Cr_2O_7$
   Observation: C change orange colouration of $K_2Cr_2O_7$ to green which D gives no change.
2. Reagent: Acidified $KMnO_4$
   Observation: C changes purple colouration of $KMnO_4$ to colourless while D gives no change.
3. Reagent: Strong electropositive metal like sodium (Na)
   Observation: D gives bubble of hydrogen gas with sodium metal while C does not.
4. Reagent: litmus paper
   Observation: D turns blue litmus paper red while C does not give any change to litmus.
5. Reagent: Phosphorous pentachloride (PCl_5)
   Observation: D gives white fumes of HCl with PCl_5 while C does not.

(b)

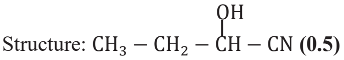
(i) Structure: $CH_3-CH_2-CH_2-OH$**(0.5)**

Type of reaction: Reduction **(0.5)**

(ii) 

Structure: $CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$**(0.5)**

Type of reaction: Oxidation **(0.5)**

(iii) 

Structure: $CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{CH}-CN$ **(0.5)**

Type of reaction: Nucleophilic addition **(0.5)**

(c)

(i)

$$CH_3OH \xrightarrow[\text{Reflux}]{PCl_5} CH_3Cl \xrightarrow[\text{Reflux}]{KCN,C_2H_5OH} CH_3CN \xrightarrow{\text{Dil.HCl}} CH_3COOH \ (\mathbf{3})$$

(ii) $CH_3COOH \xrightarrow{P_4O_{10},\text{Heat}} (CH_3CO)_2O \quad (\mathbf{1})$

(iii)

$$C_6H_6 \xrightarrow[50°C]{H_2SO_4(\text{conc}),H_2SO_4(\text{conc})} C_6H_5NO_2 \xrightarrow{LiAlH_4,\text{dry ether}} C_6H_5NH_2 \ (\mathbf{2})$$

(d) Molecular formula, C_3H_6O confirms the general molecular formula of $C_nH_{2n}O$ **(0.5)**

Thus E may be carbonyl compound (aldehyde or ketone) or unsaturated alcohol with $C=C$(enol) **(0.5)**

Since E gives positive result with Brady's reagent, it cannot be enol, it must be either aldehyde or ketone. **(0.5)**

Since E does not give positive result with either Tollen's reagent or Fehling's solution it cannot be aldehyde, it must be ketone. **(0.75)**

Since there is only one isomer of ketone with thee carbon, the structure of E must be CH_3COCH_3 **(0.75)**

Compound which gives ketone on heating with CaO is carboxylic acid. **(0.5)**
Thus B is carboxylic acid with the following structure:

CH_3COOH**(0.5)**

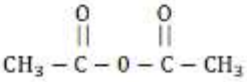
Compound which gives carboxylic acid on oxidation is either alcohol or aldehyde.
Thus D may be either alcohol or aldehyde. **(0.5)**
Compound which is formed by hydrolysis with carboxylic acid (B) as associated product is alcohol. **(0.5)**
Thus D cannot be aldehyde, it must be alcohol with the following structure:

CH_3CH_2OH **(0.5)**

Compound which gives carboxylic acid and alcohol on hydrolysis is ester. **(0.5)**
Thus C is ester with the following structure:

$CH_3COOCH_2CH_3$**(0.5)**

Compound which react with alcohol to give carboxylic acid and ester is acid anhydride.**(0.5)**
Thus A is an acid anhydride with the following structure:



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$$

(0.5)

Solutions Necta 2020

CHEMISTRY 1

SECTION A

Answer **all** questions in this section.

Question 1

(a)

(i) Amphoteric oxides are oxides, normally of weak electropositive metals which show behaviour of both acids and bases. For example, zinc oxide (ZnO) is amphoteric oxide.
As base, ZnO reacts with acids like HCl
$ZnO(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(l)$
As acid, ZnO reacts with bases like NaOH
$ZnO(s) + 2NaOH(aq) \rightarrow Na_2ZnO(aq) + H_2O(l)$

(ii) Basic oxides are oxides of strong electropositive metals which are capable of reacting with acids. For example sodium oxide (Na_2O) is basic oxide which reacts with acid like HCl.
$Na_2O(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l)$

(b) Soluble chlorides may be prepared by either displacement method or neutralisation method depending on the reactivity of metal which forms the chloride.

Metal whose reactivity is high enough to reduce (displace) hydrogen in dilute acids, its chloride is prepared by displacement method whereby the metal like magnesium (Mg) is reacted with dilute hydrochloric acid. However to avoid explosion, chlorides of extremely reactive metals like potassium are not prepared by this method.
Example;$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
Metal whose reactivity is either lower than that of hydrogen such that it has no reaction with dilute HCl or so reactive that its reaction with dilute HCl causes explosion, its chloride is prepared by neutralisation method.
Example: $KOH(aq) + HCl(aq) \rightarrow KCl(aq) + H_2O(l)$

(c) Will not work

Justification:
$AlCl_3$ will hydrolyse in water formed in step (iii) and hence crystals of $AlCl_3$ cannot be obtained.
That is;

$$Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + H_2O \text{ .... Step (iii)}$$

Then,

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3(s) + 3HCl(g) \text{..................... Hydrolysis}$$

Any further heating will end up to Al_2O_3 instead of the intended anhydrous $AlCl_3$

$$2Al(OH)_3(s) \xrightarrow[\Delta]{} Al_2O_3\ (s) + 3H_2O$$

Question 2

(a)

1. Decreased water uptake by plants: High salt concentration increases osmotic pressure of soil solution which may result to dehydration of plants.

2. Increased level of toxicity in the soil: Some salts like chlorides are toxic to plants when present in high concentration to the extent that they may kill plants.

(b)

1. Increase organic content of the soil: Increasing organic matter in agricultural soil improve the soil structure, creates more air space, increases CEC thus improving minerals and water retention within the soil
2. Reduce soil erosion: A higher proportion of organic material in the soil (as result of application of manure) will also prevent soil erosion.
3. Lead to healthy ecosystem: Manure is gentler on microorganisms and earthworms living in the soil, creating a healthy ecosystem that is sustainable and conducive to long term use.
4. Steady realize of nutrients: Through this, there is reduced risk of nutrient burn from over fertilization. Also being slow in nutrient uptake means nutrients are preserved in the soil rather than leaching away with rainwater.

(c) Number of moles of NaOH $= \frac{27}{1000} \times 0.1\text{mol} = 2.7 \times 10^{-3}\text{mol}$

NaOH reacts with HCl according to the following equation:

$NaOH + HCl \rightarrow NaCl + H_2O$

From which mole ratio of NaOH to HCl is 1:1

Thus number of moles of HCl reacted with NaOH in the titration was also 2.7×10^{-3} mol

But total number of moles of HCl was $\frac{40}{1000} \times 0.1\text{mol} = 4 \times 10^{-3}\text{mol}$

Thus; $(4\times 10^{-3} - 2.7 \times 10^{-3})$ mol

Or 1.3×10^{-3} mol of H^+exchange base cations present in 20g of the soil sample

Number of equivalents of $H^+ = 1.3\times 10^{-3}$ eq $= 1.3$meq

But number of equivalents of H^+ = Number of equivalents of any base cations

Thus number of exchangeable base cations in 20g of soil sample was also 1.3 meq

And number of exchangeable base cations in 100g of soil will be

$\frac{100\times 1.3}{20}$meq or 6.5meq

Using; percentage base saturation

$= \frac{\text{number of exchangeable bas cations}}{\text{CEC of the soil}} \times 100 = \frac{6.5}{29} \times 100\% = 22.4\%$

Hence the percentage base saturation of the soil is 22.4%

Question 3

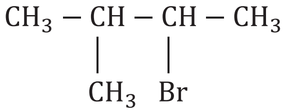
(a) (i) Plants and animals

(ii)

1. Ability to form multiple bonds.
   Apart from single bond, carbon can form double bond and triple bond. This enables carbon to combine in different overlapping ways depending on other's atom requirement and hence larger number of compounds of carbon.
2. Ability to undergo different types of hybridisation.
   Carbon can undergo sp^3 hybridisation, sp^2 hybridisation, and sp hybridisation. As result, ability of carbon to form covalent bonds has been increased in three different ways and hence largger number of compounds of carbon.
3. Ability to undergo catenation.
   Carbon can form very long and stable carbon chain. This ability, enables carbon to form different compounds with different lengths of carbon chain and hence large number of compounds of carbon.

(b)

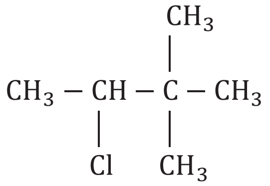
(i) Structure:



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-CH_3$$

Name: 2-bromo-3-methylbutane

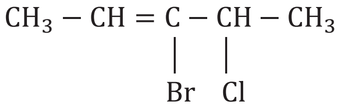
(ii) Structure:



$$CH_3-\underset{Cl}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$$

Name: 3-chloro-2,2-dimethylbutane

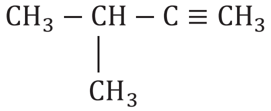
(iii) Structure:



$$CH_3-CH=\underset{Br}{\underset{|}{C}}-\underset{Cl}{\underset{|}{CH}}-CH_3$$

Name: 3-bromo-4-chloro-2-pentene

(iv) Structure:



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-C\equiv CH_3$$

Name: 3-methyl-1-butyne

(c)

(i) Methylpropane being more branched has smaller surface area and less compact package of carbon chains and therefore it has weaker Van-der-Waals dispersion forces. This makes 2-methylpropane to have lower boiling point than n-butane despite their equality in molecular mass.

(ii) Petrol mostly contains hydrocarbons which are highly combustible and thus it is so flammable that ignition sources will cause explosion

Question 4

(a) Given that:

$2B(s)+\frac{3}{2}O_2(g)\rightarrow B_2O_3(s) \quad \Delta H=-1272kJ$ ……………………… (i)

$B_2H_6(g)+3O_2(g)\rightarrow B_2O_3(s)+3H_2O(g) \quad \Delta H=-2035kJ$ ………… (ii)

$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(g) \quad \Delta H=-286kJ$ ………………………..…. (iii)

$H_2O(l)\rightarrow H_2O(g) \quad \Delta H=+44kJ$ …………………………………...…. (iv)

Reversing (ii) gives;

$B_2O_3(s)+3H_2O(g)\rightarrow B_2H_6(g)+3O_2(g) \quad \Delta H=+2035kJ$ ………..... (v)

Taking 3(iii) gives;

$3H_2(g)+\frac{3}{2}O_2(g)\rightarrow 3H_2O(g) \quad \Delta H=-858kJ$ ……………………..…. (vi)

Taking (i) + (vi) gives;

$2B(s)+\frac{3}{2}O_2(g)+\frac{3}{2}O_2(g)+3H_2(g)\rightarrow B_2O_3(s)+3H_2O(l); \Delta H=-(1273+858k)J$

From which;

$2B(s)+3O_2(g)+3H_2(g)\rightarrow B_2O_3(s)+3H_2O(l); \ \Delta H=-2131kJ$ …. (vii)

(v)+(vii) gives;
$\cancel{B_2O_3(s)} + 3H_2O(g) + 2B(s) + \cancel{3O_2(g)} + 3H_2(g) \rightarrow B_2H_6(g) + 3\cancel{O_2(g)} + \cancel{B_2O_3}(s) + 3H_2O(l) \quad \Delta H = (2035 - 2131)kJ$
From which:
$2B(s) + 3H_2(g) + 3H_2O(g) \rightarrow B_2H_6(g) + 3H_2O(l) \quad \Delta H = -96kJ$ …. (viii)
Taking $3\times$ (vi) gives;
$3H_2O(l) \rightarrow 3H_2O(g); \Delta H = 3 \times 44kJ = +132kJ$ ……………………… (ix)
Taking (viii) + (ix) gives;
$2B(s) + 3H_2(g) + 3H_2O(g) + \cancel{3H_2O(l)} \rightarrow B_2H_6(g) + \cancel{3H_2O(l)} + \cancel{3H_2O(g)}; \Delta H = (-96 + 132)kJ$
From which; $2B(s) + 3H_2(g) \rightarrow B_2H_6(s); \quad \Delta H = +36kJ$
Hence the enthalpy change of formation of B_2H_6 is $+36kJ$

(b) Total volume of the solution $= (100 + 100)cm^3 = 200\ cm^3$

Then using; $m = \rho V$
Total mass of contents = $1\ gcm^{-3} \times 200\ cm^3 = 200\ g$
Heat rise in solution contents $= M_cC_c\Delta T$

$= 200g \times 4.2Jg^{-1}K^{-1} \times 6.25K = 5250J = 5.25kJ$

Heat rise in calorimeter = Heat capacity × Temperature rise

$= 95JK^{-1} \times 6.25K = 593.75J = 0.59373kJ$

Total heat rise $= (5.25 + 0.59375)kJ = 5.84375kJ$
KOH reacts with HCl according to the following equations:
$KOH(aq) + HCl(aq) \rightarrow KCl(s) + H_2O(g)$
From which mole ratio of KOH (or HCl) to H_2O is 1:1
Since nothing was in axcess;
$n_{HCl} = n_{KOH} = \frac{100}{1000}dm^3 \times 1\ moldm^{-3} = 0.1mol = n_{H_2O}$
Using; Enthalpy of neutralisation $= \frac{\text{Heat change}}{\text{Number of moles of water produced}}$
The Enthalpy of neutralisation $= -\frac{5.84375kJ}{0.1mol} = -58.4375kJ/mol$
The standard enthalpy of neutralisation is $-58.4375kJ/mol$

Question 5

(a)
(i)
1. Matter is made up of very small indivisible particles called atoms.
2. Atoms can neither be created nor destroyed.
3. Atoms of the same element are all alike but differ from the atoms of all other elements.
4. Chemical combination takes place between small whole numbers of atoms.

(ii) Different atoms have different atomic number and hence different number of electrons. Different number of electrons means different electronic configuration and therefore different chemical properties.

(b)

s/n	Number of neutrons	Number of electrons	Atomic number	Mass number	Symbol	Electronic configuration
(i)	13	11	11	24	${}^{24}_{11}X$	$1s^22s^22p^63s^1$
(ii)	7	8	8	15	${}^{15}_{8}X$	$1s^22s^22p^4$
(iii)	17	18	18	35	${}^{35}_{18}X$	$1s^22s^22p^63s^23p^6$
(iv)	16	16	16	32	${}^{32}_{16}X$	$1s^22s^22p^63s^23p^4$

(c) From Plank's equation

$E = hf = \frac{hc}{\lambda}$

But from Rydberg equation:

$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Thus $E = hcR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

In removing an electron from hydrogen in ground state, the electron move from $n = 1$ to $n = \infty$.

Thus, $n_1 = 1$ and $n_2 = \infty$

Substituting:

$E = 6.63 \times 10^{-34}Js \times 3 \times 10^8 m/s \times 1.09678 \times 10^7 \times m^{-1}\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$

$= 2.18 \times 10^{-18}J$

The minimum energy required is $2.18 \times 10^{-18}J$

Question 6

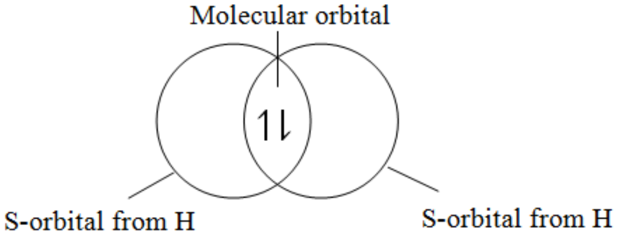
(a)

(i) Is the type of bond which is formed by transfer of electrons from metals to non-metals while octet rule governs atoms during their electrovalent (of course and covalent) bond formation by stating that both transfer and sharing of electrons between atoms is done in such a way that the atoms attain stable electron configuration of the nearest noble gas.

(ii) Lone pair are valence electrons of an atom which have not shared with another atom and thus they experience nuclear attractive force from one nucleus only while bonding electrons are valence electrons which have been shared between two atoms during the covalent bond formation and therefore they experience nuclear attractive force from two nuclei.

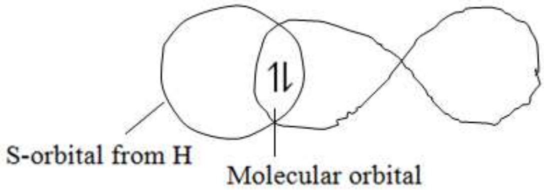
(b) First possibility: When s-orbital overlap with another s-orbital.

For example in H_2

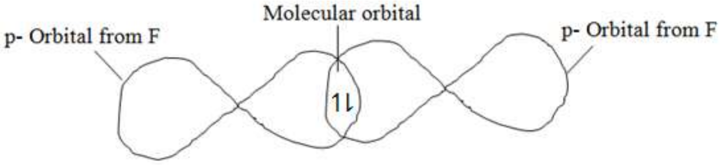


Second possibility: When s-orbital overlap with p-orbital.

For example, in the formation of HF



Third possibility: When p-orbital overlap with another p-orbital through end to end. For example, in the formation of F_2.



(c)

1. Sigma bonds are formed by head to head overlapping of atomic orbitals which have greater region of interaction than π-bond which is formed through side-way overlapping. This makes sigma bond to be stronger than pie bond.
2. Sigma bonds are commonly formed between hybrid orbitals which have lower energy than unhybridised orbitals used to form pi bond. This also makes sigma bond to be stronger than pie bond.

(d) With **three** bonded electron pairs and **one** lone pair in the central atom, N, whereby the lone pair exert stronger repulsion than the bonded pairs, the four electron pairs will be arranged around the central atom (according to VSEPR theory) in **trigonal pyramidal** geometry so as to minimize repulsion between them. **(1)**

Question 7

(a)

(i) From ideal equation:

$$V = \frac{nRT}{P} = \frac{0.25\text{mol}\times 8.31\text{Jmol}^{-1}\text{K}^{-1}\times 300\text{K}}{1.05\times 10^5\text{Pa}}$$

$$= 5.94\times 10^{-3}\text{m}^3 \text{ or } 5.94\text{L}$$

The volume it occupies is 5.94L

(ii) Since the number of moles was kept constant, combined gas law is applicable.

That is $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Where: $P_1 = 1.05\times 10^5\text{Pa}, T_1 = 300\text{K}, V_1 = V$

$P_2 = 7\times 10^6\text{Pa}, T_2 = ?, V_2 = \frac{V}{20}$

Substituting: $\frac{1.05\times 10^5\text{Pa}\times V}{300\text{K}} = \frac{7\times 10^6\text{Pa}\times V}{20T_2}$

From which; $T_2 = 1000\text{K}$ or $727°\text{C}$

The new temperature is 727°C

(b) From ideal gas equation: $P = \frac{nRT}{V}$

Thus $P_{N_2} = \frac{n_{N_2}RT}{V} = \frac{m_{N_2}RT}{M_{N_2}V} = \frac{42\text{g}\times 0.0821\text{atmmol}^{-1}\text{K}^{-1}\times 293\text{K}}{28\text{gmol}^{-1}\times 10\text{L}} = 3.6 \text{ atm}$

The partial pressure of nitrogen gas is 3.6 atm

Also $P_{H_2} = \frac{n_{H_2}RT}{V} = \frac{m_{H_2}RT}{M_{H_2}V} = \frac{8g\times0.0821atmmol^{-1}K^{-1}\times293K}{2gmol^{-1}\times10L} = 9.6$ atm

The partial pressure of nitrogen gas is 9.6 atm

By using Dalton's law of partial pressure;

$P_T = P_{H_2} + P_{N_2} = (3.6 + 9.6)\text{atm} = 13.2$ atm

The total pressure is 13.2 atm

Question 8

(a)

(i) Cryoscopic constant is related to freezing point; it is the depression (decrease) in freezing point of the solvent in the solution which is obtained when one mole of non-volatile solute is dissolved in 1kg (1000g) of the solvent while ebullioscopic constant is related to boiling point; it is the boiling point elevation of the solvent in the solution which is obtained when one mole of non-volatile solute is dissolved in 1kg (1000g) of solvent.

(ii) Consider one molecule of hypothetical compound $A_{XN}B_{YN}$ is dissociated into N molecules of A_XB_Y.

Then the equation to show the dissociation will be represented as follows:

	$A_{XN}B_{YN}(g)$	$\rightleftharpoons$	NA_XB_Y
Initial number of molecules before dissociation	1		0
Number of molecules after dissociation	$1-\alpha$		$N\alpha$

Where α is numerically equal to degree of dissociation = fraction of the molecules dissociated.

From the above equation:

Expected number of molecules (without dissociation) = 1

Observed number of molecules (after dissociation) = $1-\alpha+N\alpha = 1+\alpha(N-1)$

$$\text{Then } i = \frac{\text{Observed number of paricles}}{\text{Expected number of particles}} = \frac{1+\alpha(N-1)}{1}$$

$$\text{Or } i = 1+\alpha(N-1)$$

$$\text{Hence } \alpha = \frac{i-1}{N-1}$$

(iii) When the degree of dissociation is high, more solute particles will go to the solution leading to higher boiling point elevation and hence the boiling point of the solution will be high too.

(b) Using: $\Delta T = K_f \times \text{molality} = \frac{K_f\times m_{Su}}{M_{Su}\times m_{Sv}\text{ in Kg}}$

From which: $m_{Su} = \frac{\Delta T\times M_{Su}\times m_{Sv}\text{ in kg}}{K_f}$

Where:

$\Delta T = 0°C - (-23.3°C) = 23.3°C$

$M_{Su} = 62gmol^{-1}$

$m_{Sv} = 1g/ml \times 10 \times 10^3ml = 1 \times 10^4g = 10kg$

$K_f = 1.86°Ckgmol^{-1}$

Substituting;

$m_{Su} = \frac{23.3°C\times62gmol^{-1}\times10kg}{1.86°Ckgmol^{-1}} = 7767g = 7.767kg$

The mass of ethylene glycol is 7.767kg

(c) Using $\pi V = nRT = \frac{m_{Su}RT}{M_{Su}}$

From which: $M_{Su} = \frac{m_{Su}RT}{\pi V}$

Where:

$T = 20°C = 293$
$R = 8.31 J mol^{-1} K^{-1}$
$\pi = 25.6 \text{ Pa}$
$V = 200 \text{ cm}^3 = 200 \times 10^{-6} m^3$

Substituting:

$M_{Su} = \frac{0.12g \times 8.31 J mol^{-1} K^{-1} \times 293K}{25.6 \text{ Pa} \times 200 \times 10^{-6} m^3} = 5.7 \times 10^4 g mol^{-1}$

The molecular mass of haemoglobin is $5.7 \times 10^4 g mol^{-1}$

(d) Using $\Delta T = iK_f m = \frac{i \times K_f \times m_{su}}{M_{Su} \times m_{Sv} \text{ in kg}}$

Where:

$m_{su} = 1g$ and $m_{Sv} = 99g = 0.099kg$ (1% solution means that mass of solute in 100g of the solution is 1g).

Substituting:

$0°C - (-0.604°C) = \frac{i \times 1.86°C kg mol^{-1} \times 1g}{58.5 g mol^{-1} \times 0.099kg}$

From which $i = 1.88$

NaCl dissociates according to the following equation;

$NaCl(aq) \rightleftharpoons Na^+(aq) + Cl^-(aq)$; $N = 2$

Using $\alpha = \frac{1.88-1}{2-1} = 0.88$ or 88%

The degree of dissociation of NaCl is 88%

Question 9

(a)

(i) When chemical system is at equilibrium and the pressure of the system is increased or decreased, Le Chatelier's principle requires the position of chemical equilibrium to shift so as to decrease the added pressure or to increase the pressure respectively in order to re-store the equilibrium.

If the pressure of the system is increased, the position of chemical equilibrium shifts to the side with fewer gaseous molecules while decreasing pressure of the system shifts position of chemical equilibrium to the side with greater number of gaseous molecules.

(ii) In the coca cola soda, carbon dioxide is dissolved at high pressure and form the following equilibrium:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Opening the bottle decreases the pressure in the bottle, shifts the equilibrium position to $CO_2(g)$ side, thereby the solubility of the gas is decreased and hence gas bubbles are suddenly escaping the bottle.

(b)

(i) Addition of NaOH is equivalent to removal of H^+ thus shifting the position of equilibrium to the left and hence yellow colouration of CrO_4^{2-} will be observed.

(ii) Addition of HCl(aq) shift the position of chemical equilibrium to the right and hence Orange colouration of $Cr_2O_7^{2-}$ will be observed.

(c)

(i) Since the forward reaction is exothermic, the increase in temperature will shift the equilibrium position to the left hand (PCl_3) side and hence the amount of PCl_3 will increase.

(ii) Since the forward reaction is exothermic, the decrease in temperature will shift the equilibrium position to PCl_5-side and hence the amount of PCl_3 will decrease.

(d)

(i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Equilibrium concentration 0.85 0.031 0.031

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(0.031\text{moldm}^{-3}\right)^2}{(0.85\text{moldm}^{-3})(0.031\text{moldm}^{-3})^3} = 37.950.031\text{mol}^{-2}\text{dm}^6$$

The equilibrium constant is $37.950.031\text{mol}^{-2}\text{dm}^6$

(ii) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

Equilibrium concentration 0.031 0.85 0.031

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{(0.85\text{moldm}^{-3})\left(0.031\text{moldm}^{-3}\right)^3}{(0.031\text{moldm}^{-3})^2} = 0.02635\text{mol}^2\text{dm}^{-6}$$

The equilibrium constant is $0.02635\text{mol}^2\text{dm}^{-6}$

Question 10

(a) This is due stabilization of its pie bonds by mesomerism.

Explanation

For benzene to undergo addition reaction, pie bond must be broken. However pie bonds in benzene have been delocalised in mesomerism. So for benzene to undergo addition reaction high amount of energy (resonance energy) must be absorbed to stop the resonance before breaking π -bonds so as to add atoms to carbon atoms. This makes more difficult for it to undergo addition reaction.

(b)

(i) Examples of ortho-para directors:

1. Hydroxyl group
2. Amino group

(ii) Examples of meta-directors:

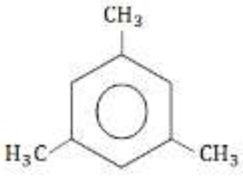
1. Carboxylic group
2. Nitro group

(c) Ortho-para directors increase electron density in benzene ring through either positive inductive effect or positive mesomerism. So they are said to activate the reactivity of benzene toward the electrophile in electrophilic substitution reactions and hence they are known as activating groups.

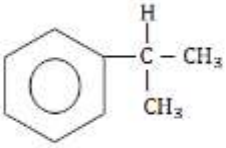
Meta directors withdraw electron from benzene ring by negative mesomerism and therefore they decrease reactivity of benzene toward electrophile. So they are said to deactivate electrophilic substitution reactions in benzene and hence they are called deactivating groups.

(d)

(i)



(ii)



(e)
(i) 1,2-dimethylbenzene
(ii) 4-nitrotoluene
(iii) 1,3,5-trichlorobenzene

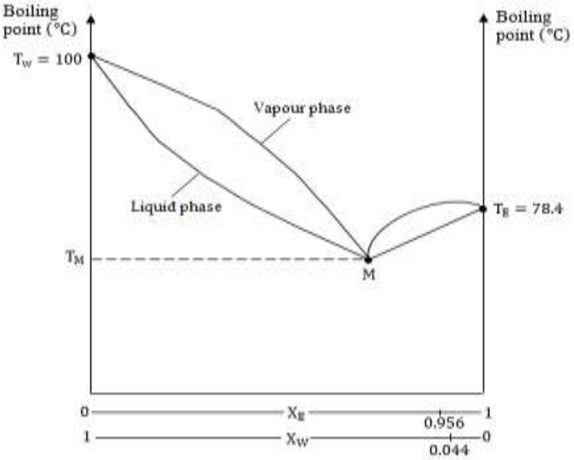
Solutions Necta 2020
CHEMISTRY 2

Answer **five (5)** questions

Question 1

(a)

(i)



Where: T_W is the boiling point of pure water

T_E is the boiling point of pure ethanol

T_M is the boiling point of azeotropic mixture (azeotropic point)

M is the azeotropic mixture

X_E is the mole fraction of ethanol

X_W is the mole fraction of water

(ii) The solution will boil in such a way that the vapour formed is richer in ethanol until its percentage in the collector rises to 95.6%. Finally on successive distillation and condensation the filtrate in the collector will be azeotropic mixture with 95.6% ethanol and the residue in the distillation flask will be pure water.

(iii) By introducing suitable dehydrating agent like calcium oxide (CaO) so as to remove water which is only 4.4%.

(b) Using; $K_d = \frac{\text{Mass concentration of G in pentan−1−ol (in gdm}^{-3})}{\text{Mass concentration of G in aqueous solution (in gdm}^{-3})}$

Where: Mass concentration of G in pentan-1-ol $= \frac{\text{mass of G}}{V_{\text{Soln}} \text{ in dm}^3}$

But $V_{\text{Soln}} = 100 \text{ cm}^3 = \frac{100}{1000} \text{dm}^3 = 0.1\text{dm}^3$

The mass concentration of G in pentan-1-ol $= \frac{1.5\text{g}}{0.1\text{dm}^3} = 15\text{gdm}^{-3}$

Original mass of G in 500cm^3 of aqueous solution$= \frac{500}{1000} \times 4\text{g} = 2\text{g}$

Then mass of G in 500cm^3 of aqueous solution after extraction $= (2 - 1.5)\text{g} = 0.5\text{g}$

Mass concentration of G in aqueous solution $= \frac{0.5\text{g}}{0.5\text{dm}^3} = 1\text{gdm}^{-3}$

Substituting:

$$K_d = \frac{15gdm^{-3}}{1gdm^{-3}} = 15$$

The partition coefficient of the solute G between pentan-1-ol and water is 15.

Let mass (in grams) of G remained in the aqueous solution be x

Then mass of G which will be extracted in the propan-1-ol will be $0.5 - x$

$$\text{Then } K_d = 15 = \frac{\frac{(0.5 - x)g}{0.1dm^3}}{\frac{xg}{0.5dm^3}} = \frac{5(0.5 - x)}{x}$$

From which; $20x = 2.5; x = 0.125g$

The mass of G remained in aqueous layer after further extraction is 0.125g.

(c)

1. Solvent extraction
2. Partition chromatography

Question 2

(a)

(i) Catalyst lowers activation energy of the reaction by providing an alternative mechanism for the reaction with smaller energy.

(ii)

Temperature

The increase in temperature increases both collision frequency and collision energy of reacting particles and hence the rate of chemical reaction increases with rise in temperature.

Concentration

The increase in concentration of reactants increases collision frequency and hence the reaction rate will increase as the reactants concentration increases.

Light

The increase in the light intensity increases the number of photons in light and therefore more number of reactant molecules gets energy by absorbing more number of photons and undergo chemical change. Consequently, the rate of photochemical reactions, increase with increase in the intensity of suitable light used.

Pressure

The increase in partial pressure of gaseous reactants increases collision frequency and hence the reaction rate will increase as the pressure increases.

Surface area

The greater surface area exposed, the greater chance of collisions between reacting particles leading to higher collision frequency and hence the rate of a reaction increases with increase in the surface area of solid reactant.

(b) $KMnO_4$ was used to oxidise the undecomposed H_2O_2

So the volume of $KMnO_4$ used in the titration varies directly proportional to the concentration of the undecomposed H_2O_2 (Greater amount of H_2O_2 needs larger volume of $KMnO_4$ for its oxidation)

Thus if a and V_o are respectively representing the original concentration of H_2O_2 and the original volume of $KMnO_4$ used for the titration (to oxidise the H_2O_2)
And $a - x$ and V_t are respectively representing concentration of H_2O_2 and volume of $KMnO_4$ used to oxidise the H_2O_2 after any time, t, of its (H_2O_2) decomposition'
Then $a \propto V_o$ or $a = kV_o$
And $a - x \propto V_t$ or $a = kV_t$
Thence $\frac{a}{a-x} = \frac{kV_o}{kV_t} = \frac{V_o}{V_t}$
But from the differential rate equation of first order
$\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$
But $\frac{a}{a-x} = \frac{V_o}{V_t}$ (As shown above)
Thus $\log\left(\frac{V_o}{V_t}\right) = \frac{kt}{2.303}$
From which $k = \frac{2.303}{t}\log\left(\frac{V_o}{V_t}\right)$
Where $V_o = 70\ cm^3$
When $t = 6$ min, $V_t = 47\ cm^3$
Then $K_1 = \frac{2.303}{6}\log\left(\frac{70}{47}\right) = 0.0664\ min^{-1}$
When $t = 9$ min, $V_t = 30\ cm^3$
Then $K_2 = \frac{2.303}{9}\log\left(\frac{70}{30}\right) = 0.0942\ min^{-1}$
When $t = 20$ min, $V_t = 13\ cm^3$
Then $K_3 = \frac{2.303}{20}\log\left(\frac{70}{7.2}\right) = 0.0842\ min^{-1}$
When $t = 29$ min, $V_t = 7.2\ cm^3$
Then $K_4 = \frac{2.303}{29}\log\left(\frac{70}{7.22}\right) = 0.0784\ min^{-1}$
Since the rate constants do not differ much, the given data obey differential rate equation of first order and hence the reaction is of the first order.
Rate constant, $k = \frac{k_1+k_2+k_3+k_4}{4}$
$= \frac{(0.0664+0.0942+0.0842+0.0784)min^{-1}}{4}$
$= 0.0808\ min^{-1}$
The rate constant is $\mathbf{0.0808\ min^{-1}}$

(c)

(i) Using the equation; $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

Where: $k = 2.2 \times 10^{-5} sec^{-1}, t = 90 minutes = 9 \times 60 sec = 5400 sec$
If a is the initial percentage $= 100$
Then x will be the percentage decomposed
Thence $\log\left(\frac{100}{100 - x}\right) = \frac{2.2 \times 10^{-5} sec^{-1} \times 5400 sec}{2.303} = 0.0516$
From which $\frac{100}{100 - x} = \log^{-1}(0.0516) = 1.126$
Thus $1.126x = 12.6$; $x = 11.19$

The percentage of NH_2NO_2 decomposed is approximately 11%

(ii) Using;

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.30R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Where: $T_1 = 20°C = 293K$ and $T_2 = 323K$

Since reaction rate varies directly proportional to the rate constant; $\frac{k_2}{k_1} = \frac{R_2}{R_1} = 3$

Substituting $\log(3) = \frac{E_a}{2.303 \times 8.31 Jmol^{-1}K^{-1}}\left(\frac{(323-293)K}{293K \times 323K}\right)$

From which $E_a = 28805 J/mol$ or $28.805 kJ/mol$

The activation of the reaction is $28.805 kJ/mol$

Question 3

(a)

(i) Using $n = MV$;

Then number of moles of NaOH, $n_{NaOH} = \frac{1}{1000} dm^3 \times 0.1 moldm^{-3} = 1 \times 10^{-4} mol$

And number of moles of HCl, $n_{HCl} = \frac{100}{1000} dm^3 \times 0.001 moldm^{-3} = 1 \times 10^{-4} mol$

NaOH react with HCl according to the following equation:

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

From which mole ratio of NaOH to HCl is 1: 1

Thus with equal number of moles of NaOH and HCl, the given amount satisfy the mole ratio and therefore nothing present in excess.

Since neither acid nor base present in excess and the salt that has been formed (NaCl) is strong ionic salt which does not hydrolyse in water, the resulting solution is neutral with pH of 7

Hence the pH of the solution obtained is 7

(ii) $n_{HCl} = \frac{1}{1000} dm^3 \times 1 moldm^{-3} = 1 \times 10^{-3} mol$

Then $[HCl] = \frac{n_{HCl}}{V_{soln}}$; where $V_{soln} = (1 + 1000)cm^3 = 1001 cm^3 = 1.001 dm^3$

Substituting $[HCl] = \frac{1 \times 10^{-3} mol}{1.001 dm^3}$

Also $[CH_3COOH] = \frac{n_{CH_3COOH}}{V_{soln}} = \frac{0.04 mol}{1.001 dm^3} = 0.04M$

CH_3COOH being weak acid ionises partially according to the following equation:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

At equilibrium $\quad 0.04 - x \quad x \quad x$

HCl being strong acid ionises completely according to the following equation:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

After ionisation $\quad 0 \quad 0.001M \quad 0.001M$

Thus in $CH_3COOH|HCl$ mixture:

$[CH_3COOH] = 0.04 - x$

$[CH_3COO^-] = x$

$[H^+] = x + 0.001$

Then from the equation of ionisation of CH_3COOH;

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH\,]}$$

Substituting $1.84 \times 10^{-5} = \frac{x(x+001)}{0.04-x}$

From which: $x^2 + 0.0010184x - 7.36 \times 10^{-7} = 0$

From the above quadratic equation; practical value of $x = 4.88 \times 10^{-4}$

Thus $[H^+] = x + 0.001 = (4.88 \times 10^{-5} + 0.001)M = 1.488 \times 10^{-3}M$

$pH = -\log[H^+] = -\log(1.488 \times 10^{-3}) = 2.83$

Hence pH of the solution is 2.83

(b) According to Bronsted-Lowry theory, if an acid has high ability of donating its hydrogen proton as strong acid then its conjugate base will have low ability of accepting hydrogen proton and therefore behaving as weak base.

Also if a base has high ability of accepting hydrogen proton as strong base then its conjugate acid will have high hydrogen proton donating ability and therefore it becomes strong acid.

(c)

(i) NH_4^+/NH_3 and H_3O^+/H_2O acid – base conjugate pairs.

(ii) H_2SO_4/HSO_4^- and H_3O^+/H_2O acid – base conjugate pairs.

(iii) AH/A^- and H_3O^+/H_2O acid – base conjugate pairs.

Question 4

(a)

1. Due to their weak metallic bond, s-block elements are soft metals possessing low melting point and low boiling point.
2. Due to their small atomization energy and low ionisation energy, s-block elements are generally very reactive. They are normally not found in free state due to their reactive nature.
3. Due to their weak metallic bond and low electronegativity, s-block metals (except beryllium) dissolve readily in water to give strong alkaline solution.
4. Due to their large metallic radius accompanied with high ionisation energy, alkali metals (except beryllium and magnesium) impart characteristic colour to the flame.

(b)

(i) Electronegativity is the measure of the tendency of an atom to attract a shared pair of electrons in covalent bond towards itself. It is the measure atom's ability to form covalent bond whereby atoms with high electronegativity have high ability to form covalent bond.

(ii)

1. The size of charge in the nucleus

The greater number of protons present in the nucleus, the higher nuclear charge is and hence high electronegativity of the atom.

2. **The distance from the nucleus**

   The shorter distance of bonding pair electrons from nucleus of the atom the more attraction to the electrons and hence high electronegativity of the atom.

3. **The amount of screening by inner electrons**

   The greater screening effect exerted by inner electrons of the atom to the bonding pair of electrons, the less attraction to the bonding electrons and hence low electronegativity

(c) Stable hydrides of period 2 are LiH, B_2H_6 (or BH_3), CH_4, NH_3, H_2O and HF.

LiH is basic. Being basic; it dissolves in water to give basic solution, reacts with acids like HCl and has no reaction with another basic solution like NaOH.
With water: $LiH + H_2O \longrightarrow LiOH + H_2$
With acid: $2LiH + 2HCl(aq) \longrightarrow LiCl + H_2$
With Base: $LiH + NaOH(aq) \longrightarrow$ No reaction
B_2H_6 is acidic. Being acidic; it dissolves in water to give acidic solution, reacts with basic solution like NaOH and has no reaction with acidic solution like HCl.
With water: $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$
With base: $B_2H_6 + 2NaOH + 6H_2O \longrightarrow 2Na[B(OH)_4] + H_2$
With acid: $B_2H_6(aq) + HCl(aq) \longrightarrow$ No reaction
CH_4 is neutral. It does not react with all water, acid and base.
NH_3 is basic. Being basic, it dissolves in water to give basic solution, reacts with acids like HCl and does not react with another basic solution like NaOH.
With water: $NH_3 + H_2O \longrightarrow NH_4^+(aq) + OH^-(aq)$
With acid: $NH_3(aq) + HCl(aq) \longrightarrow NH_4OH + H_2O$
With base: $NH_3 + NaOH \longrightarrow$ No reaction
H_2O is amphoteric; it can react with both acid and base depending on the strength of the acid or base it react with.
With water itself: It undergoes self ionisation to give hydronium ion and hydroxide ion.

$$H_2O + H_2O \longrightarrow H_3O^+ + OH^-$$

With base: it reacts with stronger base (than itself) like SO_4^{2-}.

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$

With acid: it reacts with stronger acid like HCl

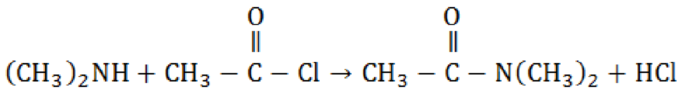
$$H_2O + HCl \rightarrow H_3O^+ + Cl^-$$

HF is acidic. Being acidic, it dissolves in water to give acidic solution, reacts with basic solution like NaOH and it has no reaction with another acidic solution like HNO_3.
With water: $HF + H_2O \longrightarrow H_3O^+ + F^-$
With base: $HF + NaOH \rightarrow NaF + H_2O$
With acid: $HF + HNO_3 \rightarrow$ No reaction

Question 5

(a)

(i) With limited amount of dimethylamine, the dimethylamine will react with CH_3COCl via nucleophilic substitution mechanism.

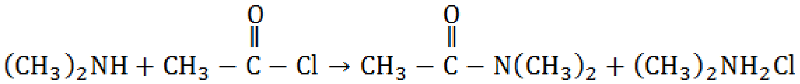


$$(CH_3)_2NH + CH_3 - \overset{\overset{O}{\|}}{C} - Cl \rightarrow CH_3 - \overset{\overset{O}{\|}}{C} - N(CH_3)_2 + HCl$$

If the amine present in excess, acid-base reaction between the amine (base) and HCl (acid) occurs.

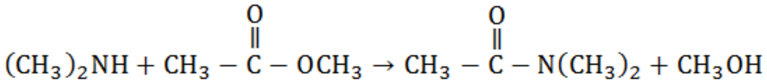
$(CH_3)_2NH + HCl \rightarrow (CH_3)_2NH_2Cl$

Overall reaction equation:



$$(CH_3)_2NH + CH_3 - \overset{\overset{O}{\|}}{C} - Cl \rightarrow CH_3 - \overset{\overset{O}{\|}}{C} - N(CH_3)_2 + (CH_3)_2NH_2Cl$$

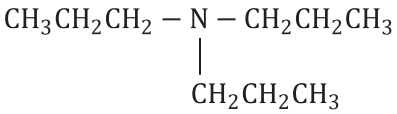
(ii) Dimethyl reacts with CH_3COOCH_3 via nucleophilic substitution mechanism.



$$(CH_3)_2NH + CH_3 - \overset{\overset{O}{\|}}{C} - OCH_3 \rightarrow CH_3 - \overset{\overset{O}{\|}}{C} - N(CH_3)_2 + CH_3OH$$

(b)

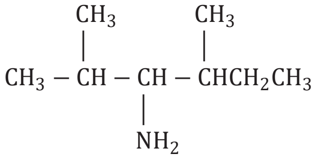
(i)



$$CH_3CH_2CH_2 - \underset{\underset{CH_2CH_2CH_3}{|}}{N} - CH_2CH_2CH_3$$

(ii) $CH_3CH_2CH_2CH_2CH_2 - NH - CH_2CH_2CH_2CH_2CH_3$

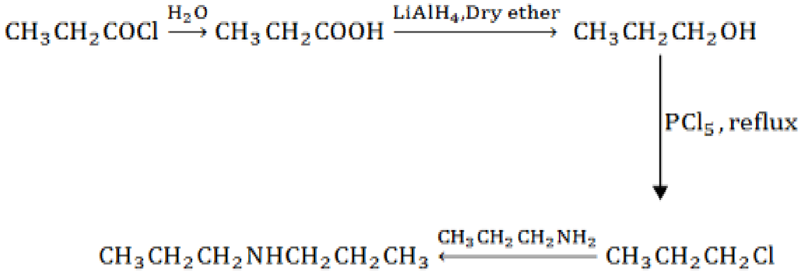
(iii)



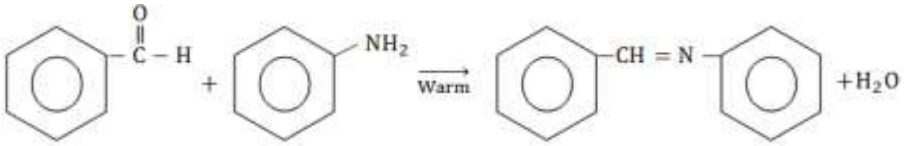
$$CH_3 - \overset{\overset{CH_3}{|}}{CH} - \underset{\underset{NH_2}{|}}{CH} - \overset{\overset{CH_3}{|}}{C}HCH_2CH_3$$

(c)

(i)



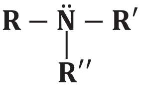
(ii)



(iii) **Primary amine:**

General formula: $\mathbf{R - \ddot{N}H - R'}$ where R and R$'$ are carbon containing substituents.
Functional group is $\mathbf{-\ddot{N}}$

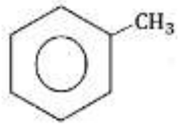
Secondary amine:

General formula: 
$\mathbf{R - \underset{\textstyle R''}{\underset{|}{\ddot{N}}} - R'}$

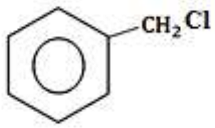
Where R, R$'$ and R$''$ carbon containing substituents.
Functional group is $\mathbf{-\ddot{N}}$

(iv) $(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$

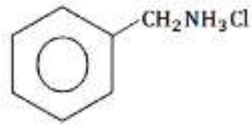
(d) Structure of B:



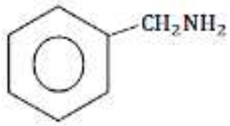
Structure of C:



Structure of D



Structure of E



Question 6

(a)

(i) Thermoplastic polymers are polymer materials which soften when heated without decomposition and become hard when cooled. Are polymers whose strength of their intermolecular forces of attraction lies between those of elastomers and fibers. Their chains have no cross links and therefore thermoplastics can be moulded on heating. An example of thermoplastic polymer is polystyrene.

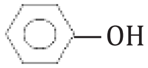
(ii) Thermosetting polymers are polymer materials which are hard and soften when heated with decomposition. Once hardened, they cannot be softened by re-heating. They have massive cross-links between different polymer chains forming three dimensional networks of bonds and therefore very strong physical properties for them. An example of thermosetting polymer is bakelite plastic.

(iii) Natural polymers are polymers occurring in nature in plants and animals. They are not man made polymers; they are made by either addition polymerisation or condensation polymerisation naturally. Most of them are water-based polymers made by condensation polymerisation. An example of natural polymers is protein.

(b)

(i) $CH_2 = CH - Cl$ (Vinyl chloride/1-chloroethane)

(ii) $F_2C = CF_2$ (tetrafluoroethylene/tetrafluoroethene)

(iii) HCHO and 

(methanal and phenol)

(c)

(i) Through positive inductive effect, electron donating group makes the intermediate carbenium ion (carbocation) less negative and hence more stable. So the cationic polymerisation is more favoured due to this stability of cationic propagating species.

(ii) In styrene, the phenyl group which is an electron withdrawing group is attached to doubly bonded carbon of the side chain ($C_6H_5 - CH = CH_2$) and therefore stabilizing the intermediate carbanion by making it less negative. This stabilization of anionic propagating species favours anionic polymerisation.

(iii) Addition polymers are chain growth polymers formed from unsaturated monomers by addition reaction whereby only one molecule is formed while condensation polymers are step growth polymers formed from active groups containing monomers by condensation reaction with evolvement of small molecules like H_2O and HCl.

Example of addition polymer is polyvinyl chloride.

Example of condensation polymer is protein.

(d)

(i) Butyl-rubber

Use: In inner tube of tyre.

Reason: It has good impermeability (air retention) and good flex properties, resulting from low levels of unsaturation between long polyisobutylene segments.

(ii) Polyacrylonitriles

Use: In making automobile body parts.

Reason: Due to high polarity of nitrile group of its acrylonitrile units there is very strong intermolecular forces existing between its chains and therefore making the polymer to have strong physical properties.

(iii) Polyhaloalkene

Use: In packaging

Reason: They are generally unreactive as they are composed of very long saturated carbon chain containging non- polar $C - C$ bond and hence they are good inert material.

Solutions Necta 2021
CHEMISTRY 1

SECTION A

Answer **all** questions in this section.

Question 1

(a)

(i) Isotopy is the tendency of an element to show the property of possessing atoms with different mass numbers while isotopes are those atoms of the elements with different mass number.

(ii) Atomic spectrum is the arrangement of electromagnetic radiations emitted or absorbed by an electron during transitions between different energy levels within an atom formed after the atom absorbing or emitting discrete packets of energy while photon is that single packet of energy contributing to atomic spectrum.

(iii) Continuous spectrum is the arrangement of all possible radiation of all frequencies over a wide range of frequencies with no clear cut way between one radiation and other while line spectrum consists of separate lines with clear cut separating radiations.

(b) Using $f = \frac{c}{\lambda}$

But from Rydberg equation:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

It follows that; $f = cR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

The visible region of atomic spectrum is found when an electron falls from higher energy level (in this case $n = 4$) to $n = 2$.

Thus $n_2 = 4$ and $n_1 = 2$

Substituting $f = 3x10^8 ms^{-1} \times 1.09678m^{-1} \times 10^7\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 6.17 \times 10^{14}s^{-1}$

Hence the frequency is 6.17×10^{14}Hz

(c)

1. In determination of masses of atoms and molecules.
2. In measurement of abundances of atoms and molecules.

Question 2

(a)

(i) It requires smaller amount of energy to ionize Na to Na^+ (more stable oxidation state for Na is +1) in NaBr than Na^{2+} in $NaBr_2$. Thus NaBr is more stable.

(ii) With total of 32 valence electrons, electronic structure of ClO_4^- is more stable than ClO_4 which has a total of 31 valence electrons. Thus ClO_4^- is more stable.

(iii) Se is large enough and has vacant d orbitals for expansion of valence shell so as to accommodate four F atoms unlike O which is too small and has no d sub-energy level to accommodate those F atoms. Thus SeF_4 is more stable.

(iv) With a total of 32 valence electrons, XeO_4 has more stable electronic structure than SO_4 which has a total of 30 valence electrons. Thus XeO_4 is more stable.

(b) In CH_4 all electron domains around the central atom, C, are bonded electron pairs exerting equal amount of repulsion resulting to tetrahedral arrangement with bond angle of 109.5°.

In NH_3 there is one lone pair in the central atom, N. Unlike bonded electron pair which are shared between two nuclei of bonded atoms, the lone pair are localized only around the nucleus of N atom exerting stronger repulsion than bonded electron pairs making bonds to be squeezed inward and consequently the bond angle in NH_3decreases from tetrahedral angle of 109.5° to 107.3°.

(c)

(i) Ionic bond.
Reason: The bond is between Ca which is strong electropositive metal and Cl which is strong electronegative non-metal.

(ii) Covalent bond.
Reason: The bond is between H and F which are both non-metals.

Question 3

(a) $n_{methanol} = \frac{m_{methanol}}{M_{methanol}} = \frac{32g}{32g/mol} = 1mol$

$$n_{water} = \frac{m_{water}}{M_{water}} = \frac{36g}{18g/mol} = 2mol$$

$$X_{water} = \frac{n_{water}}{n_{methanol} + n_{water}} = \frac{2mol}{1mol + 2mol} = \frac{2}{3}$$

Mixture of water and methanol ideal solution, so it obeys Raoult's law.

Then $P'_{water} = X_{water}P^{o}_{water} = \left(\frac{2}{3} \times 3.2\right) kPa = 2.13kPa$

Partial vapour pressure of water in the mixture is 2.13kPa

(b) Using $M_{su} = \frac{m_{su}\times M_{sv}\times P^{0}_{sv}}{m_{sv}\times \Delta P}$

From which; lowering in vapour pressure of carbon tetrachloride (solvent), ΔP

$$= \frac{m_{su} \times M_{sv} \times P^{0}_{sv}}{m_{sv} \times M_{su}}$$

Where:

$$m_{su} = 10g, M_{sv} = 154g/mol, P^{0}_{sv} = 100mmHg, m_{sv} = 40g, M_{su} = 310g/mol$$

Substituting $\Delta P = \frac{10g\times 154g/mol\times 100mmHg}{40g\times 310g/mol} = 12.42mmHg$

Then $P_{soln} = P^{0}_{sv} - \Delta P = (100 - 12.42)mmHg = 87.58mmHg$

Vapour pressure of the solution is 87.58mmHg

(c)Further dilution increases degree of dissociation of KCl. Furthermore the dilution makes the amount of solvent to be such large compared to the amount of solute that ions interaction and hence the ion pairing becomes difficult because ions are more distant apart as solvent-solvent interactions are more dominant in the diluted solution. Consequently the Van't Hoff's factor approaches the ideal value of 2 and hence the relative molecular mass approaches the ideal value too.

Question 4

(c) Given that:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H = -68.3kCal \ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$$

$$Ca(s) + H_2O(l) \longrightarrow Ca(OH)_2(s); \Delta H = -15.3kCal \ldots\ldots\ldots\ldots\ldots. (ii)$$

From (i); $\Delta H_f(H_2O) = -68.3kCal$

Then using;

$$\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

The equation (ii) becomes;

$$-15.3\text{kCal} = \Delta H_f(Ca(OH)_2) - \Delta H_f(H_2O) \qquad (\Delta H_f(Ca) = 0)$$

Substituting $-15.3\text{kCal} = \Delta H_f(Ca(OH)_2) - (-68.3\text{kCal})$

From which; $\Delta H_f(Ca(OH)_2) = -83.6\text{kCal}$

Heat of formation of $Ca(OH)_2$ is $= -83.6\text{kCal}$.

(d) Given that:

$2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s) \qquad \Delta H = -1272\text{kJ}$ ……………………… (i)

$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g) \quad \Delta H = -2035\text{kJ}$ ………… (ii)

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \quad \Delta H = -286\text{kJ}$ ……………………..…. (iii)

$H_2O(g) \rightarrow H_2O(l) \quad \Delta H = +44\text{kJ}$ …………………………………...…. (iv)

Reversing (ii) gives;

$B_2O_3(s) + 3H_2O(g) \rightarrow B_2H_6(g) + 3O_2(g) \quad \Delta H = +2035\text{kJ}$ ………..... (v)

Taking 3(iii) gives;

$3H_2(g) + \frac{3}{2}O_2(g) \rightarrow 3H_2O(g) \quad \Delta H = -858\text{kJ}$ ……………………..…. (vi)

Taking (i) + (vi) gives;

$2B(s) + \frac{3}{2}O_2(g) + \frac{3}{2}O_2(g) + 3H_2(g) \rightarrow B_2O_3(s) + 3H_2O(l); \Delta H = -(1273 + 858k)J$

From which;

$2B(s) + 3O_2(g) + 3H_2(g) \rightarrow B_2O_3(s) + 3H_2O(l); \ \Delta H = -2131\text{kJ}$ …. (vii)

(v)+(vii) gives;

$\cancel{B_2O_3(s)} + 3H_2O(g) + 2B(s) + \cancel{3O_2(g)} + 3H_2(g) \rightarrow B_2H_6(g) + 3\cancel{O_2(g)} + \cancel{B_2O_3}(s) + 3H_2O(l) \quad \Delta H = (2035 - 2131)\text{kJ}$

From which:

$2B(s) + 3H_2(g) + 3H_2O(g) \rightarrow B_2H_6(g) + 3H_2O(l) \quad \Delta H = -96\text{kJ}$ …. (viii)

Taking 3× (iv) gives;

$3H_2O(l) \rightarrow 3H_2O(g); \Delta H = 3 \times 44\text{kJ} = +132\text{kJ}$ ……………………… (ix)

Taking (viii) + (ix) gives;

$2B(s) + 3H_2(g) + 3H_2O(g) + \cancel{3H_2O(l)} \rightarrow B_2H_6(g) + \cancel{3H_2O(l)} + \cancel{3H_2O(g)}; \Delta H = (-96 + 132)\text{kJ}$

From which; $2B(s) + 3H_2(g) \rightarrow B_2H_6(g); \qquad \Delta H = +36\text{kJ}$

Hence the heat change for the synthesis of B_2H_6 is $+36\text{kJ}$

Question 5

(a)

(i) All ions in soil solution are moving constantly: the ion exchange can be undertaken in either way until the equilibrium is established. Hence the process is reversible.

(ii) Magnesium and calcium ions from these compounds are basic and are capable of replacing acidic cations in the soil, mainly H^+ and Al^{3+}. Simultaneously anionic part of these compounds hydrolyse in the solution to give hydroxide (OH^-) ions which in turn either precipitate out $Al(OH)_3$ or combine with H^+ to give H_2O. The two processes makes magnesium and calcium compounds capable of neutralizing acidity and therefore they are good liming materials.

(iii) In soil water solution, Al^{3+} from hexaaqua complex which tends to hydrolyse in ligand substitution reaction thus forming acidic solution and hence soil acidity.

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_3O^+$$

(b) Molar mass of $(NH_4)_2SO_4$ is 132g/mol = 0.132 kg/mol
Mass of nitrogen in one mole of ammonium sulphate = 28g =0.028kg
Thus, 0.028kg of nitrogen is produced by 0.132kg of ammonium sulphate.
And 100kg of the required nitrogen will be produced by $\frac{100\times0.132}{0.028}$kg $=$ 471.43kg of $(NH_4)_2SO_4$.
Thus 471.43kg of ammonium sulphate fertilizer is required per hectare.
So 60 hectares will require $471.43\text{kg} \times 60 = 28285.8\text{kg}$ of the fertilizer.
But one bag of fertilizer weighs 25kg.
It follows that;
Number of bags $= \frac{28285.8\text{kg}}{25\text{kg/bag}} = 1132\text{bags}$
(estimated to the nearest whole number after 1131.432)
Amount of amount of the fertilizer required to meet the demand is 1132 bags of ammonium sulphate.

Question 6

(a) When dilute hydrochloric acid is added to potassium, chemical equilibrium is established as per the following ionic equation:

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O$$

Therefore:

(i) The addition of HCl(aq) shift the position of chemical equilibrium to the dichromate side and orange colouration of potassium dichromate will be observed.

(ii) The addition of NaOH is equivalent to removal of H^+ thus shifting the position of equilibrium to the chromate side and yellow colouration of potassium chromate will be observed.

(iii) Anhydrous $CaCl_2$ absorbs water, thus its addition shifts position of chemical equilibrium to the dichromate side and orange colouration of potassium will be observed.

(b)

(i) NH_4Cl contain strong acidic cation (NH_4^+) and weak basic anion (Cl^-) , so in aqueous solution it undergo cationic hydrolysis yielding acidic solution which is responsible of evolving hydrogen gas when magnesium (metal) is introduced in the solution.
That is $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$
Then $2H^+ + Mg \rightarrow Mg^{2+} + H_2$

(ii) $AlCl_3$ is amphoteric salt with covalent characters as it contains strong acid cation, Al^{3+}, of high polarizing power making it to have high degree of polarization. So with water, the salt undergo cationic hydrolysis yielding acidic solution while NaCl being more ionic as it contains weak acid cation, Na^+, of very weak polarizing power, does not hydrolyse in water.
i.e. $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3H^+ + 3Cl^-$

While $NaCl + H_2O \rightarrow$ No reaction

Question 7

(a)

1. Their combustion are highly exothermic.
2. Their combustion can be controlled.

(b) Compared to conventional fuels, compressed natural gas have the following benefits:

1. Their combustion release greater amount of energy (they have higher energy density).
2. They are lighter and therefore easier to transport.
3. They combust more cleanly and therefore contributing less to air pollution (they produce less toxic pollutants and green house gases than gasoline and diesel).
4. They are not stored in the underground tanks like gasoline and diesel and therefore avoiding land pollution (soil contamination) and water pollution.

(c)

(i) Bromine water test: With bromine water, butane gives positive test by decolourising reddish-brown colouration of bromine water while butane does not.

(ii) Ammonical silver nitrate test: With Ammonical silver nitrate, propyne gives positive test by producing white precipitate of silver propynide while propene does not.

(iii) Ammonical silver nitrate test: With Ammonical silver nitrate, pent-1-yne gives positive test by producing white precipitate of silver pent-1-ynide while pent-2-yne does not.

(iv)Alcoholic silver nitrate test: With alcoholic silver nitrate test, 1-bromopropane gives light yellow precipitate of silver bromide while propane does not.

Question 8

(a)

(i) It states that: "If a chemical system is in equilibrium and one of the factors involved in the equilibrium is altered, the equilibrium will shift so as to tend to annul the effect of the change."

(ii) In homogenous chemical equilibrium, all reagents present in the system are at the same phase while in heterogeneous chemical equilibrium, more than one phase present in the system.

(b)

(i) Forward direction.

Reason: The right hand side has fewer gas particles, so to reduce the effect of the increased pressure, the reaction should proceed toward the direction with fewer gas particles.

(ii) No effect.

Reason: The reaction has the same number of gas particles in both direction and therefore it is not accompanied with change in pressure.

(iii) No effect.

Reason: The reaction has the same number of gas particles in both direction and therefore it is not accompanied with change in pressure.

(c)

(i) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

(ii) $Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2\times10^{-2}}{V}\right)^2}{\left(\frac{1\times10^{-2}}{V}\right)\left(\frac{3\times10^{-2}}{V}\right)} = 1.33$

The value of reaction quotient is 1.33.

(iii) The reaction will proceed to the right of the equation to reach the equilibrium.

Reason: the calculated value of reaction quotient (Q =1.33) is smaller than the given value of equilibrium constant ($K_c = 50.5$).

(iv) No effect.

Reason: The reaction has the same number of gas particles in both direction and therefore it is not accompanied with change in pressure.

(d) Using $K_p = K_c(RT)^{n-m}$

Where number of gas particles in the reactants side is equal to that of products side; that is $m = n = 2$

Thus $K_p = K_c(RT)^{2-2}$ or $K_p = K_c$

Hence the value of K_p is 10.

Question 9

(a)

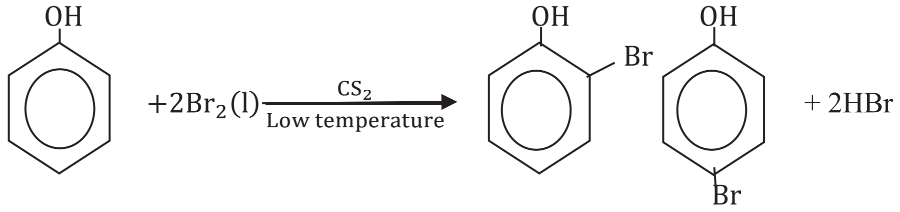
(i) 1,1,1-trichloroethane

(ii) 1,1,22,33-hexachloropropane

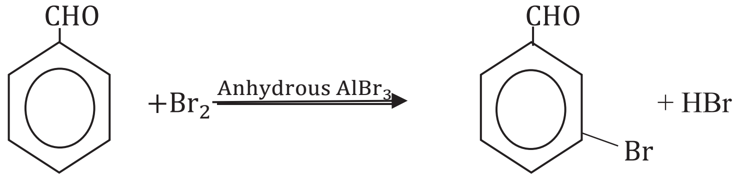
(iii) 1-bromo-4-chlorobenzene

(iv) 1,1,1,3,3,3-hexachloropropane

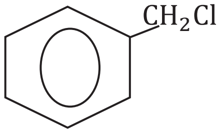
(i) Hydroxyl group in phenol is ortho-para director, so it will direct the Br atom at ortho and para position as per the following equation:



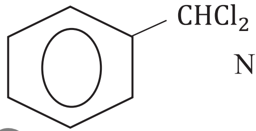
(ii) Carbonyl group in benzene carbaldehyde is meta director, directing the Br atom at meta position as per the following equation:



(c)

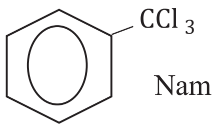


Name: (1-chloromethyl)benzene

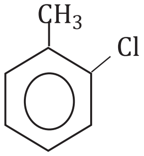


Name: (1,1-dichloromethyl)benzene

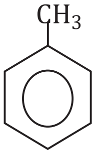
(b)



Name: (1,1,1-trichloromethyl)benzene



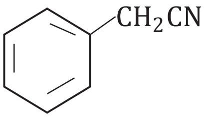
Name: 2-chlorotoluene (or o-chlorotoluene)



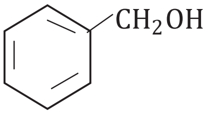
Name: 4-chlorotoluene (or p-chlorotoluene)

(c)

(i)



(ii)



(d)

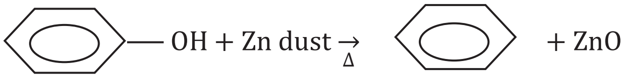
(i) **Sodium hydroxide followed by silver nitrate solution test:** With solution of sodium hydroxide followed by an addition of silver nitrate solution at room temperature, 1-chloro-1,1-diphenylmethane (the later) gives white precipitate of silver chloride while bromobenzene (the former) does not.

(ii) **Liquid bromine test:** With liquid bromine under presence of anhydrous aluminium bromide, chlorobenzene decolourise reddish-brown colouration of bromine while vinyl bromide does not.

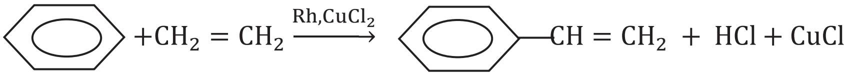
(e)

(i)

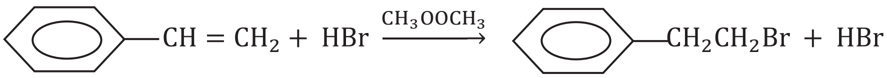
Step 1: Converting phenol into benzene



Step 2: Converting benzene into vinylbenzene

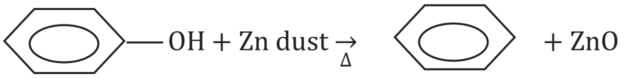


Step 3: Anti-Markonikoff's addition of vinylbenzene

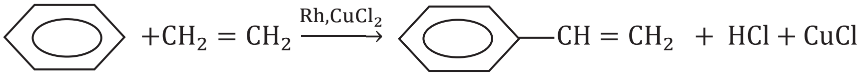


(ii)

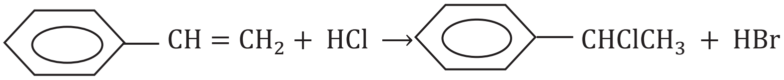
Step 1: Converting phenol into benzene



Step 2: Converting benzene into vinylbenzene



Step 3: Markonikoff's addition of vinylbenzene



Question 10

(a) **For Boyles's law:**

From ideal gas equation: $PV = nRT$

For fixed mass of a gas, n is constant

So if T (temperature) is constant, nRT must be also constant.

Thus $PV = \text{constant}$ or $V = \frac{\text{constant}}{P}$

And hence $V \propto \frac{1}{P}$ which is equivalent to Boyle's law and states that: The volume of fixed mass of a gas varies inversely proportional to its pressure at constant temperature.

For Charles's law:

From ideal gas equation: $PV = nRT$

For fixed mass of a gas, number of moles, n is constant

So if P (pressure) is constant, $\frac{nR}{P}$ must be also constant

Thus from $PV = nRT$ or $V = \left(\frac{nR}{P}\right)T$ but $\frac{nR}{P}$ constant

Then $V = \text{constant} \times T$ or $V \propto T$ which is equivalent to Charles's law and it states that: The volume of fixed mass of a gas varies directly proportional to its absolute temperature at constant pressure.

(b)

(i) No; the gas will not occupy zero volume.

Reason: As temperature decreases, strength of intermolecular forces between gas particles increases and consequently gases becomes liquefied before reaching $-273.15°C$.

(ii) Both have the same kinetic energy.

Reason: Kinetic energy of gas depends only upon temperature. (So at any given temperature different gas molecules have the same kinetic energy regardless to their molecular masses).

(c)

(i) At room temperature, liquid ammonia is very volatile due to its high vapour pressure. To decrease its volatility, the temperature is lowered so that ammonia remains in the liquid state even after opening the bottle.

(ii) Due to higher temperature found in summer, speed of gas molecules inside the tyre increases which in turn increases pressure in the tyre in accordance to Gay Lussac's law. So to avoid bursting of the tyre, it should be inflated at lower temperature.

(d)

(i) But from ideal gas equation: $P_TV = n_TRT$

From which $n_T = \frac{P_TV}{RT} = \frac{786\times1}{760\times0.0821\times298}\text{mol} = 0.0423\text{mol}$

But $n_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{0.925}{28}\text{mol} = 0.033\text{mol}$

Then $X_{N_2} = \frac{n_{N_2}}{n_T} = \frac{0.033\text{mol}}{0.0423\text{mol}} = 0.78$

The mole fraction is 0.78

(ii) Then $P_{N_2} = X_{N_2}P_T = 0.78 \times 786\text{mmHg} = 613\text{mmHg}$

The partial pressure is 613mmHg.

(e) From Grahm's law of diffusion: $\frac{t_Z}{t_{O_2}} = \sqrt{\frac{M_Z}{M_{O_2}}}$

Or $M_Z = 32\text{g/mol} \times \left(\frac{177}{250}\right)^2 = 16\text{g/mol}$

The relative molecular mass of gas Z is 16.

Solutions Necta 2021
CHEMISTRY 2

Answer **five (5)** questions

Question 1

(a)

(i) Electrolytic cell is a device which uses electricity to produce non – spontaneous redox reaction while galvanic cell is a device which uses spontaneous redox reaction to produce electricity.

(ii) Only metals with less negative or more positive electrode potential than lead, are less reactive (than lead) and therefore they will be displaced by lead resulting to the coating of the metal the lead rod. Thus for given solutions, copper and silver having larger electrode potential; only in $AgNO_3$ and $CuSO_4$ solution, the coating will be observed according to the following equations:

$$Pb(s) + AgNO_3(aq) \longrightarrow PbNO_3(aq) + Ag(s) \ldots\ldots \text{silver coating on lead rod}$$
$$Pb(s) + CuSO_4(aq) \longrightarrow PbSO_4(aq) + Cu(s) \ldots\ldots \text{copper coating on lead rod}$$

While:

$$Pb(s) + FeSO_4(aq) \longrightarrow \text{No reaction} \ldots\ldots\ldots \text{no coating}$$
$$Pb(s) + ZnSO_4(aq) \longrightarrow \text{No reaction} \ldots\ldots\ldots \text{no coating}$$

(b) At infinite dilution, the dissociation of the electrolyte is complete with ions possessing limiting molar conductivity, and hence each ion makes definite contribution to the molar conductivity of the electrolyte irrespective of the nature of other ions associated with it.

(c) Cell diagram corresponding to the given cell reaction is as follows: $Zn\,|\,Zn^{2+}(aq)||Cu^{2+}(aq)\,|\,Cu(s)$

Anode reaction (oxidation half reaction)

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e$$

From which; $n = 2$ and $R_Q = \frac{1}{[Zn^{2+}(aq)]}$

And $E_{Anode} = E^{\theta}_{Anode} - \frac{RT}{nF}\ln\frac{1}{[Zn^{2+}(aq)]}$ (From Nernst equation)

Cathode reaction (reduction half reaction)

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$$

From which $n = 2$ and $R_Q = \frac{1}{[Cu^{2+}(aq)]}$

And $E_{Cathode} = E^{\theta}_{Cathode} - \frac{RT}{nF}\ln\frac{1}{[Cu^{2+}(aq)]}$ (From Nernst equation)

But cell potential, $E = E_{Cathode} - E_{Anode}$

Thus $E = \left(E^{\theta}_{Cathode} - \frac{RT}{nF}\ln\frac{1}{[Cu^{2+}(aq)]}\right) - \left(E^{\theta}_{Anode} - \frac{RT}{nF}\ln\frac{1}{[Zn^{2+}(aq)]}\right)$

$$= \left(E^{\theta}_{Cathode} - E^{\theta}_{Anode}\right) + \left(\frac{RT}{nF}\ln\frac{1}{[Zn^{2+}(aq)]}\right) - \left(\frac{RT}{nF}\ln\frac{1}{[Cu^{2+}(aq)]}\right)$$

$$= \left(E^{\theta}_{Cathode} - E^{\theta}_{Anode}\right) + \frac{RT}{nF}\left(\ln\frac{1}{[Zn^{2+}(aq)]} - \ln\frac{1}{[Cu^{2+}(aq)]}\right)$$

$$= \left(E^{\theta}_{Cathode} - E^{\theta}_{Anode}\right) - \frac{RT}{nF}\left(\ln\frac{1}{[Cu^{2+}(aq)]} - \ln\frac{1}{[Zn^{2+}(aq)]}\right)$$

$$= \left(E^{\theta}_{Cathode} - E^{\theta}_{Anode}\right) - \frac{RT}{nF}\ln\left(\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}\right)$$

Where $E^{\theta}_{Cathode} - E^{\theta}_{Anode} = E^{\theta}_{cell}$, $R = 8.31JK^{-}mol^{-}, T = 298K, F = 96500C, n = 2$ and $\ln = 2.303\log$

Substituting $E = E^{\theta}_{cell} - \frac{2.303 \times 8.31 \times 298}{2 \times 96500} \log\left(\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}\right)$ gives;

$$E = E^{\theta}_{cell} - 0.0295\log\left(\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}\right)$$

Hence the cell potential is given by; $E = E^{\theta}_{cell} - 0.0295\log\left(\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}\right)$

(d)

(i) Zinc having more negative electrode potential, it is an anode of the galvanic cell while lead is cathode.

Anode reaction:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e$$

Cathode reaction:

$$Pb^{2+}(aq) + 2e \longrightarrow Pb(s)$$

(ii) Cell notation: $Zn \mid Zn^{2+}(0.1M) \| Pb^{2+}(0.02M) \mid Pb(s)$

(iii) Cell reaction:

$$Zn(s) + Pb^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Pb(s)$$

From which $n = 2$ and $R_Q = \frac{[Zn^{2+}]}{[Pb^{2+}]} = \frac{0.1M}{0.02M} = 5$

And $E^{\theta}_{cell} = E^{\theta}_{cathode} - E^{\theta}_{anode} = -0.13V - (-0.76V) = 0.63V$

From Nernst equation: $E_{cell} = E^{\theta}_{cell} - \frac{0.0591}{n}\log R_Q$

Substituting $E_{cell} = 0.63 - \frac{0.0591}{2}\log 5 = 0.6093V$

Hence the e.m.f of the cell is 0.6093V

Question 2

(a) $K_d = \frac{\text{Concentration of the solute in the first solvent}}{\text{Concentration of the solute in the second solvent}}$

Where K_d is distribution constant.

(b) $K_d = \frac{\text{Concentration of P in ethoxyethane}}{\text{Concentration of P in water}}$

(i) Let mass of A extracted in grams be x

Then: $4 = \frac{x/50}{2-x/50} = \frac{x}{2-x}$

$5x = 8, x = 1.6g$ g

Mass of A extracted by $50cm^3$ of ethoxyethane is 1.6g.

(ii) Let mass of A extracted in the first extraction be m_1

Then $4 = \frac{m_1/25}{2-m_1/50} = \frac{2m_1}{2-m_1}$

$6m_1 = 8, m_1 = 1.33g$

Mass of P remained after the first extraction = $2 - m_1 = (2 - 1.33)\,g = 0.67g$

Let mass of A extracted in the second extraction be m_2

Then $4 = \frac{m_2/25}{0.67-m_2/50} = \frac{2m_2}{0.67-m_2}$

$6m_2 = 2.68, m_2 = 0.45g$

Total mass extracted = $m_1 + m_2 = (1.33 + 0.45)\,g = 1.78g$

Hence mass of A extracted by two successive portions of $25\ cm^3$ of ethoxyethane is 1.78g.

(c) The greater amount of P is extracted when the volume of extracted solvent is divided into small portions (in (ii)) rather than using the whole volume at once (in (i)).

(d) Using; $K_d = \frac{\text{Mass concentration of G in pentan-1-ol (in gdm}^{-3})}{\text{Mass concentration of G in aqueous solution (in gdm}^{-3})}$

Where: Mass concentration of G in pentan-1-ol $= \frac{\text{mass of G}}{v_{Soln}\text{ in dm}^3}$

But $V_{Soln} = 100\text{ cm}^3 = \frac{100}{1000}\text{dm}^3 = 0.1\text{dm}^3$

The mass concentration of G in pentan-1-ol $= \frac{1.5\text{g}}{0.1\text{dm}^3} = 15\text{gdm}^{-3}$

Original mass of G in 500cm^3 of aqueous solution$= \frac{500}{1000} \times 4\text{g} = 2\text{g}$

Then mass of G in 500cm^3 of aqueous solution after extraction $= (2 - 1.5)\text{g} = 0.5\text{g}$

Mass concentration of G in aqueous solution $= \frac{0.5\text{g}}{0.5\text{dm}^3} = 1\text{gdm}^{-3}$

Substituting:

$$K_d = \frac{15\text{gdm}^{-3}}{1\text{gdm}^{-3}} = 15$$

(i) The partition coefficient of the solute G between pentan-1-ol and water is 15.

Let mass (in grams) of G remained in the aqueous solution be x

Then mass of G which will be extracted in the propan-1-ol will be $0.5 - x$

$$\text{Then } K_d = 15 = \frac{\frac{(0.5 - x)\text{g}}{0.1\text{dm}^3}}{\frac{x\text{g}}{0.5\text{dm}^3}} = \frac{5(0.5 - x)}{x}$$

From which; $20x = 2.5; x = 0.125\text{g}$

(ii) The mass of G remained in aqueous layer after further extraction is 0.125g.

Question 3

(a)

(i) For AgCl

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

From which $K_{sp} = [Ag^+][Cl^-]$ or $[Ag^+] = \frac{K_{sp}}{[Cl^-]}$

Thus minimum $[Ag^+]$ required to precipitate AgCl $= \frac{2.72\times10^{-10}}{0.1}\text{M} = 2.72 \times 10^{-9}\text{M}$

For Ag_2CrO_4

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

From which $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$ or $[Ag^+] = \sqrt{\frac{K_{sp}}{[CrO_4^{2-}]}}$

Thus minimum $[Ag^+]$ required to precipitate $Ag_2CrO_4 = \sqrt{\frac{2.4\times10^{-12}}{0.01}}\text{M} = 1.55 \times 10^{-5}\text{M}$

Therefore AgCl will precipitate first because it requires lower concentration of Ag^+ ions. On addition of silver ions (from silver nitrate solution), AgCl starts precipitating when silver ion concentration reaches 2.72×10^{-9}M while until concentration of silver ions reaches up to 1.55×10^{-4} M, Ag_2CrO_4 will also starts precipitating.

(ii) Remaining concentration of Cl^- when Ag_2CrO_4 starts precipitating

$$= \frac{K_{sp}\text{ of AgCl}}{[Ag^+]\text{ when }Ag_2CrO_4\text{ starts precipitating}} = \frac{2.72 \times 10^{-10}}{1.55 \times 10^{-5}} = 1.75 \times 10^{-5}\text{M}$$

Hence the concentration of the ion that will precipitate first (Cl^-) at the time CrO_4^{2-} start to precipitate was 1.75×10^{-5}M.

(b) If S represents solubility of Ag_2CrO_4 in mol/L, then:

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

$$\text{From which } K_{sp} = \underset{2S}{[Ag^+]^2}\underset{S}{[CrO_4^{2-}]} = (2S)^2 \times S = 4S^3$$

$$S = \sqrt[3]{\frac{1.3 \times 10^{-11}(\text{mol/L})^3}{4}} = 1.48 \times 10^{-4}\ \text{mol/L}$$

But molar mass of $Ag_2CrO_4 = \big((2 \times 108) + 52 + (4 \times 16)\big)\text{g/mol} = 332\text{g/mol}$

Thus the solubility of $Ag_2CrO_4 = 1.48 \times 10^{-4}\ \text{mol/L} \times 332\text{g/mol} = 0.049\text{g/L}$

Hence the solubility is 0.049g/L.

(c) AgCl being sparingly soluble electrolyte;

molar conductivity of its saturated solution = molar conductivity at infinite dilution

Thus molar conductivity of its saturated solution was also $120\Omega^{-1}\text{cm}^2\text{mol}^{-1}$

Using $V = \frac{\Lambda_m}{\kappa} = \frac{120\Omega^{-1}\text{cm}^2\text{mol}^{-1}}{1.32\times10^{-6}\Omega^{-1}\text{cm}^{-1}} = 9.09 \times 10^7\text{cm}^3\text{mol}^{-1} = 9.09 \times 10^4\text{dm}^3\text{mol}^{-1}$

Then molar solubility of AgCl $= \frac{1}{9.09\times10^4\text{dm}^3\text{mol}^{-1}} = 1.1 \times 10^{-5}\text{moldm}^{-3}$

(i) But molar mass of AgCl $= (108 + 35.5)\text{g} = 143.5\text{g}$

Thus mass solubility of AgCl $= 1.1 \times 10^{-5}\text{moldm}^{-3} \times 143.5\text{g/mol} = 1.58 \times 10^{-3}\text{g/L}$

Hence the solubility of AgCl is $1.58 \times 10^{-3}\text{g/L}$

(ii) If S represents molar solubility of AgCl, then:

$$AgCl(s) \rightleftharpoons \underset{S}{Ag^+(aq)} + \underset{S}{Cl^-(aq)}$$

From which;

$$K_{sp} = [Ag^+][Cl^-] = S \times S = S^2 = (1.1 \times 10^{-5}\text{moldm}^{-3})^2$$
$$= 1.21 \times 10^{-10}(\text{moldm}^{-3})^2$$

Hence the solubility product is $1.21 \times 10^{-10}(\text{moldm}^{-3})^2$

Question 4

(a)

(i) Ions of different atoms have different number of protons. So with the same number of electrons (the same electronic configuration), different number of protons means different ionic charges whereby ions with higher ionic charge have stronger nuclear attractive force per electron leading to smaller ionic radius.

(ii) At ordinary temperature, PCl_5 exists in ionic form as $[PCl_4]^+[PCl_6]^-$; so there is strong electrostatic force of attraction between cation and anion and not weaker Van-der-Waals force of attraction between covalent bonded molecules of PCl_5 as expected.

(iii) Covalent characters and hence ability to undergo hydrolysis of chlorides of period three increases as you across the period (from left to right). Na being on the left of the period, its chloride is strongly ionic as result of its lower degree of polarization which is brought about by weaker polarising power of larger sized and lower charged Na^+ than Al^{3+}in $AlCl_3$ which is more covalent in characters.

(iv) With electronic configuration $[Ne]3s^2$ and $[Ne]3s^2 3p_x^1$ for magnesium and aluminium respectively, the first ionisation energy of magnesium is larger due to:

- Shorter distance of the most loosely electron in Mg from the nucleus.
- More stable electronic configuration of Mg.
- Weaker screening effect experiencing the most loosely electron in Mg.

(v) Lithium being on the top of the group IA its ion has greater degree of hydration in aqueous solution as result of its smaller cationic radius thus lowering its mobility as the ions become heavy and hence Li^+ ions are not free to move in aqueous solution which account for its poor conduction of electricity.

(vi) Oxygen being above sulphur in group IV, has higher electronegativity and therefore there is strong intermolecular hydrogen bonding existing between water molecules resulting to higher boiling point of water than that of hydrogen sulphur which has Van-der-Waals dispersion forces.

(b)

(i) The factors are:

- Periodicity of outermost electronic configuration of elements and
- Periodicity of properties of elements.

(ii) Eight electrons in the third period corresponds to the filling of electrons in one 3s orbital and three 3p orbitals. To have eighteen electrons, extra ten electrons should be added in the five 3d orbitals which would against Aufbau principle as according to the principle, after 3p sub-shell, the next sub-shell is 4s sub-shell of the fourth period.

(c)

(i) Ammonia is capable of making intermolecular hydrogen bonding between its molecules which is stronger intermolecular forces than Van-der-Waals intermolecular forces present in phosphine.

(ii) Unlike phosphine, ammonia is capable of making intermolecular hydrogen bonding with water molecules.

(d) As you go across the period and down the group in adjacent groups and periods, there is a cancellation of changes of general periodic properties. This makes elements in those positions to have similar polarising power, similar atomic radius, similar electronegativity values, similar effective nuclear charge and hence exhibiting diagonal relationship. Example of pair of elements which shows diagonal relationship is lithium and magnesium. Another example is beryllium and aluminium.

Question 5

(a)

(i) $CH_3CH_2CH_2OH + HBr \xrightarrow{\text{Reflux}} CH_3CH_2CH_2Br + H_2O$

1-bromopropane

(ii) $CH_3CH_2CH_2OH + H_2SO_4(\text{limited}) \longrightarrow CH_3CH_2CH_2OCH_2CH_2CH_3 + H_2O$

Propoxypropane

(iii) $CH_3CH_2CH_2OH + KMnO_4 \overset{H^+}{\rightarrow} CH_3CH_2COOH$

Propanoic acid

(iv) $CH_3CH_2CH_2OH + CH_3COOH \xrightarrow{H_2SO_4(\text{conc})} CH_3COOCH_2CH_2CH_3 + H_2O$

Propyl ethanoate

(v) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$

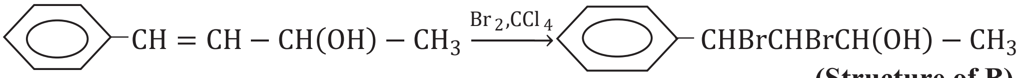
1-chloropropane

(b)

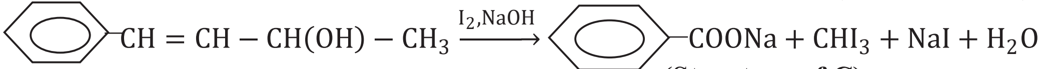
- With more than six carbons in its molecular formula, A may be aromatic compound.
- Since the compound has only one oxygen in its formula; it may be alcohol, ether or carbonyl compound.
- Since the compound gave off oxygen with sodium metal, it cannot be alcohol or carbonyl compound. Thus compound A must be alcohol.
- Since the compound decolourises bromine under presence of carbon tetrachloride, there is double bond in A. Thus A is unsaturated alcohol with double bond.
- Since A gives iodoform with mixture of iodine and sodium hydroxide, there is CH_3 group bonded to carbon with OH group in A. Thus A must be unsaturated secondary alcohol with CH_3CH-OH group.

– With above information and given molecular formulae, structure of A must be as follows:

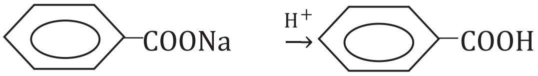
(Structure of A)



(Structure of B)



(Structure of C)



(Structure of D)

Question 6

(a)

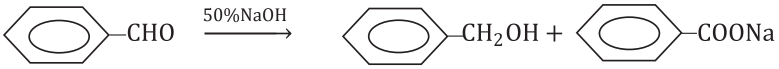
(i) By using silver mirror test: With Tollen's reagent, propanal gives positive test by giving silver deposit which appears as silver mirror while propanone does not.
That is; $CH_3CH_2CHO + 2[Ag(NH_3)_2]NO_3 + H_2O \rightarrow CH_3CH_2COONH_4 + 2Ag + 3NH_3 + 2HNO_3$
While; $CH_3COCH_3 \ + \ \text{Tollen's reagent} \ \rightarrow \ \text{No reaction (gives negative test)}$

(ii) By using Fehling's solution test: With Fehling's solution, ethanol gives positive test by producing brick-red precipitate of copper (I) oxide while benzaldehyde does not.
That is; $CH_3CHO + 2Cu^{2+} + 4OH^- \rightarrow CH_3COOH + Cu_2O + 2H_2O$
While, $C_6H_5CHO + 2Cu^{2+} + 4OH^- \rightarrow$ No reaction (negative test)

(iii) By using silver mirror test: With Tollen's reagent, pentanal gives positive test by giving silver deposit which appears as silver mirror while pentan-2-one does not.
That is;
$$CH_3CH_2CH_2CH_2CHO + 2[Ag(NH_3)_2]NO_3 + H_2O \rightarrow CH_3CH_2CH_2CH_2COONH_4 + 2Ag + 3NH_3 + 2HNO_3$$
While; $CH_3COCH_2CH_2CH_3 \ + \ \text{Tollen's reagent} \ \rightarrow \ \text{No reaction (gives negative test)}$

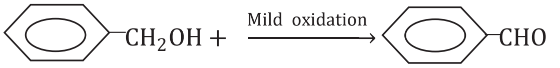
(iv) By using iodoform test: With mixture of iodine and sodium hydroxide, 2-pentanone gives positive test by producing yellow precipitate of iodoform while 3-pentanone does not.
That is; $CH_3CH_2CH_2COCH_3 + I_2 \xrightarrow{NaOH(aq)} CHI_3 + CH_3CH_2CH_2COONa + NaI + H_2O$
While; $CH_3CH_2COCH_2CH_3 + I_2 \xrightarrow{NaOH(aq)}$ No reaction (negative test)

(b)

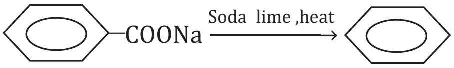


(Cannizaro reaction)

Strucure of A **Strucure of B** **Structure of C**



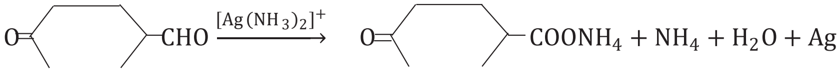
Strucure of A **Strucure of B**



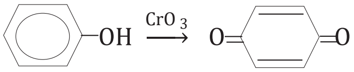
Strucure of C **Strucure of D**

(c)

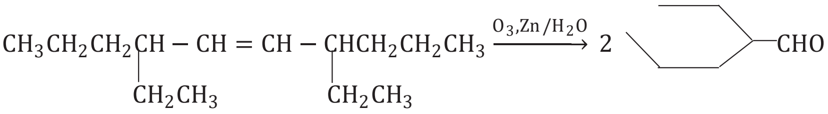
(i)



(i)

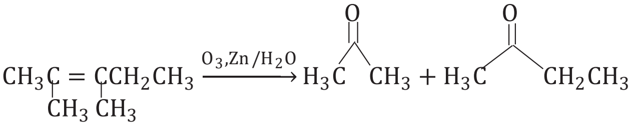


(ii)



$CH_3CH_2CH_2\underset{\displaystyle CH_2CH_3}{CH} - CH = CH - \underset{\displaystyle CH_2CH_3}{C}HCH_2CH_2CH_3 \xrightarrow{O_3,Zn/H_2O} 2$

(iii)



$CH_3\underset{\displaystyle CH_3}{C} = \underset{\displaystyle CH_3}{C}CH_2CH_3 \xrightarrow{O_3,Zn/H_2O} H_3C\overset{\displaystyle O}{\overset{\|}{C}}CH_3 + H_3C\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$

Solutions Necta 2022

CHEMISTRY 1

SECTION A

Answer **all** questions in this section.

Question 1

(a)

(i) $\Delta E = E_3 - E_1 = \frac{-1.312\times10^6}{3^2}\text{J/mol} - \frac{-1.312\times10^6}{1^2}\text{J/mol} = 1.166\times10^6\text{J/mol}$

Thus to promote one mole of electrons $(6.02\times10^{23}\text{electrons})$, $1.166\times10^6\text{J}$ is required.

So energy required for an (one) electron

$$= \frac{1.166\times10^6\text{J/mol}}{6.02\times10^{23}\text{electron/mol}} = 1.937\times10^{-18}\text{J/electron}$$

Hence the amount of energy required is $1.937\times10^{-18}\text{J}$

(ii) This is because at ground state, an electron is attracted toward the nucleus and therefore making the energy of the electron to be negative.

(b)

(i) For neutral atom: total number of electrons is equal to atomic number of the atom.

X has a total of 18 electrons. So its atomic number is 16 and hence it is argon (Ar).

Y has a total of 12 electrons. So its atomic number is 12 and hence it is magnesium (Mg).

Z has a total of 19 electrons. So its number is 19 and hence it is potassium (K).

Element	First ionization energy	Atomic radius
Argon	1500kJ/mol	0.94A°
Magnesium	740kJ/mol	1.6A°
Potassium	420kJ/mol	1.97A°

(ii) Using $E = hf = 6.626\times10^{-34}\text{Js}\times3\times10^8/\text{s} = 1.9878\times10^{-25}\text{J}$

The energy of the photon is $1.9878\times10^{-25}\text{J}$

(c)

(i) Continuous spectrum is the arrangement of all possible radiation of all frequencies over a wide range of frequencies with no clear cut way between one radiation and other while line spectrum consists of separate lines with clear cut separating radiations.

(ii) Absorption spectrum are formed when substances are made to absorb radiation during excitation of electrons while emission spectra are obtained from substances causing them to emit radiation during de-excitation of electrons.

Question 2

(a)

Change	**H_2**	**Br_2**	**HBr**	**K_c value**
Addition of some H_2	Increase	Decrease	Increase	No change
Removal of some HBr	Decrease	Decrease	Decrease	No change
Rise in temperature	Increase	Increase	Decrease	Decrease
Increase in pressure	No change	No change	No change	No change

(b) $K_p = \frac{(P_{NOCl})^2}{(P_{NO})^2(P_{Cl_2})} = \frac{(12\text{atm})^2}{(5\times10^{-2}\text{atm})^2(3\times10^{-1}\text{atm})} = 192000\text{atm}^{-1}$

Thus K_p is 192000atm^{-1}

Question 3

(a)

(i) Relative lowering of vapour pressure $= \frac{\Delta P}{P^o_{sv}} = \frac{0.061\text{mmHg}}{17.5\text{mmHg}} = 0.003486$

The relative lowering of vapour pressure is approximately 0.0035

(ii) $P_{soln} = P^o_{sv} - \Delta P = 17.5\text{mmHg} - 0.061\text{mmHg} = 17.439\text{mmHg}$

The vapour pressure of the solution is 17.439mmHg

(iii) $X_{su} = $ Relative lowering of vapour pressure $= 0.0035$

But $X_{sv} = 1 - X_{su} = 1 - 0.0035 = 0.9965$

Mole fraction of sugar (solute) is 0.0035

Mole fraction of water (solvent) is 0.9965

(b) From $\Delta T = K_f \times m = \frac{K_f \times m_{su}}{M_{su} \times m_{sv} \text{ in kg}}$;

$$M_{su} = \frac{K_f \times m_{su}}{\Delta T \times m_{sv} \text{ in kg}} = \frac{3.9°\text{Ckg/mol} \times 2.5\text{g}}{(16.63 - 14.48)°\text{C} \times 0.04\text{kg}} = 113\text{g/mol}$$

Hence the relative molecular mass of the compound is 113.

(c) Using $\Delta T = K_f m$ or $m = \frac{\Delta T}{K_f}$

But freezing point of pure water is 273K

And freezing point of the solution is 272.07K

And thus $\Delta T = (273 - 272.07)\text{K} = 0.93\text{K}$

Then $m = \frac{0.93\text{K}}{1.86\text{Kkgmol}^{-1}} = 0.5\text{mol/kg}$

The molality is $\mathbf{0.5mol/kg}$

Then using $\Delta T = K_b m$;

Substituting $\Delta T = K_b m = 0.512\text{Kkgmol}^{-1} \times 0.5\text{mol/kg} = 0.256\text{K}$

But boiling point of pure water is 373K.

Thus boiling point of the solution= $(373 + 0.256)\text{K} = 373.256\text{K}$

Hence the boiling point is 373.256K.

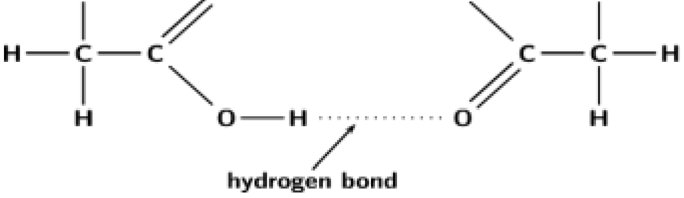
Question 4

(a)

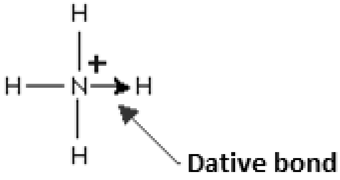
(i)

Cation/anion	Ionic radius(nm)	Chemical bond
C^{4+}	0.015	Covalent
I^-	0.216	Covalent
Na^+	0.095	Ionic
F^-	0.136	Ionic

(ii) Intermolecular hydrogen bonding occur when partially positively charged hydrogen in one molecule attracts lone pair of strong electronegative atom (mainly F, O or N) in neighbor molecule. For example, different molecules of ethanoic acid are held together by hydrogen bonding.



On another hand, dative bond is formed when one atom with lone pair donate all two electrons to be shared in covalent bond formation with another atom with empty orbital. For example, during the formation of ammonium ion from ammonia and hydrogen ion, the fourth bond is dative bond.



(b)

(i) Among the given three elements, fluorine has highest electronegativity which makes hydrogen bonded to it to have highest partial positive charge to enable hydrogen bond formation.

(ii) Hydrogen chloride is polar molecule, so their molecules exhibit permanent dipole-dipole interactions. But when they are mixed with argon which is non-polar, these permanent dipole distort arrangement of electrons around argon leading to the formation of induced dipole interactions.

(c)

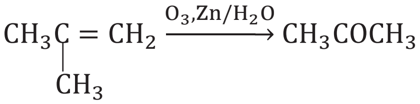
(i) sp^2 hybridisation is formed when one s-orbital is mixed with two p-orbitals to give three sp^2 hybrid orbitals in trigonal planar arrangement while sp hybridisation is formed when one s-orbital is mixed with one p-orbital to give two sp hybrid orbitals in linear arrangement.

(ii) Between $C \equiv O$ and $C = O$, $C \equiv O$ is stronger.
Reason: the triple bond in $C \equiv O$ has greater number of electron pairs and it is shorter than $C = O$.
Between $C - N$ and $C - O$, $C - O$ is stronger.
Reason: O in $C - O$ has smaller atomic radius than N in $C - N$.
Between $C - C$ and $C = C$; $C = C$ is stronger.
Reason: the double bond in $C = C$ has greater number of electron pairs and it is shorter than $C - C$.

Question 5

(a)

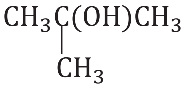
(i) $CH_3CH = CH_2 \xrightarrow{KMnO_4(Dilute),KOH(aq),cold} CH_3CH(OH)CH_2\ (OH)$

(ii) 
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2 \xrightarrow{O_3,Zn/H_2O} CH_3COCH_3$

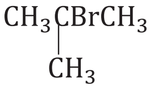
(iii) $CH_3CH_2CH_3 \xrightarrow{Br_2,UV} CH_3CHBrCH_3 \xrightarrow{KOH(conc),C_2H_5OH,\Delta}) CH_3CH = CH_2 \xrightarrow{O_3,H_2O} CH_3COOH$
$\xrightarrow{LiAlH_4} CH_3CH_2OH$

(iv) $CaC_2 \xrightarrow{H_2O,\Delta} CH \equiv CH$

(b) Product for each of the given reaction is as follows:

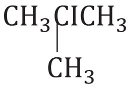
(i) 
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)CH_3$

(ii)



$CH_3C(CH_3)BrCH_3$

(iii)



$CH_3C(CH_3)ICH_3$

(c) To prepare asymmetrical alkane by Wurtz reaction, two different haloalkanes are required. This would give mixture of alkanes whose separation (to get the intended asymmetrical alkane) is difficult due to their similarity in boiling point and physical properties in general. For example, to prepare pentane, one may need ethane and propane which would give three different alkanes according to the following equations:

$$CH_3CH_2Br + CH_3CH_2CH_2Br + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Pentane}}{CH_3CH_2CH_2CH_2CH_3} + 2NaBr$$

$$CH_3CH_2CH_2Br + CH_3CH_2CH_2Br + 2Na \xrightarrow{\text{Dry ether}} CH_3CH_2CH_2CH_2CH_2CH_3 + 2NaBr$$

Hexane

$$CH_3CH_2Br + CH_3CH_2Br + 2Na \xrightarrow{\text{Dry ether}} CH_3CH_2CH_2CH_3 + 2NaBr$$

Butane

Question 6

(a)

(i) Using;

$$\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

$$\Delta H_r^\theta = \Delta H_f^\theta\big(H_2O(g)\big) + \Delta H_f^\theta(CO(g)) - \Delta H_f^\theta(CO_2(g)) - \Delta H_f^\theta(H_2(g))$$

Where $\Delta H_f^\theta\big(H_2(g)\big) = 0$ (heat of formation of an element in its natural state is zero)

Then substituting;

$$\Delta H_r^\theta = \big(-241.8 + (-121.31) - (-393.5)\big)\text{kJ/mol} = +30.39\text{kJ/mol}$$

The enthalpy change for the reaction is $+30.39\text{kJ/mol}$.

(ii)

1. Amount of reactants and products.
2. Physical state of reactants and products.
3. Temperature of the reaction.
4. Specific heat capacity of the container and substances involved in the transformation.

(b) Using $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$

So from equation **D**;

$$\Delta H_c = 2\Delta H_f(CO_2) + \Delta H_f(H_2O) - \Delta H_f(C_2H_2) - \tfrac{5}{2}\Delta H_f(O_2)$$

But $\Delta H_f(O_2) = 0$

Then substituting given values gives: $-1323 = (2 \times -393) + -286 - \Delta H_f(C_2H_2)$

From which $\Delta H_f(C_2H_2) = 251\text{kJ/mol}$

Hence heat of formation of ethyne is $+251$ kJ/mol

Question 7

(a)

1. **Introducing measures of treating sewage before damping them.**
   This will employ chemical treatment methods like redox, hydrolysis, acid-base neutralization, chemical precipitation and incineration to treat hazardous waste.

2. **Encouraging the use of alternative source of energy which are environmental friendly.**
   This will involve introduction of measures which will reduce the use of conventional fuel like gasoline and diesel while expanding the utilization of better options sources of energy like solar energy and compressed natural gas.
3. **Introducing measures which will reduce the use of agricultural chemicals.**
   This will include encouraging the use of organic manures while discouraging the use of inorganic fertilizers. Also less needed or harmful pesticides and insecticides will be restricted.
4. **Introducing measures which will reduce the use of chlorofluorocarbons (CFCs).**
   This will involve the use of less harmful substitutes of these CFCs like hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs).

(b)

1. **Burning of fossil fuels**
   Burning fuels in vehicles and other related machines like generator produce carbon dioxide gas.
   $$C_xH_y(\text{Fossil fuel}) + O_2 \longrightarrow CO_2 + H_2O$$
2. **Deforestation**
   Whether through cutting or burning trees, deforestation disturb ecological balance leading to more carbon dioxide in the atmosphere. Burning trees for example, produce carbon dioxide according to the following equation:
   $$CH_2O(\text{tree}) + O_2 \longrightarrow CO_2 + H_2O$$

(c) The four reactions are:

1. $SO_2 + H_2O \rightarrow H_2SO_3$
2. $2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$
3. $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$
4. $CO_2 + H_2O \rightarrow H_2CO_3$

Question 8

(a)

(i) Not applicable.
Explanation:
Pumping air into a ball, increases mass (number of moles) of air (gas) in the container and hence high pressure. This is against Boyle's law which needs amount of the air to be fixed which in turn would lead to decrease in pressure as volume increases.

(ii) Reason: So that they can float in the air.
Explanation:
According to Charles's law; hot air inside the balloon has larger volume than cold air outside the balloon and therefore it has lower density than the air outside and hence the balloon floats.

(iii) To be true, Dalton's law of partial pressure requires the gases not to react. SO_2 and O_2 react to give SO_3 and hence their mixture will not obey Dalton's law of partial pressure.

(iv) The observed (real) pressure of the gas would be smaller than the ideal pressure because inelastic collision leads to decrease in speed of gas particles making collision between gas particles and container's wall to be less energetic and less frequent.

(b) From ideal gas equation; $PV = nRT$
From which; $PV = \frac{m}{M_r}RT$ or $\frac{m}{V} = \rho = \frac{PM_r}{RT}$
Then $\frac{\rho_2}{\rho_1} = \frac{P_2M_r}{RT_2} \times \frac{RT_1}{P_1M_r} = \frac{P_2T_1}{P_1T_2}$

Where:

$$\mathrm{T_1 = 27°C = 300K, P_1 = 1520mmHg, \rho_1 = 5.46\times10^{-3}g/cm^3 = 5.46g/dm^3, T_2 = 273K, P_2 = 760mmHg}$$

Substituting $\frac{\rho_2}{5.46\mathrm{g/dm^3}} = \frac{760\mathrm{mmHg}\times300\mathrm{K}}{1520\mathrm{mmHg}\times273\mathrm{K}}$

From which; $\rho_2 = 3\mathrm{g/dm^3}$

The density at **s.t.p** will be $3\mathrm{g/dm^3}$

(c)

(i) From Grahm's law of diffusion: $\frac{R_{O_2}}{R_{CO_2}} = \sqrt{\frac{(R.D)_{CO_2}}{(R.D)_{O_2}}}$

But the rate of diffusion $= \frac{\text{Volume diffused}}{\text{Time taken}}$

Then $\frac{R_{O_2}}{R_{CO_2}} = \frac{V_{O_2}/t_{O_2}}{V_{CO_2}/t_{CO_2}} = \frac{V_{O_2}t_{CO_2}}{V_{CO_2}t_{O_2}} = \sqrt{\frac{(R.D)_{CO_2}}{(R.D)_{O_2}}}$

Substituting $\frac{V_{O_2}\times75}{25\times96} = \sqrt{\frac{22}{16}}$

From which; $V_{O_2} = 37.52\mathrm{cm^3}$

The volume of oxygen gas is $37.52\mathrm{cm^3}$

(ii)

1. In separation of gases with different densities.
2. In determination of densities and molecular masses of unknown gases.

Question 9

(a)

1. **In extraction of metals**
   Metals oxides can be useful as ore or in removing gangue in blast furnace. For example, bauxite is the oxide of aluminium ($Al_2O_3.XH_2O$) is used for extracting aluminium and haematite (Fe_2O_3) for iron. Also CaO is used to eliminate sand, SiO_2 (gangue) as slag.
2. **In soil liming**
   Calcium oxide and magnesium oxide are good liming materials which are used to eliminate excess acid in the soil.
3. **As oxygen source**
   Peroxides especially sodium peroxide is used in confined spaces (for example in emergency breathing devices on submarines) because it absorbs carbon dioxide and liberates oxygen at the same time.
   $$2Na_2O_2(s) + 2CO_2(g) \longrightarrow 2Na_2CO_3(s) + O_2(g)$$
4. **In manufacture of glass**
   Several metals oxides like trilead tetraoxide (Pb_3O_4), manganese (IV) oxide, calcium oxide and sodium oxide are used in the glass industry.
5. **As catalysts**
   Some metal oxides are very useful catalysts for important chemical reactions. As an example, both manganese (IV) oxide and copper (II) oxide may be used to catalyse thermolysis of potassium chlorate to give potassium chloride and oxygen gas.

(b) A gas which forms with lime water is carbon dioxide. Thus **R** is carbon dioxide(CO_2).
Since the carbon dioxide was evolved from the reaction between dilute nitric acid and solid P, there is carbonate ion in **P**.
Brown fumes of gas **T** is nitrogen dioxide confirming that, solution **Q** is nitrate (has nitrate ion as anion).

Formation of brown fumes (nitrogen dioxide) on decomposition of the product suggest that the solid **S** must oxide (if it would partial decomposition that gives nitrite, brown fumes could not be produced).

The metal whose carbonate is green, its nitrate is blue and its oxide is black is copper. So **P** is copper (II) carbonate.

(i) Hence:

P is copper (II) carbonate ($CuCO_3$).

S is copper (II) oxide (CuO)

R is carbon dioxide(CO_2)

T is nitrogen dioxide (NO_2)

(ii) $CuCO_3(s) + 2HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + CO_2(g) + H_2O(l)$

(c)

(i) Lime stone: It is of great importance in different aspects of live, from agriculture where it is used as liming material in the soil, to industries where it has different uses like in the manufacture of glass and even to construction and architecture where it has number of uses including in manufacture of cement.

(ii) Plaster of Paris: It has many uses including in building material as protective coating on the walls and ceiling before painting is done. Also in surgery to maintain joints in a fixed position and in dentistry for taking impressions.

Question 10

(a)

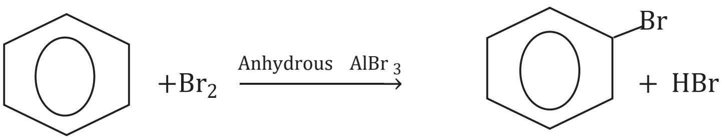
(i) Sulphuric acid is helping the formation of NO_2^+ electrophile which is easy to substitute on benzene.

(ii) The hydroxyl group in hydroxylbenzene is activator, making benzene more reactive toward electrophile.

(iii) Presence of lone pair in chlorine make it capable of stabilizing intermediate carbenium ion when an electrophile is substituted at ortho and para carbons.

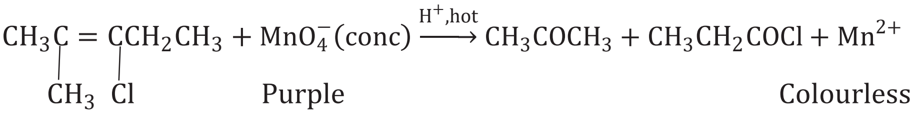
(b)

(i) With liquid bromine under presence $FeBr_3$, benzene ring decolourise reddish-brown colouration the bromine while ethane does not.



While; ethane $+Br_2 \xrightarrow{\text{Anhydrous AlBr}_3}$ No reaction

(i) With hot concentrated solution of acidified potassium permanganate,3-chloro-2-methylpent-2-en decolourises purple colouration of the permanganate while 1-chloropropane does not.



$$\underset{CH_3}{CH_3C} = \underset{Cl}{C}CH_2CH_3 + \underset{\text{Purple}}{MnO_4^-(conc)} \xrightarrow{H^+,hot} CH_3COCH_3 + CH_3CH_2COCl + \underset{\text{Colourless}}{Mn^{2+}}$$

$$CH_3CH_2CH_2Cl + MnO_4^-(conc) \xrightarrow{H^+,hot} \text{No reaction}$$

(ii) With $NaOH(aq)$ at room temperature followed by addition of $AgNO_3(aq)$, bromomethane gives light yellow precipitate of $AgBr$ while bromobenzene does not.

i.e $CH_3Br + NaOH(aq) \xrightarrow[25^\circ C]{} CH_3OH + NaBr$

Then $NaBr + AgNO_3(aq) \rightarrow NaNO_3 + AgBr$

Light yellow precipitate

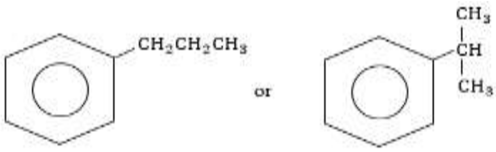
While Bromobenzene + NaOH(aq) $\xrightarrow[25^\circ C]{}$ No reaction

(c)

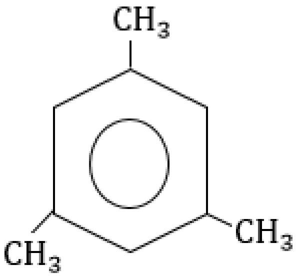
(i) Firstly the intermediate tertiary (3°) carbenium ion, $(CH_3)_3C^+$ formed by $(CH_3)_3CBr$ is more stable than the primary (1°) carbenium ion, $CH_3CH_2^+$ formed by CH_3CH_2Br.
Secondly the three alkyl groups surrounding carbon with Br in $(CH_3)_3CBr$ exert stronger steric hindrance than one alkyl group in CH_3CH_2Br.
The two factors make $(CH_3)_3CBr$ to undergo S_N1 mechanism while CH_3CH_2Br undergoes S_N2.

(ii) In haloalkane, carbon with halogen (in $C - X$ bond) is positively polarized and therefore it becomes good site for nucleophile and hence nucleophilic substitution reaction. In halobenzene, due to involvement of halogen (X) in mesomerism, there is a formation of $C = X$ which is too difficult to break for it undergo nucleophilic substitution reaction like haloalkane. However benzene ring being nucleophilic in nature, it choose the easier option of reacting with electrophile in electrophilic substitution reaction occurring in benzene ring.

(d) Structure of K is;



Structure of L is



Solutions Necta 2022
CHEMISTRY 2

Answer **five (5)** questions

Question 1

(a)

(i) $K_d = \frac{\text{Concentration of } \mathbf{Y} \text{ in benzene}}{\text{Concentration of } \mathbf{Y} \text{ in water}}$

$$= \frac{0.13\text{g}/10\text{cm}^3}{0.22\text{g}/100\text{cm}^3} = 5.9$$

The distribution coefficient of **Y** between benzene and water is 5.9

(ii) **Y** is more soluble in benzene than in water (solubility of **Y** in benzene is 5.9 times its solubility in water).

(b)

(i) 1. **In separation of substances:** Fractional distillation can be used to separate components of mixture. As an example, crude oil is separated to various components (fractions) like paraffin wax, diesel, lubricating oil, gasoline, kerosene and naphtha. Gases such as argon, nitrogen and oxygen can also be extracted (separated) from air by fractional distillation.

2. **In purification of substances:** Fractional distillation can be used to remove unwanted material from a substance so as to get pure form of the substance or the form of which the substance has higher concentration. As an example, water is commonly purified by fractional distillation. Purified or concentrated silicon is also obtained by fractional distillation from chlorosilanes.

(ii) The molar mass of bromobenzene (C_6H_5 Br)is 157g/mol

Let mass percentage of bromobenzene be y

Then mass of water in 100g of the distillate will be (100-y)

So using: $\frac{m_b}{m_{H_2O}} = \frac{P_bM_b}{P_{H_2O}M_{H_2O}}$

$$\frac{y}{100-y} = \frac{1.59\times10^4\times157}{8.5\times10^4\times18} = 1.63$$

$y = 163 - 1.63y$ or $2.63y = 163$; $y = 62$

Hence the percentage by mass of bromobenzene in distillate is 62%

(c) Using; $n = \frac{m}{M_r}$

Number of moles of heptane, $n_H = \frac{26\text{g}}{100\text{gmol}^{-1}} = 0.26\text{mol}$

Number of moles of octane, $n_O = \frac{35\text{g}}{114\text{gmol}^{-1}} = 0.31\text{mol}$

Using; Mole fraction, $X = \frac{n}{n_T}$

$$X_H = \frac{0.26\text{mol}}{(0.26 + 0.31)\text{mol}} = 0.4561$$

And $X_O = 1 - X_O = 1 - 0.4561 = 0.5439$

Since the solution is ideal, it obeys Raoult's law;

Thus $P_{soln} = X_HP_H^o + X_OP_O^o$

Substituting $P_{soln} = (0.4561 \times 105.2)\text{kPa} + (0.5439 \times 46.8)\text{kPa} = 73.4362\text{kPa}$

The vapour pressure of the mixture is approximately 73.4kPa.

Question 2

(a) Water undergo self-ionization according to the following equation:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Where $[OH^-\ ] = [H_3O^+]$

Then $K_w = [OH^-\ ][H_3O^+] = [H_3O^+]^2$ or $[H_3O^+] = \sqrt{K_w}$

And $pH = -\log[H_3O^+] = -\log\sqrt{K_w}$

But at 25°C; $K_w = 1 \times 10^{-14}$

Substituting $pH = -\log\sqrt{1 \times 10^{-14}} = 7$

Hence the pH of pure water at 25°C is 7.

(b) $n_{HCl} = \frac{500}{1000}dm^3 \times 0.1moldm^{-3} = 0.05mol = n_{CH_3COOH}$

Then $[HCl] = \frac{n_{HCl}}{V_{soln}}$; where $V_{soln} = (500 + 500)cm^3 = 1000cm^3 = 1dm^3$

Substituting $[HCl] = \frac{0.05mol}{1dm^3} = 0.05M = [CH_3COOH]$

CH_3COOH being weak acid ionises partially according to the following equation:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

At equilibrium $0.05 - x$ x x

HCl being strong acid ionises completely according to the following equation:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

After ionisation 0 $0.05M$ $0.05M$

Thus in $CH_3COOH|HCl$ mixture:

$[H^+] = (x + 0.05)M \approx 0.05M$ (with equal concentration of CH_3COOH which is weak acid and HCl which is strong acid, amount of H^+ from the weak acid can be neglected).

Thus $pH = -\log[H^+] = -\log 0.05M = 1.3$

Hence the pH of the mixture before addition of NaOH is 1.3.

Using; $n = \frac{m}{M_r}$

Number of moles of NaOH added $= \frac{3g}{40g/mol} = 0.075mol$

NaOH will react with HCl in the mixture according to the following equation:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

From which; mole ratio of NaOH to HCl is 1:1.

Thus NaOH is in excess with $(0.075 - 0.05)mol$ or $0.025mol$ of it remaining unreacted with HCl.

The unreacted NaOH and CH_3COOH reacts according to the following equation:

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

From which; mole ratio is also 1:1

Thus CH_3COOH was in excess with $(0.05 - 0.025)mol$ or $0.025mol$ of it remaining unreacted.

Thus:

Number of moles of CH_3COONa produced (deduced from NaOH, the limiting reactant) was 0.025mol

Number of moles of CH_3COOH unreacted was 0.025mol

The unreacted CH_3COOH and the produced CH_3COONa forms buffer solution whose is given by the following equation:

$pH = pKa + \log\frac{[Salt]}{[Acid]}$ or $pH = pKa + \log\frac{\text{Number of moles of salt}}{\text{Number of moles of acid}}$

Substituting $pH = pKa + \log\frac{0.025mol}{0.025mol} = pKa$

Hence pH of the mixture after addition of NaOH was equal to pKa of acetic acid.

(In this question neither Ka value nor pKa value of acetic acid was given. With practical Ka value of acetic acid which is about 1.8×10^{-5} at 25°C, the numerical answer would be about 4.7).

(c)

(i) Lead (II) chloride which is insoluble in water due to its high lattice energy accompanied with high covalent character. However in concentrated hydrochloric acid, there is enough concentration of Cl^- to form soluble complex with Pb^{2+} and hence $PbCl_2$ appears to dissolve in the concentrated hydrochloric acid .

That is $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ ………… (i)
Insoluble

Then $Pb^{2+}(aq) + 4Cl^-(aq) \rightarrow [PbCl_4]^{2-}(aq)$……......(ii)

Where the formation of the complex in (ii) is equivalent to removal of Pb^{2+} in equilibrium (i) and therefore the position of the equilibrium (i) will shift to the right hand side by dissolving more $PbCl_2$.

(ii) With addition of ammonium hydroxide followed by addition of ammonium chloride, zinc is capable of forming soluble tetrammine complex while aluminium which has smaller ability of forming complex, cannot form similar complex, it only ends forming insoluble aluminium hydroxide.

That is; $Zn^{2+}(aq) + NH_4OH \longrightarrow Zn(OH)_2(s) \downarrow + NH_4^+(aq)$

Then $Zn(OH)_2(s) + NH_4Cl \longrightarrow [Zn(NH_3)_4]^{2+}(aq) + Cl^-(aq) + H_2O(l)$

(d) Let the volume taken for each solution be Vdm^3

Then:

Number of moles of barium nitrate ($Ba(NO_3)_2$) will be $0.025V$ moles

Number of moles of sodium fluoride (NaF) will be $0.01V$ moles

Total volume of the solution mixture will be $V + V = 2Vdm^3$

Since both barium nitrate and sodium fluoride are soluble salts;

$$[Ba^{2+}] = [Ba(NO_3)_2] = \frac{0.025Vmol}{2Vdm^3} = 0.0125moldm^{-3}$$

And $[F^-] = [NaF] = \frac{0.01Vmol}{2Vdm^3} = 0.005moldm^{-3}$

Barium fluoride ionizes according to the following equation:

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$$

From which;

Ionic product, $Q_{sp} = [Ba^{2+}][F^-]^2 = 0.0125moldm^{-3} \times (0.005moldm^{-3})^2 = 3.125 \times 10^{-7}mol^3/dm^9$

But the given K_{sp} value is $1.7 \times 10^{-6}mol^3/dm^9$ which greater than the calculated Q_{sp}. Since the ionic product is less than the solubility product, the solution is unsaturated.

Question 3

(a)

(i) Ester

(ii) By gently heating mixture of ethanoic acid and methanol under presence of concentrated sulphuric acid catalyst.

(iii) Ethyl methanoate

(iv) $HCOOCH_2CH_3 + NaOH \longrightarrow HCOONa + CH_3CH_2OH$

(b)

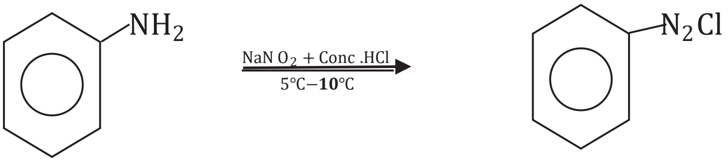
(i) Ethanoic acid forms stronger intermolecular hydrogen bonding between its molecules. This is due to presence of more oxygen in carboxylic group which makes O-H bond in ethanoic more positive polarized and also makes ethanoic acid to have greater number of hydrogen bonds per molecule. The stronger intermolecular hydrogen bonding means higher boiling point of ethanoic acid.

(ii) Lone pair on nitrogen (N) of methylamine are more available for the donation to Lewis acid due to positive inductive effect exerted by methyl group. The positive inductive effect increases electron density on N and also stabilizes the positive charge that is formed after ammine donating its lone pair and hence higher basic strength for methylamine.

(iii) Nitrogen in trimethylamine which is tertiary amine has no hydrogen (all three hydrogen atoms of ammonia have been replaced methyl groups) and therefore unlike in propylamine (which is primary amine) where there is hydrogen bonding there is no hydrogen bonding at all between molecules of trimethylamine. The absence of intermolecular hydrogen bonding between trimethylamine molecules, makes the amine to have lower boiling point.

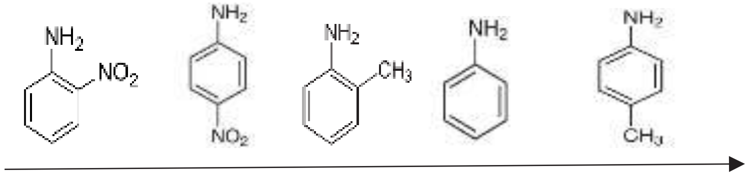
(c)

(i)



(ii) $CH_3CH_2NH_2 + CHCl_3 + KOH \xrightarrow{\text{Alcohol}} CH_3CH_2NC + KCl + H_2O$

(d)



Increase in basic strength

Question 4

(a)

1. **Temperature:** When iron is exposed at higher temperature due to machine operations, the active centre of corrosion in the metal increases and hence extent of corrosion becomes high.
2. **Humidity:** Moisture content tend to increase the oxidation rate and hence the extent of corrosion rate of iron is high in places with more humidity.
3. **Presence of impurities in atmosphere:** Atmosphere in industrial areas contains corrosives substances (fumes and gases) like $H_2S, HCl, SO_2,$ and H_2SO_4 whose presence increases both acidity of the liquid adjacent to the metal surfaces and electrical conductivity of the iron and hence the rate of corrosion increases.

(b) Oxidation half reaction:

Balancing oxygen atoms: $HNO_2 + H_2O \longrightarrow NO_3^-$

Balancing hydrogen atoms: $HNO_2 + H_2O \longrightarrow NO_3^- + 3H^+$

Balancing charges: $HNO_2 + H_2O \longrightarrow NO_3^- + 3H^+ + 2e$

Balanced oxidation half reaction: $HNO_2 + H_2O \longrightarrow NO_3^- + 3H^+ + 2e$ … … … … … (i)

Reduction half reaction:

Balancing material: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$

Balancing oxygen atoms: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

Balancing hydrogen atoms: $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

Balancing charges: $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$

Balanced reduction half reaction:

$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \ldots\ldots\ldots\ldots$ (ii)

Overall reaction equation:

Taking 3(i)+(ii) gives;

$3HNO_2 + 3H_2O + Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 3NO_3^- + 9H^+ + 6e + 2Cr^{3+} + 7H_2O$

Hence by cancelling and combining like terms, the overall balanced chemical equation becomes;

$$3HNO_2 + Cr_2O_7^{2-} + 5H^+ \longrightarrow 3NO_3^- + 2Cr^{3+} + 4H_2O$$

(c) Molar mass of $H_2C_2O_4.2H_2O$ is $126gmol^{-1}$

Using; $[\quad] = \frac{m}{M_rV}$,

Then $[H_2C_2O_4.2H_2O] = \frac{0.95}{126 \times 0.25}M = 0.03M$

Number of moles of $H_2C_2O_4.2H_2O$ in $25cm^3$ of its solution

$= \frac{25}{1000} \times 0.03mol = 7.5 \times 10^{-4}mol$ = number of moles of $C_2O_4^{2-}$

$C_2O_4^{2-}$ reacts with MnO_4^- according to the following equation:

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

From which mole ratio of MnO_4^- to $C_2O_4^{2-}$ is $2:5$

Thus number of moles of manganate (VII) solution

$= \frac{2}{5} \times 7.5 \times 10^{-3}mol = 3 \times 10^{-4}mol$

Then $[MnO_4^-] = \frac{3 \times 10^{-4} \times 10^3}{33}M = 0.009M$

Hence the concentration of potassium permanganate (VII) solution is 0.009M

(d) The reaction will occur between bromine and iodide ions whereby the bromine will displace iodide from the solution according to the following equation:

$$Br_2 + 2I^- \longrightarrow Br^- + I_2$$

Reason:

Non-metals with more positive electrode potential are stronger oxidizing agents and therefore more reactive. Bromine having larger electrode potential, oxidizes iodide into iodine while itself becomes reduced to bromide thereby displacing iodide from the solution. Iodine having smaller electrode potential, is less reactive and thus cannot displace bromide from the solution.

That is; $I_2 + Br^- \longrightarrow$ No reaction

Question 5

(a)

(i) Periodicity is the similarity in properties between elements which are found in similar positions in the periodic table while diagonal relationship is the similarity in properties between the first element in a group and the second element in the next group.

(ii) The reduction is done by mixing carbon and tin ore (SnO_2) at 1200°C in the reverberator furnace. The ore is reduced to tin while SiO_2 is removed as slag.

$SnO_2 + 2C \xrightarrow[1200°C]{} Sn + 2CO$

$CaCO_3 \underset{\Delta}{\rightarrow} CaO + CO_2$

$CaO + SiO_2 \longrightarrow CaSiO_3(slag)$

(b)

1. They both combine with oxygen gas to form normal oxide only (Li_2O and MgO).
   $4Li + O_2 \longrightarrow 2Li_2O$
   $2Mg + O_2 \longrightarrow 2MgO$
2. They both react with nitrogen gas forming nitrides which react with water liberating ammonia.
   $6Li + N_2 \underset{\Delta}{\rightarrow} 2Li_3N$
   Then $Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$
   And $Mg + N_2 \underset{\Delta}{\rightarrow} Mg_3N_2$
   Then $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$
3. Their compounds have similar thermal stability. For example; hydroxides, carbonates of both lithium and magnesium decompose on heating.
   $2LiOH \underset{\Delta}{\rightarrow} Li_2O + H_2O$
   $Li_2CO_3 \underset{\Delta}{\rightarrow} Li_2O + CO_2$
   $Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g)$
   $MgCO_3(s) \underset{\Delta}{\rightarrow} MgO(s) + CO_2(g)$

(c) **Action of water on chlorides of period 3**

Chloride of period 3 are $NaCl, MgCl_2, AlCl_3, SiCl_4, PCl_5$ (or PCl_3), S_2Cl_2 and Cl_2

NaCl does not react with water; i.e. does not hydrolyse either in cold water or steam. It is only dissolve in water to give neutral solution of its aqueous ions.

$$NaCl(s) + H_2O \rightarrow Na^+(aq) + Cl^-(aq)$$

Action of $MgCl_2$ with water depend on whether the water is cold or hot.

- With cold water**,** the chloride does not undergo hydrolysis. It is only dissolve to give neutral solution of its aqueous ions without any chemical reaction.

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

- With hot water or steam, the chloride undergoes partial hydrolysis to give basic chloride and hydrogen chloride gas.

$$MgCl_2 + H_2O \underset{\Delta}{\rightarrow} Mg(OH)Cl + HCl$$

The remaining chloride undergo hydrolysis to give acidic solution

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3H^+ + 3Cl^-$$

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

$$PCl_5 + 4H_2O \underset{\Delta}{\rightarrow} H_3PO_4 + 5HCl$$

S_2Cl_2 (disulphur dichloride) reacts with water in complex way. It undergoes hydrolysis and redox reaction in water, yielding mixture of products ($HCl, H_2S, S, H_2SO_3, H_2SO_4, SO_2$) which is very acidic.

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

Conclusion

Ability of chloride of period 3 element to hydrolyse in water increases as you go across the period from NaCl which does not hydrolyse at all via $MgCl_2$ which undergo partial hydrolysis in hot water to other chlorides which undergo complete hydrolysis to give acidic solution. This confirms that covalent characters of chlorides increases as you go across the period and hence metallic characters of the elements decrease to the same direction.

Action of water on hydrides of period 3

Period 3 elements which form hydrides are Na, Mg, Al, Si, P, S, Cl and their respective hydrides are $NaH, MgH_2, AlH_3, SiH_4, PH_5$, (or PH_3), H_2S and HCl.

The first two hydrides and react with water to give basic solution (hydroxide) according to the following equations:

$$NaH + H_2O \rightarrow NaOH + H_2$$
$$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2$$

AlH_3 reacts with water to give amphoteric hydroxide according to the following equation:

$$AlH_3 + 3H_2O \rightarrow Al(OH)_3 + 2H_2$$

SiH_4 (name: **silane**) and **phosphane**, PH_5 (or **phosphine**, PH_3) do not react with water:

$SiH_4 + H_2O \rightarrow$ No reaction

PH_5 (or PH_3) $+ H_2O \rightarrow$ No reaction

H_2S and HCl dissolve in water to give acidic solution according to the following equation:

$$H_2S + H_2O \rightarrow H_3O^+ + HS^-$$
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Conclusion

- The hydrides of first two elements (Na and Mg) gives basic solution suggesting that the period 3 elements are stronger electropositive (less electronegative) than hydrogen.
- Hydride of Al gives amphoteric solution suggesting that electronegativities of Al and H do not differ much.
- Hydrides of Si and P have no reaction with water suggesting that their electronegativities are almost equal to that of hydrogen.
- The last two hydrides of S and Cl give acidic solution suggesting that the elements are more electronegative than hydrogen.

The above facts justify that electronegativity increases as you go across the period from left to right and hence metallic characters of elements decrease at the same direction

Question 6

(a) $\underrightarrow{[Fe(CN)_6]^{4-} < [FeF_6]^{4-} < [MnCl_4]^{2-}}$

Increase in magnetic properties

Reason: Consider outermost electronic configuration of Fe^{2+} and Mn^{2+} as shown below:

$[Fe^{2+}]$ =

3d					4s	4p		
1⇂	1	1	1	1				

$[Mn^{2+}]$ =

3d					4s	4p		
1	1	1	1	1				

Magnetic properties increases as number of unpaired electrons increases. The first complex has zero unpaired electron due to rearrangement of electrons brought about by CN which is strong ligand. Both F and Cl are weak ligands (they do not cause electron rearrangement), so the second complex has four unpaired electrons while the last one has five unpaired electrons.

(b)

(i) After addition of water through dilution, there is formation of hexaaquacobalt(II) complex in which water is weak ligand leading to the formation of light colour which is light blue.

$$CuCl_2(aq) + 6H_2O(l) \longrightarrow [Cu(H_2O)_6]^{2+} + 2Cl^-$$

(ii) With electronic configuration of Cu^{2+} which is [Ar] $3d^9$ with one unpaired d-orbital; copper is transition element with unlike zinc whose electronic configuration of both neutral atom and ion are all paired with electrons in d-orbitals

(c)

1. In Haber process
   Iron is used as catalyst in industrial manufacture of ammonia by Haber process.

$$N_2\,(g) + 3H_2(g) \overset{\text{Fe}}{\rightleftharpoons} 2NH_3(g)$$

2. In hydrogenation of unsaturated hydrocarbon.
   Nickel can be used as catalyst in hydrogenation of alkene or alkyne into alkane.
   For example:

$$CH_2 = CH_2 + H_2 \overset{\text{Ni}}{\rightarrow} CH_3CH_3$$

3. In contact process
   Oxide of vanadium (V_2O_5) is used as catalyst in production of sulphur trioxide as important step in the manufacture of sulphuric acid.

$$2SO_2\,(g) + (g) \overset{V_2O_5}{\rightleftharpoons} 2SO_3(g)$$

4. In the preparation of carbonyl compounds by heating carboxylic acids.
   Oxide of manganese (MnO_2) is used as catalyst in the preparation of carbonyl cmpounds.
   Example; $2CH_3COOH \xrightarrow{MnO_2} CH_3COCH_3 + CO_2 + H_2O$

(d)

(i) **1.** Elastomers: These are polymers in which the polymer chains are held by weakest intermolecular forces of attraction. As result, they possess so weak physical properties that they can be stretched, they can be melted easily without decomposition and they show elasticity at room temperature. A good example of elastomer is rubber.

2. Fibers: These are polymers with strong physical properties like high tensile strength and high modulus due to presence of strong intermolecular forces like hydrogen bonding. An example of fiber is Dacron.

(ii) Reason: They are non-biodegradable (they are not decomposed easily by living organisms) and therefore they constitute to an enviromental hazard.

Explanation:

Polyethylene are commonly very long saturated hydrocarbon containging non- polar $C - C$ bond and hence are very unreactive. Their little reactivity means that they persist in the environment for long time and therefore become serious environmental pollutant.

(iii) HDP have longer straight chain with no branches while LDP are usually shorter and more branched. This means that HDP chains are larger in size and more compact leading to stronger Van-der-Waals of attraction which account for their stronger physical properties like higher melting and boiling point, higher density, greater stiffness accompanied with higher tensile strength and hardness than LDP whose chains are loosely packed due to presence of branches.

Solutions Necta 2023
CHEMISTRY 1

SECTION A

Answer **all** questions in this section.

Question 1

(a) Using $m = \rho V$;

Mass of oxygen gas in the stomach $= 1.149\text{gcm}^{-3} \times 0.05\text{cm}^3 = 0.05745\text{g}$

Using $PV = \frac{m}{M_r} \times RT$ or $V = \frac{mRT}{M_rP}$;

$$\text{Volume of oxygen produced} = \frac{0.05745\text{g} \times 0.0821\text{atmdm}^3\text{mol}^{-1}\text{K}^{-1} \times 310\text{K}}{32\text{gmol}^{-1} \times 1\text{atm}}$$

$$= 0.04569\text{dm}^3 = 45.69\text{cm}^3$$

The volume produced is 45.69cm^3.

(b) $\%H + \%N = 100\%$ or $\%H = 100 - \%N = (100 - 87.4)\% = 12.6\%$

Calculating empirical formula of the given compound:

Composition by element	N	H
Percentage of each by mass	87.4	12.6
Mass of each in 100g of the compound	87.4g	12.6g
Number of moles of each. Using: $n = \frac{m}{M_r}$	$\frac{87.4\text{g}}{14\text{g/mol}}$ $= 6.24286\text{mol}$	$\frac{12.6\text{g}}{1\text{g/mol}}$ $= 12.6\text{mol}$
Dividing by the smallest number of moles in each so as to get simpler ratio	$\frac{6.24286\text{mol}}{6.24286\text{mol}} = 1$	$\frac{12.6\text{mol}}{6.24286\text{mol}} = 2$

Hence the empirical formula of the compound is NH_2

Calculating molar mass of the compound:

From ideal gas equation: $PV = nRT$ but $n = \frac{m}{M_r}$

Then $PV = \frac{m}{M_r}RT$ or $M_r = \frac{mRT}{PV}$ but $\frac{m}{V} = \rho$

Thus $M_r = \frac{\rho RT}{P}$

Where $\rho = 0.977\text{g/L}, R = 0.0821\text{atmLmol}^{-1}\text{K}^{-1}, T = 100^\circ\text{C} = 373\text{K},$

$P = 710\text{mmHg} = \frac{710}{760}\text{atm}$

Then $M_r = \frac{0.977\text{g/L} \times 0.0821\text{atmLmol}^{-1}\text{K}^{-1} \times 373\text{K}}{\frac{710}{760}\text{atm}} = 32\text{g/mol}$

Calculating molecular formula:

Let molecular formula of the compound be $(NH_2)_n$

Then $14n + 2n = 32$ or $16n = 32$ or $n = n$

Hence the molecular formula of the compound is $(NH_2)_2$ or N_2H_4.

(c) By Dalton's law of partial; pressure: $P_T = P_{Cl_2} + P_{H_2O} = 764$ torr

But $P_{H_2O} = 17.5\text{mmHg}$

Then $P_{Cl_2} = P_T - P_{H_2O} = (760 - 17.5)\text{mmHg} = 742.5\text{mmHg}$

Using $PV = \frac{m}{M_r} \times RT$ or $m = \frac{M_r PV}{RT}$;

$$\text{Mass of chlorine} = \frac{71\text{gmol}^{-1} \times \frac{742.5}{760}\text{atm} \times 2.5 \times 10^{2} \times 10^{-3}\text{L}}{0.0821\text{atmLmol}^{-1}\text{K}^{-1} \times 293\text{K}} = 0.72\text{g}$$

The chlorine mass is 0.72g.

Question 2

(a)

(i) When a non-volatile solute like sodium chloride is dissolved in a solvent, the vapour pressure decreases. The lowering in vapour pressure means that the liquid solution will need higher temperature to raise its vapour pressure so that it equalises to atmospheric pressure and hence its boiling point elevates. Also the lowering in vapour pressure means that the solid phase of the solution will need lower temperature to raise its vapour pressure so that it equalises to the vapour pressure of liquid solution and hence lowering in freezing point.

(ii) The ethylene glycol is non-volatile solute which causes freezing point depression of water and therefore it acts as anti-freeze to prevent freezing of radiator in the car.

(iii) 1.2% sodium chloride solution is hypertonic with respect to 0.9% sodium chloride solution or blood cells. So when red blood cells are placed in this solution, water flows out of the cell and they shrink due to loss of water by osmosis.

(iv) Fresh water is hypotonic with respect to the fruits and vegetables. So when dehydrated fruits and vegetables are placed in fresh water, they absorb water by osmosis and hence they regain their firmness.

(b)

(i) $\Delta T = K_b m = \frac{K_b \times m_{su}}{M_{su} \times m_{sv} \text{in kg}} = \frac{0.52°\text{Ckg/mol} \times 18\text{g}}{180\text{g/mol} \times 1\text{kg}} = 0.052°\text{C}$

Boiling point of solution $= T_o + \Delta T = (100 + 0.052)°\text{C} = 100.052°\text{C}$

(ii) $\Delta T = K_b m = \frac{K_b \times m_{su}}{M_{su} \times m_{sv} \text{in kg}} = \frac{1.15°\text{Ckg/mol} \times 5\text{g}}{60\text{g/mol} \times 0.075\text{kg}} = 1.3°\text{C}$

The boiling point elevation is 1.3°C.

Question 3

(a) **Conditions:**

1. Hydrogen atom must be bonded to strong electronegative atom, mainly N, O or F. This ensures the formation of strong partial positive charge in hydrogen atom.
2. The strong electronegative atom must possess at least one lone pair. This ensures strong electrostatic force of attraction between the partial positively hydrogen atom and negatively charged lone pair.

(b)

(i) **Compound I:** Intramolecular hydrogen bonding. **Compound II:** Intermolecular hydrogen bonding.

(ii) Compound II

(iii) Compound II

(c) There are three types of bonds as outlined below:

- **Bond between N and H:** (Three) covalent bonds and (one) coordinate (or dative) bond.
- **Bond between N and O:** Covalent bonds.
- **Bond between ammonium radical and nitrate radical:** Ionic bond.

The mode of hybridisation: sp^2 hybridisation.

Question 4

(a)

(i) $f = \frac{c}{\lambda}$

(ii) $\lambda = \frac{1}{\nu}$

(iii) $E = hf$

(iv) $E = \frac{hc}{\lambda}$

(b)

(i) Impossible. Rule violated: Hund's rule of maximum multiplicity

(ii) Impossible. Rule violated: Aufbau principle,

(iii) Impossible. Rule violated: Hund's rule of maximum multiplicity

(iv) Possible

(v) Impossible. Rule violated: Aufbau principle,

(c)

(i) Three.

(ii) Five.

Question 5

(a)

(i) In air, unburnt sodium reacts with oxygen from air to give normal sodium oxide which in turn gives sodium hydroxide after addition of water.

That is; $4Na + O_2 \rightarrow 2Na_2O$
Then; $Na_2O + H_2O \rightarrow 2NaOH$

(ii) At high temperature of burnt sodium, the sodium metal forms sodium peroxide which in turn gives sodium hydroxide and hydrogen peroxide when water is added.

That is; $2Na + O_2 \xrightarrow[\Delta]{} Na_2O_2$
Then; $Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$

(b)

(i) With dilute sulphuric acid.

For lead oxide and calcium oxide: They form very thin layer of insoluble sulphates which prevents further reaction. Thus the reactions stop immediately after starting to take place.
$PbO(s) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + H_2O(l)$
$CaO(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + H_2O(l)$
For aluminium oxide: It forms solution of aluminium sulphate (and water) and the reaction continues until all aluminium oxide is consumed.
$Al_2O_3(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$

(ii) With dilute nitric acid. All given oxides react completely to give solutions of their nitrates and water.

$PbO(s) + 2HNO_3(aq) \longrightarrow Pb(NO_3)_2(aq) + H_2O(l)$
$CaO(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2O(l)$
$Al_2O_3(s) + 6HNO_3(aq) \longrightarrow Al(NO_3)_3(aq) + 3H_2O(l)$

Question 6

(a)

(i) Born-Haber cycle is the enthalpy diagram used in calculation of lattice energy by showing all necessary steps in the formation of ionic compounds while heat of formation is the net heat change obtained in all necessary steps of the formation of a compound from its elements in their normal physical states. So Born-Haber cycle deals with ionic compounds only while heat of formation is for both ionic and covalent compounds.

(ii) Heat of neutralisation is the heat evolved when two reacting dilute solutions of acid and base are mixed to give water while heat of solution is the heat absorbed or evolved when any solute (not necessary to be acid or base) is mixed with water to give a solution.

(b) In reactants side there are:

One $C = C$, four $C - H$, one $H - H$

In products side there are:

One $C - C$, six $C - H$

Using $\Delta H_r = \sum B.E(\text{reactants}) - \sum B.E(\text{products})$

$= (C = C) + 4(C - H) + (H - H) - (C - C) - 6(C - H)$

$= (C = C) + (H - H) - 2(C - H) - (C - C)$ (By combining like terms)

$= 612 + 436 - (2 \times 416) - 348 = -132\text{kJ/mol}$

So the standard enthalpy of the given reaction is -132kJ/mol.

Question 7

(a)

(i) Bromine water test: With bromine water, $CH_3CH = CH_2$ gives positive test by decolourising reddish-brown colouration of bromine water while $CH_3CH_2CH_3$ does not.

That is $CH_3CH = CH_2 + \underset{\text{Reddish brown}}{Br_2 \mid H_2O} \longrightarrow \underset{\text{colourless}}{CH_3CH(OH)CH_2Br}$

While $CH_3CH_2CH_3 + Br_2 \mid H_2O \longrightarrow$ No reaction

(ii) Ammonical silver nitrate test: With ammonical silver nitrate, $CH_3CH_2C \equiv CH$ gives positive test by producing white precipitate of silver but-1-ynide while $CH_3C \equiv CCH_3$ does not.

That is; $CH_3CH_2C \equiv CH + Ag(NH_3)_2NO_3 \longrightarrow \underset{\text{White precipitate}}{CH_3CH_2C \equiv CAg} + 2NH_3 + HNO_3$

While $CH_3C \equiv CCH_3 + Ag(NH_3)_2NO_3 \longrightarrow$ No reaction

(b)

(i) $CH_3COCH_2CH_3$

(ii) $CH_3CH_2CH_2CH_3$

(iii) $CH_3CH_2NO_2$

(iv) $CH_2BrCH = CH_2$

(c) $(CH_3)_3CC \equiv CH < CH_3C \equiv CH < CH \equiv CH < ClC \equiv CH < NO_2C \equiv CH$

Reasons:

1. Positive inductive effect: The longer the carbon chain, the stronger the positive inductive effect and consequently the corresponding terminal hydrogen becomes less acidic.
2. Negative inductive effect: As the substituent possess more ability of withdrawing electrons, negative inductive becomes stronger and consequently the corresponding terminal hydrogen becomes more acidic.

Question 8

(a)

(i) The chemical equilibrium involves balance of the rate of the two reactions which are proceeding at the same time in opposite directions. So it is dynamic in a sense that reactants continue to change into products and products continue change into reactants even after achieving the equilibrium.

(ii) Since pressure exerted by gas varies directly proportional to the number of moles of the gas; $\text{pressure ratio} = \text{mole ratio}$

Thus pressure can be treated as number of moles as follows:

	$CCl_4(g)$	$\rightleftharpoons C(s) +$	$2Cl_2(g)$
Pressure at $t = 0$	P		0
Pressure at equilibrium	$P - x$		$2x$

From the above equation; $K_p = \frac{\left(P_{Cl_2}\right)^2}{P_{CCl_4}} = \frac{(2x)^2}{P-x} = \frac{4x^2}{P-x}$

Substituting $0.76 = \frac{4x^2}{P-x}$

From which; $4x^2 + 0.76x - 0.76P = 0; \ldots\ldots\ldots\ldots$ (i)

But equilibrium total pressure is 1.2atm

Thus $P - x + 2x = 1.2$ or $P + x = 1.2$

From which; $P = 1.2 - x \ldots\ldots\ldots\ldots$. (ii)

Substituting (ii) to (i) gives; $4x^2 + 1.52x - 0.912 = 0$

Solving above quadratic equation gives the practical value of x which is 0.3239

Then $P = 1.2 - x = (1.2 - 0.3239)\text{atm} = 0.8761\text{atm}$

The initial pressure is 0.8761atm.

(b)

(i) This is because at higher temperature, kinetic energy and thus speed of gas molecules become higher thus making gas particles to escape from the solution.

(ii) Catalyst enables the equilibrium to be reached in shorter time. However, it has no effect in equilibrium position because it increases the rate of both forward and reverse reaction by equal amount.

(iii) Raising the temperature in the exothermic reaction shifts the equilibrium position to the reactants side and hence the equilibrium constant value will decrease.

(c)

(i) Concentration of Fe^{2+} will decrease. This is because, the addition of KSCN disturbs the chemical equilibrium by increasing concentration of SCN^- appearing in Fe^{2+} side and thus to restore the equilibrium, more Fe^{2+} must combine with added SCN^-.

(ii) No effect on equilibrium position. This is because, the given equilibrium involves liquid solutions which are not compressible like gases (pressure may affect equilibrium position of chemical system involving gases only).

(iii) The fading of red colour suggests that equilibrium position shifted to the reactants side (Fe^{2+} side) at lower temperature of ice-water bath. This implies that K_c value is low at low temperature and hence the reaction is endothermic.

Question 9

(a)

(i) Soil reaction is the reaction of soil solution which represents the degree of acidity or basicity caused by the relative concentration of hydronium ions, H_3O^+, (acidity) or hydroxide ions, $\mathrm{OH^-}$, (basicity) present in the soil. For example; if the soil contains more acidic cations like $\mathrm{H^+}, \mathrm{Al^{3+}}$ and $\mathrm{Fe^{3+}}$, then the concentration of hydronium ions will be greater than that of hydroxide ions and hence the soil reaction will be acidic.

(ii) Soil colloids are very small organic and inorganic particles present in the soil which are responsible for potential fertility of the soil. They are very small particles whose size is less than 0.001mm, for example; layer silicate clays.

(iii) Liming is the application of calcium and magnesium rich materials with anions capable of producing hydroxide ions $(\mathrm{OH^-})$ to neutralize acidity of the solution. For example; the addition of calcium oxide to the soil.

(iv) Organic fertilizers are any natural organic matter that is added to the soil to supply plant nutrients essential to plant growth. For example; feces from cattle.

(v) Artificial fertilizer is any synthetically produced inorganic material that is added to a soil to supply one or more plant nutrients essential to the growth of plants. For example; NPK fertilizer.

(b) It is important to measure soil pH due to the following reasons:

1. Soil pH determine the availability (solubility) of plant nutrients to the plants. So knowing soil pH will help us to understand the appropriate measure to take so as to increase the yield of crops.
2. Soil pH determines level of hydrogen, aluminium and manganese toxicity. So to combat these toxicities, it is important to know soil pH.

(c) Molar mass of $Ca(NO_3)_2$ is 164g/mol or 0.164kg/mol

Mass of nitrogen in one mole of $Ca(NO_3)_2$ is 28g or 0.028kg
Thus 0.028kg of N is contained in 0.164kg of $Ca(NO_3)_2$
And 200kg of N will be contained in $\frac{200\times0.164}{0.028}$ or 1171.43kg of $Ca(NO_3)_2$
But the fertilizer is 60% $Ca(NO_3)_2$
Then 60kg of $Ca(NO_3)_2$ is contained in 100kg of the fertilizer;
And 1171.43kg of $Ca(NO_3)_2$ will be contained in $\frac{1171.43\times100}{60}$ or 1952kg of the fertilizer
Hence 1952kg of the fertilizer is required to meet the requirement.

Question 10

(a)

(i) The two effects are:

1. **Activating effect:** Substituents which increase electron density in benzene ring through either positive inductive effect or positive mesomerism, are said to increase (activate) the reactivity of benzene toward the electrophile in electrophilic substitution reactions. These substituents are known as activating groups or simply activators, for example: carboxylic group and nitro group.
2. **Deactivating effect:** Substituents which withdraw electron from benzene ring by negative mesomerism, they decrease reactivity of benzene toward electrophile. These substituents are therefore said to deactivate electrophilic substitution reactions in benzene and hence they are called deactivating groups or deactivators; for example: hydroxyl group and amino group.

(ii) In alkenes pie bonds are localised while in benzene pie bonds have been delocalised in mesomerism making them more stable and hence it become more difficult for benzene to undergo addition reactions like alkenes. For example; bromination of alkene gives dibromoalkane which is an additional product while that of benzene gives bromobenzene which is substitutional product.

$C_nH_{2n} + Br_2 \xrightarrow[A_E]{} C_nH_{2n}Br_2$

Alkene

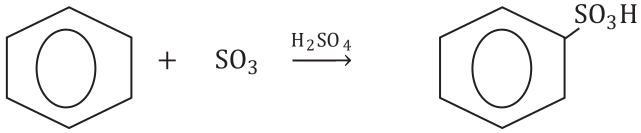
$C_6H_6 + Br_2 \xrightarrow[S_E]{} C_6H_5Br + HBr$

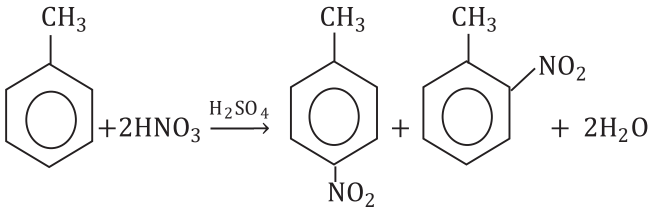
Benzene

(b) This is due to two reasons:

1) **Position of carbanion:** Activators increase more electron density in ortho and para carbons than meta carbon. This makes them (ortho and para carbons) negatively charged and hence better position for incoming electrophile.
2) **Stability of intermediate carbenium ion:** Activators do more stabilisation of intermediate carbenium ion when the electrophile is substituted to ortho and para carbon than in meta carbon.

(c) Both nitration and sulphonation of given compounds are electrophilic substitution reactions. However, presence of methyl group which is electron releasing group (activator) in methylbenzene, activates its reaction towards electrophile and hence nitration of methylbenzene becomes faster than sulphonation of benzene.





Solutions Necta 2023

CHEMISTRY 2

Answer **five (5)** questions

Question 1

(a)

(i) No.

Explanation

For mixture to be separated into pure components by fractional distillation, vapour composition should change compared to liquid composition upon boiling. Azeotropes boil at constant temperature making the vapour composition the same as liquid composition and hence they cannot be separated by fractional distillation.

(ii) The reduction in volume suggests that there are stronger intermolecular forces in the acetone-chloroform mixture than in pure acetone and pure chloroform. The stronger intermolecular forces mean that the vapour pressure in the mixture is smaller than that which would be predicted by Raoult's law and hence the mixture shows negative deviation from Raoult's law.

(b) Since M and N formed ideal solution, then Raoult's law is applicable.

Thus $P_{soln} = X_M^L P_M^o + X_N^L P_N^o$

For the first case;

$$550\text{mmHg} = \left(\frac{3\text{mol}}{3\text{mol} + 1\text{mol}}\right) P_M^o + \left(\frac{1\text{mol}}{3\text{mol} + 1\text{mol}}\right) P_N^o$$

From which;

$$\frac{3}{4} P_M^o + \frac{1}{4} P_N^o = 550 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. \text{(i)}$$

For the second case;

$$560\text{mmHg} = \left(\frac{4\text{mol}}{4\text{mol} + 1\text{mol}}\right) P_M^o + \left(\frac{1\text{mol}}{4\text{mol} + 1\text{mol}}\right) P_N^o$$

From which;

$$\frac{4}{5} P_M^o + \frac{1}{5} P_N^o = 560 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. \text{(ii)}$$

Solving the two equations above gives;

$$P_M^o = 600\text{mmHg and } P_N^o = 400\text{mmHg}$$

The vapour pressure of pure M is 600mmHg.

The vapour pressure of pure N is 400mmHg.

(c)

(i) Below are conditions that govern distribution law:

1) **Constant temperature:** Solubility and hence partition coefficient is temperature dependent. So the temperature must be kept constant while doing experiment involving the distribution law.
2) **Same molecular state**: The molecular state of the solute must be the same in the two solvents. The law does not hold if there is dissociation or association or any other chemical reaction in one of the solvents.

3) **Equilibrium concentration:** The concentration of the solute must be noted after equilibrium has been established.
4) **Dilute solution:** The concentration of the solute in the two solvents must be low. The law does not hold when the concentration is high.
5) **Non miscibility of solvents**: The two solvents must be immiscible or only slightly soluble in each other.

(ii) Given that: $K_d = \frac{\text{Concentration of succinic acid in water}}{\text{Concentration of succinic acid in ether}} = 5.2$

Let weight of the acid in water layer (aqueous solution) be x.

Then $\frac{x/_{50\text{cm}^3}}{0.092\text{g}/_{20\text{cm}^3}} = 5.2, \quad 20x = 23.92\text{g or } x = 1.196\text{g}$

Hence the weight of the acid in the aqueous solution is 1.196g.

Question 2

(a)

(i) The Lewis concept expands list of acids and bases by including species with neither ionisable hydroxyl group (Arrhenius bases) nor ionisable hydrogen (Arrhenius acids). It also includes species which are insoluble in water unlike Arrhenius acids and bases which must be water soluble.

(ii) Hydrogen sulphate ions (HSO_4^-) can do both losing a hydrogen ion to form sulphate ions (SO_4^{2-}) and accepting the hydrogen ion to form sulphuric acid (H_2SO_4).

$HSO_4^- + OH^- \rightarrow H_2O + SO_4^{2-}$ (with base, it loses hydrogen ion).

$HNO_3 + HSO_4^- \rightarrow H_2SO_4 + NO_3^-$ (with strong acid, it accepts hydrogen ion).

(iii) High energy released during thunderstorms enables oxygen and nitrogen in the atmosphere to react to give nitrogen dioxide which in turn react with water to give acidic solution and hence the rain water becomes more acidic.

That is; $N_2(g) + O_2(g) \xrightarrow[\text{High energy of lightning}]{} 2NO$

Then, $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Finally, $2NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$

(b)

(i) Hydrochloric acid (HCl) being strong electrolyte (strong acid), ionises completely (its according to the following equation: $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

From which mole ratio of HCl to H^+ is 1:1

And hence for HCl, initial $[H^+] = [HCl] = 0.1M$

Also sulphuric acid (H_2SO_4) being strong electrolyte, ionises completely according to the following equation: $H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$

From which mole ratio of H_2SO_4 to H^+ is 1: 2

And hence for H_2SO_4, initial $[H^+] = 2[H_2SO_4] = 2 \times 0.5M = 1M$.

Using, concentration of the mixture $= \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$;

New $[H^+]$ in the mixture $= \frac{1cm^3 \times 1M + 2cm^3 \times 0.1M}{1cm^3 + 2cm^3} = 0.4M$

Hence pH of the mixture $= -\log[H^+] = -\log 0.4M = 0.4$

(ii) Ethanoic acid being weak electrolyte, (weak acid) ionises in aqueous solution according to the following equation:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

From which; $K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$; where $[CH_3COO^-] = [H_3O^+]$ (From mole ratio)

It follows that; $K_a = \frac{[H_3O^+]^2}{[CH_3COOH]} = \frac{(0.001M)^2}{0.1M} = 1 \times 10^{-5}M$

(c) The mixture of HCN and NaCN is acidic buffer solution whose pH value is given by the following equation: $pH = pK_a + \log\frac{[salt]}{[acid]}$

But $[salt] = \frac{\text{number of moles of salt}}{\text{volume of buffer solution}}$

And $[Acid] = \frac{\text{number of moles of acid}}{\text{volume of buffer solution}}$

It follows that: $\frac{[salt]}{[acid]} = \frac{\text{number of moles of salt}}{\text{number of moles of acid}}$

Thus for acidic buffer solution:

$$pH = pK_a + \log\frac{\text{number of moles of salt}}{\text{number of moles of acid}}$$

If V is the volume of the acid (HCN) required.

Then $4.91 = 4.76 + \log\frac{0.2M\times50cm^3}{0.1M\times V}$ (n = [ ]V)

From which; $V = 70.79cm^3$

Hence $70.79cm^3$ of HCN is required.

Question 3

(a)

(i) 2,4-dimethyl-2-pentanone

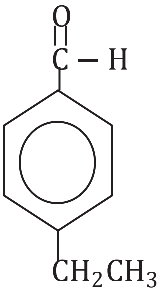
(ii) 3-phenylprope-2-enal

(b)

(i) The molecular formula $C_9H_{10}O$ confirms the general molecular formula of $C_nH_{2n-8}O$.

- Thus with 9 carbons, E may be aromatic aldehyde or ketone.

- The formation of 2,4-DNP confirms that E is the carbonyl compound.
- Since E can reduce Tollen's reagent, it cannot be ketone; it must be aldehyde.
- Since E undergoes Cannizzaro's reaction and gives two carboxylic groups (in the first and fourth carbon) upon oxidation, its carbonyl group must be directly bonded to benzene ring and ethyl group as attached groups as per the following structure:

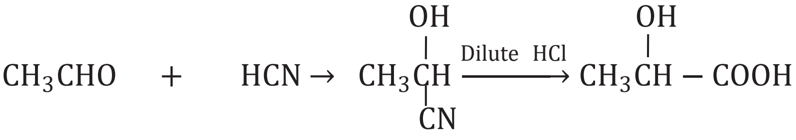


Structure of **E**

(ii) The polar nature of $O-H$ group in alcohols and carboxylic acids, enables them to exhibit intermolecular hydrogen bonding while in aldehyde and ketone, the polar nature of $C = O$ group (carbonyl group) does not allow the formation of hydrogen bonding. The presence of hydrogen bonds means stronger intermolecular forces and hence higher boiling point for alcohols and carboxylic acids.

(iii) $CH_3CHO + [O] \longrightarrow CH_3COOH$

B **C**



$$CH_3CHO + HCN \rightarrow CH_3\underset{CN}{\overset{OH}{CH}} \xrightarrow{\text{Dilute HCl}} CH_3\overset{OH}{CH}-COOH$$

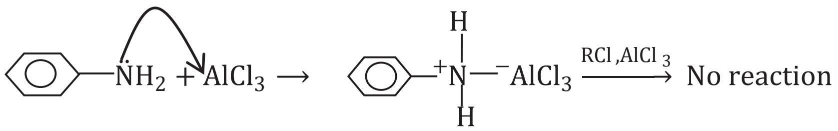
B **Z** 2-hydroxypropanoic acid

(c)

(i) In methanol, there are two lone pairs in oxygen thus making it to have two positions for making hydrogen bonding while in methylamine only one lone pair is present in the nitrogen. This makes alcohol to exhibit stronger hydrogen bonding and therefore higher boiling point for methanol than methylamine.

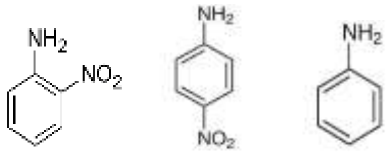
(ii) Friedel-Craft alkylation does not occur with aniline because the complex that forms between NH_2 and the $AlCl_3$ catalyst deactivate the ring towards Friedel-Craft alkylation.

That is;



(d)

(i) **A:** CH_3NH_2; **B:** CH_3Cl; **C:** CH_3CN; **D:** $CH_3CH_2NH_2$



NH_3, CH_3NH_2

Increase in basic strength →

Reasons:

- Compared to aniline, aliphatic amines have higher basic strength because in aniline lone pair electrons participate in mesomerism (and therefore they become less available to be donated to Lewis acid).
- For aliphatic amine, basic strength is increased by positive inductive effect which increases as length of carbon chain increases (that is why CH_3NH_2 has higher basic strength than NH_3).
- In aniline, basic strength is decreased by deactivating effect. If deactivator is closer to amino group, its basic strength becomes smaller.

(ii)

Step 1: Amide formation

$$CH_3CH_2COOH + NH_3 \underset{\Delta}{\rightarrow} CH_3CH_2CONH_2 + H_2O$$

Propionic acid

Step 2: Hoffmann's degradation reaction

$$CH_3CH_2CONH_2 + Br_2 + 4KOH \rightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

Question 4

(a)

(i) Potassium hexaammineferrate(III)

(ii) Ten

(iii) Geometric structure: octahedral. Hybridization: d^2sp^3 hydridization

(iv) Anionic

Explanation:

The whole compound must be electrically neutral. Since potassium ions are positively charged, the complex must be negatively charged so that the summation of charges becomes zero.

(b)

(i) $[Cu(NH_3)_4Cl_2]$ has no free Cl^- ions in the ionisation sphere to combine with Ag^+ (from $AgNO_3$) as all of its Cl^- ions are directly bonded to the central metal ion in the coordination sphere as ligands by dative bond while in $[Cu(NH_3)_5Cl]Cl$, there is free Cl^- in the ionisation sphere which may combine with Ag^+ (from $AgNO_3(aq)$) yielding a white precipitate of AgCl.

That is; $[Cu(NH_3)_5Cl]Cl + AgNO_3 \rightarrow [Cu(NH_3)_5Cl]NO_3 + AgCl(s)$

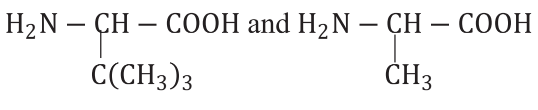
While $[Cu(NH_3)_4Cl_2] + AgNO_3 \rightarrow$ No reaction

(ii) Among the three ligands (H_2O, NH_3 and CN^-) in given complexes, H_2O is the weakest ligand exerting smallest energy gap between treble degenerate and double degenerate of d-orbitals and hence lowest energy photons are absorbed resulting to the blue colour for $[Co(H_2O)_6]^{2+}$ while CN^- is the strongest ligand exerting largest energy gap between treble degenerate and double degenerate of d-orbitals and hence highest energy photons are observed resulting to the yellow colour for $[Co(CN)_6]^{4-}$.

(c)

(i) Polypeptide.

(ii) Monomers are:

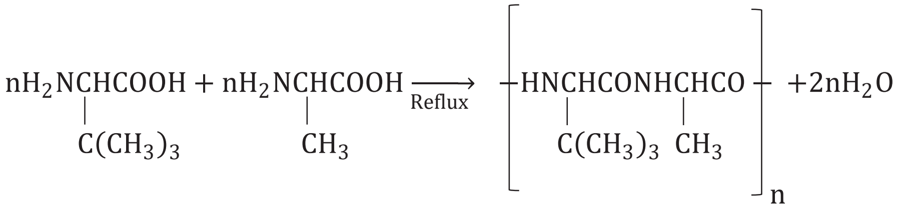


$$H_2N-\underset{\displaystyle C(CH_3)_3}{\underset{|}{CH}}-COOH \text{ and } H_2N-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$$

(iii) Condensation polymer.

Reason: Presence of amide (or peptide) link in the polymer.

(iv) Equation:



$$nH_2N\underset{\displaystyle C(CH_3)_3}{\underset{|}{C}}HCOOH + nH_2N\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH \xrightarrow[\text{Reflux}]{} \left[-HN\underset{\displaystyle C(CH_3)_3}{\underset{|}{C}}HCONH\underset{\displaystyle CH_3}{\underset{|}{C}}HCO- \right]_n + 2nH_2O$$

(d)

(i) Addition polymerization.

Reason: Absence of two different functional groups which may react in the monomer, eliminates the possibility of condensation polymerization while presence of $C = C$, makes acrylonitrile unsaturated monomer and hence the only possible type of suitable polymerization is the addition polymerization.

(ii) Homopolymer is a polymer which is formed from only one kind of monomer while copolymer is a polymer which is formed from more than one kind of monomer unit. For example; polyethylene is homopolymer as it is formed from ethylene monomers only while poly(styrene-butadiene) is copolymer as it is formed from styrene and butadiene monomers.

Question 5

(a) The characteristics:

1. They are found in the right hand side of modern periodic table and therefore p-block elements consist of non-metals with few metals.
2. Due to their small atomic size, p-block elements have high ionization energy.
3. Due to their small atomic size accompanied with low ionization energy, p-block elements do not impart characteristic colour to the flame.
4. Due to their complex valence shell electronic structure, most of p-block elements have variable oxidation states.

(b) The factors are:

1. **The charge on the nucleus**
   The more protons there are in the nucleus, the more positively charged the nucleus is, and the more strongly electrons are attracted.
2. **The distance of the electron from the nucleus**
   The nucleus attraction to valence electron decrease very rapidly as the distance of the electron from the nucleus increases. An electron close to the nucleus will be much more strongly attracted than one farther away.
3. **The number of electrons between the outer electrons and the nucleus (screening effect)**
   As the number of electrons in inner shells and sub – shells increases, screening (or shielding) effect exerted by those electrons to outer electrons also increase and hence the amount of ionisation energy also decreases.
4. **Stability of electronic configuration**
   Two electrons in the same orbital experience some repulsion from each other. This off sets the attraction of the nucleus, so that paired electrons are removed rather easily than it would be expected.

(c) Oxides of period 3 elements are $Na_2O, MgO, Al_2O_3, SiO_2, P_4O_{10}, SO_3$ and Cl_2O_7 .

The first two oxides Na_2O and MgO are basic and therefore they react with water to give alkaline solution.

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$MgO + H_2O \rightarrow Mg(OH)_2$$

Al_2O_3 is insoluble in water (because its lattice energy is very high) and therefore it has no reaction with water.

$$Al_2O_3 + H_2O \rightarrow \text{No reaction}$$

The remaining oxides; SiO_2, P_4O_{10} (or P_2O_6), SO_3(or SO_2) and Cl_2O_7 are acidic and thus with exceptional of SiO_2 which is insoluble (because its molecules are held together by giant covalent bond in three dimensional structure), they react with water to give acidic solution (oxoacids).

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$
$$\text{Or} \quad P_2O_6 + 6H_2O \rightarrow 4H_3PO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$\text{Or} \quad SO_2 + H_2O \rightarrow H_2SO_3$$
$$Cl_2O_7 + H_2O \rightarrow 2HClO_4$$
$$\text{But} \quad SiO_2 + H_2O \rightarrow \text{No reaction}$$

(d) **Drawback:** H^+ (from water) will be discharged in preference to the sodium metal (H^+ has lower discharge potential than the metal).

At cathode: $2H^+(g) + 2e \longrightarrow H_2(g)$

Way to overcome: The evaporation of sea water will firstly be done to get solid sodium chloride. The solid sodium chloride is then melted and finally the electrolysis of fused chloride will be done to get the sodium metal.

That is; sea water $\xrightarrow[\text{Evaporation}]{} NaCl(s) \xrightarrow[\text{Melting}]{} NaCl(l)$

Then at cathode: $Na^+(l) + e \longrightarrow Na(s)$

Question 6

(a)

(i) From $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$ which is first order integral equation.

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right) \quad \text{where } a = 0.4M \text{ (when } t = 0)$$

When $\mathbf{t = 20min, a - x = 0.289M}$

$$\mathbf{k_1} = \frac{2.303}{20min}\log\left(\frac{0.4}{0.289}\right) = 0.016min^{-1}$$

When $\mathbf{t = 40min, a - x = 0.209M}$

$$\mathbf{k_2} = \frac{2.303}{40min}\log\left(\frac{0.4}{0.209}\right) = 0.016min^{-1}$$

When $\mathbf{t = 60min, a - x = 0.151M}$

$$\mathbf{k_3} = \frac{2.303}{60min}\log\left(\frac{0.4}{0.151}\right) = 0.0162min^{-1}$$

When $\mathbf{t = 80min, a - x = 0.109M}$

$$\mathbf{k_4} = \frac{2.303}{80min}\log\left(\frac{0.4}{0.109}\right) = 0.0163min^{-1}$$

$$\text{Rate constant, } \mathbf{k} = \frac{\mathbf{k_1 + k_2 + k_3 + k_4}}{4}$$

$$= \frac{(0.0162 + 0.0162 + 0.0162 + 0.0163)min^{-1}}{4}$$

$$= 0.016min^{-1}$$

Hence the rate constant for the reaction is $0.016min^{-1}$

(ii) Using $\log\left(\frac{a}{a-x}\right) = \frac{kt}{2.303}$

Substituting $\log\left(\frac{0.4M}{a-x}\right) = \frac{0.016\text{min}^{-1}\times 10\text{min}}{2.303}$

From which $a - x = 0.341M$

The concentration after 20 minutes is $0.341M$.

(b) Half-life for the first order reaction is given by $t_{1/2} = \frac{0.693}{k}$

From which; $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\times 60s} = 1.155\times 10^{-3}s^{-1}$

From the Arrhenius equation: $k = Ae^{-E_a/RT}$

$\ln k = \ln A + \ln e^{-E_a/RT}$;

$\ln k = \ln A + \frac{-E_a}{RT}\ln e$

But $\ln e = 1$

Then $\ln k = \ln A + \frac{-E_a}{RT}$

$\frac{E_a}{RT} = \ln A - \ln k = \ln\left(\frac{A}{k}\right)$

From which; $T = \frac{E_a}{R\ln\left(\frac{A}{k}\right)} = \frac{98.6\times 1000\text{Jmol}^{-1}}{8.31\text{Jmol}^{-1}\text{K}^{-1}\times\ln\left(\frac{4\times 10^{13}s^{-1}}{1.155\times 10^{-3}s^{-1}}\right)} = 311.56K$

The temperature is $311.56K$.

(c) For gases, number of moles varies directly proportional to their partial pressures. So in a chemical equation, pressure may be treated like number of moles as shown below:

	$SO_2Cl_2(g)$	$\longrightarrow$ $SO_2(g)$	$+ Cl_2(g)$
Initially (At $t = 0$)	0.5	0	0
After any time, t	$0.5 - x$	x	x

Thus, **total pressure after any time**, $t = 0.5 - x + x + x = \mathbf{0.5 + x}$

Integral equation of first order reaction in terms of partial pressures is given by the following equation: $\log\left(\frac{P_o}{P_o - P}\right) = \frac{kt}{2.303}$

From which; $k = \frac{2.303}{t}\log\left(\frac{P_o}{P_o - P}\right)$ where $P_o = 0.5$ and $P_o - P = 0.5 - x$

Thus $k = \frac{2.303}{t}\log\left(\frac{0.5}{0.5-x}\right)$

When $t = 100s, 0.5 + x = 0.6$ or $x = 0.1$

Substituting $k = \frac{2.303}{100s}\log\left(\frac{0.5}{0.5-0.1}\right) = 2.2318\times 10^{-3}s^{-1}$

Then $R = k[\ SO_2Cl_2] = k(0.5 - x)$

When total pressure is 0.65atm; $0.5 + x = 0.65$ or $x = 0.15$

Substituting $R = 2.2318\times 10^{-3}s^{-1}(0.5 - 0.15)\text{atm} = 7.81\times 10^{-4}\text{atm/s}$

The rate of the reaction is $7.81\times 10^{-4}\text{atm/s}$.