THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL OF TANZANIA

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/1 **CHEMISTRY 1**

(For Both School and Private Candidates)

Time: 3 Hours **ANSWERS** **Year: 2018**

Instructions

1. This paper consists of sections A, B and C with total of Fourteen questions

2. Each question carries ten marks

1. (a) Study carefully the Bohr's atomic model of hydrogen atom shown below then answer the questions that follow.

(i) State three basic postulates which led to Bohr's atomic model. Include mathematical expressions, if any, which qualify the postulate.

1. Electrons move in fixed circular orbits around the nucleus without emitting energy. These orbits are known as stationary states or energy levels.
2. The energy of an electron in a given orbit is quantized and given by:
   $E_n = -13.6 Z^2 / n^2$ eV
   where Z is the atomic number and n is the principal quantum number.
3. Electrons can transition between energy levels by absorbing or emitting photons with an energy equal to the difference between the two levels:
   $\Delta E = h\nu = E_{final} - E_{initial}$

(ii) In a single sketch of Bohr's atom, show how Lyman and Paschen spectral series are formed.

(Sketch should show transitions from higher energy levels to n=1 for Lyman series and to n=3 for Paschen series).

(b) The energy difference between ground and excited state of atoms of a certain element was found to be 4.4×10^{-19} J. Calculate the wavelength and wavenumber of the photons that excited the atoms. Show your work clearly including manipulations of units.

Step 1: Use the equation
$E = hc/\lambda$
$\lambda = hc / E$

Given:
$h = 6.626 \times 10^{-34}$ Js
$c = 3.0 \times 10^8$ m/s
$E = 4.4 \times 10^{-19}$ J

$\lambda = (6.626 \times 10^{-34} \times 3.0 \times 10^8) / (4.4 \times 10^{-19})$
$\lambda = 4.52 \times 10^{-7}$ m or 452 nm

Step 2: Calculate the wavenumber:
Wavenumber $(\tilde{\nu}) = 1/\lambda$
$\tilde{\nu} = 1 / (4.52 \times 10^{-7})$
$\tilde{\nu} = 2.21 \times 10^6\ m^{-1}$

(c) Dalton's atomic theory consists of four main postulates. For each of the two postulates given below, briefly describe an experiment or a discovery which is against the postulate.

(i) Atoms can neither be created nor destroyed.

- This postulate was disproved by nuclear reactions, where atoms undergo fission or fusion, resulting in the creation of new atoms or destruction of existing ones.

(ii) All atoms of the same element are alike.

- Isotopes disprove this postulate, as elements exist in different isotopic forms with the same atomic number but different mass numbers (e.g., Carbon-12 and Carbon-14).

2. (a) State the following:

(i) Boyle's law.

At constant temperature, the volume of a given mass of gas is inversely proportional to its pressure.
$P_1V_1 = P_2V_2$

(ii) Charles' law.

At constant pressure, the volume of a gas is directly proportional to its absolute temperature.
$V_1 / T_1 = V_2 / T_2$

(iii) Avogadro's law.

Equal volumes of gases at the same temperature and pressure contain an equal number of molecules.
$V \propto n$

(iv) Dalton's law of partial pressure.

The total pressure of a mixture of non-reacting gases is equal to the sum of the partial pressures of the individual gases.
$P\_total = P_1 + P_2 + P_3 + \ldots$

(v) Graham's law of diffusion.

The rate of diffusion of a gas is inversely proportional to the square root of its molar mass.
$Rate_1 / Rate_2 = \sqrt{(M_2 / M_1)}$

(b) (i) A certain amount of a gas was found to occupy 100 cm^3 at 33°C and 97×10^3 Nm^{-2}. Calculate the volume of the gas at standard temperature and pressure. Show your work clearly including manipulations of units.

Step 1: Use the combined gas law equation:

$(P_1V_1)/T_1 = (P_2V_2)/T_2$

Given:
$P_1 = 97 \times 10^3$ Nm^{-2}, $V_1 = 100$ cm^3, $T_1 = 33°C = (33+273)$ K = 306 K
$P_2 = 101.3 \times 10^3$ Nm^{-2}, $T_2 = 273$ K, $V_2 = ?$

$(97 \times 10^3 \times 100) / 306 = (101.3 \times 10^3 \times V_2) / 273$

$V_2 = (97 \times 10^3 \times 100 \times 273) / (306 \times 101.3 \times 10^3)$
$V_2 = 87.1$ cm^3

(ii) At 1.0 atmosphere pressure and 30°C, 1,236 g of a gas was found to occupy a volume of 512 cm^3. Calculate the relative molecular mass of the gas.

Molar mass (M) = (mass × RT) / (PV)

Given:
P = 1 atm = 101.3 kPa, V = 512 cm^3 = 0.512 L
T = 30°C = 303 K, R = 0.0821 L atm mol^{-1} K^{-1}
Mass = 1.236 g

$M = (1.236 \times 0.0821 \times 303) / (1 \times 0.512)$
M = 60.3 g/mol

(c) The compressibility factor, Z, is used to test the ideality or non-ideality of real gases.

(i) Write an expression for compressibility factor, Z.

$Z = PV / nRT$

(ii) At what values of Z a real gas shows ideal behavior, positive and negative deviation from ideality?

- $Z = 1$ → Ideal behavior
- $Z > 1$ → Positive deviation (repulsions dominate)
- $Z < 1$ → Negative deviation (attractions dominate)

3. (a) State the meaning of an ideal gas.

An ideal gas is a hypothetical gas that obeys all gas laws perfectly under all conditions, where intermolecular forces and the volume of individual gas molecules are negligible.

(b) State two postulates of kinetic molecular theory of gases which are incorrect for real gases. Express their corresponding corrections and derive the van der Waals' equation.

1. Gas molecules do not exert attractive or repulsive forces on each other.
   - Correction: Real gases exhibit intermolecular forces, especially at high pressures and low temperatures.
2. Gas molecules have negligible volume compared to the total volume.
   - Correction: The volume of gas molecules must be accounted for at high pressures.

Van der Waals equation:
$(P + a(n/V)^2) (V - nb) = nRT$

4. Given the information that, nitric acid ($T_b = 87°C$) and water form a constant boiling mixture of $T_b = 122°C$ and composition 65% by mass nitric acid.

(a) (i) Draw the boiling temperature - composition curve for nitric acid and water.

(Plot should show the azeotropic point at 65% HNO_3 and 122°C).

(ii) State what is meant by a constant boiling point mixture.

A mixture that boils at a constant temperature and retains the same composition in the liquid and vapor phase.

(b) (i) State Raoult's law.

The partial vapor pressure of a component in a mixture is proportional to its mole fraction in the liquid phase.

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

It shows a positive deviation because the mixture has a higher boiling point than either pure component.

(iii) With reference to Raoult's law, distinguish positive deviation from negative deviation.

- Positive deviation: Higher vapor pressure, weaker intermolecular forces.
- Negative deviation: Lower vapor pressure, stronger intermolecular forces.

(iv) What interaction between nitric acid and water gives rise to this type of deviation?

Hydrogen bonding, which leads to the formation of a more volatile azeotropic mixture.

5. (a) Classify the bonds in the following compounds as ionic, polar covalent, or covalent.

(i) HCl(g) - polar covalent
(ii) NaCl(s) - ionic
(iii) NCl_3 - polar covalent
(iv) Methane (CH_4) - covalent
(v) Tetrachloromethane (CCl_4) - covalent
(vi) CO_2 - covalent

(b) For each of the following compounds, show from electron configurations the type of hybrid orbital of the underlined atom and draw the geometry of the corresponding molecule.

(i) $BeCl_2$
- Hybridization: sp
- Geometry: Linear

(ii) CCl_4
- Hybridization: sp^3
- Geometry: Tetrahedral

(iii) SF_4
- Hybridization: sp^3d
- Geometry: See-saw

(c) Study carefully the information in the following table, then answer the questions that follow.

Name	Molecular weight	Boiling point, °C
Diethyl ether	74	35
n-Butyl alcohol	74	118
Propionamide	73	213

(i) Account on the high boiling point of n-butyl alcohol compared to diethyl ether, while the two compounds have the same molecular weight.

- The high boiling point of n-butyl alcohol is due to the presence of strong intermolecular hydrogen bonding between hydroxyl (-OH) groups, which requires more energy to break, whereas diethyl ether lacks hydrogen bonding and only has weak van der Waals forces.

(ii) Account on the low boiling point of n-butyl alcohol compared to propionamide despite its higher molecular weight.

- Propionamide has stronger intermolecular hydrogen bonding due to the presence of the amide ($-CONH_2$) functional group, which can form more extensive hydrogen bonds compared to the hydroxyl (-OH) group in n-butyl alcohol. This results in a higher boiling point for propionamide.

6. (a) Briefly give the meaning of the following phrases as used in chemical energetics:

(i) Heat of solution
- The amount of heat energy released or absorbed when one mole of a substance dissolves in a given amount of solvent to form a solution at constant pressure.

(ii) Spontaneous reaction
- A reaction that occurs naturally without any external energy input because it results in a decrease in Gibbs free energy ($\Delta G < 0$).

(iii) Enthalpy change
- The total heat content change of a system at constant pressure, represented as ΔH, which can be either exothermic (negative) or endothermic (positive).

(iv) Heat of sublimation
- The amount of heat required to convert one mole of a solid directly into a gas without passing through the liquid state at a given pressure.

(v) Endothermic reaction
- A chemical reaction that absorbs heat from the surroundings, resulting in a positive enthalpy change ($\Delta H > 0$).

(b) During chemical reactions, bonds 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
- In an exothermic reaction, the bonds in the products are stronger than those in the reactants, meaning energy is released as new bonds form.
(ii) Endothermic
- In an endothermic reaction, the bonds in the reactants are stronger than those in the products, meaning energy is absorbed to break the reactant bonds.

(c) State the types of enthalpies in each of the following equations:

(i) $KOH(aq) + HCl(aq) \text{------>} KCl(aq) + H_2O(l)$
- Enthalpy of neutralization ($\Delta H = -57 \text{ kJ mol}^{-1}$)

(ii) $H_2(g) + 1/2\ O_2(g) \text{------>} H_2O(l)$
- Enthalpy of formation ($\Delta H = -286 \text{ kJ mol}^{-1}$)

(iii) $H_2(g) + Cl_2(g) \text{------>} 2HCl(aq)$
- Enthalpy of reaction ($\Delta H = -164 \text{ kJ mol}^{-1}$)

(iv) $Cl_2(g) + e^- \text{------>} Cl^-(g)$
- Electron affinity ($\Delta H = -347$ kJ mol^{-1})

(d) Two liquids, trichloromethane ($CHCl_3$) and ethoxyethane ($CH_3CH_2OCH_2CH_3$), form intermolecular hydrogen bonds when mixed. In a certain experiment, 0.5 moles of trichloromethane and 0.3 moles 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 was recorded upon mixing. Assume that the heat capacity of the calorimeter is negligible, while heat capacities of trichloromethane and ethoxyethane are 0.98 J g^{-1} K^{-1} and 2.28 J g^{-1} K^{-1}, respectively. Calculate:

(i) Heat change in this experiment.

Step 1: Find the mass of each component.
Mass of $CHCl_3$ = $0.5 \times (12 + 1 + 3\times35.5) = 0.5 \times 119.5 = 59.75$ g
Mass of $CH_3CH_2OCH_2CH_3$ = $0.3 \times (2\times12 + 6\times1 + 1\times16) = 0.3 \times 74 = 22.2$ g

Step 2: Calculate heat change for each liquid.
$Q = mc\Delta T$

For $CHCl_3$:
$Q_1 = (59.75 \times 0.98 \times 5.4) = 316.6$ J

For $CH_3CH_2OCH_2CH_3$:
$Q_2 = (22.2 \times 2.28 \times 5.4) = 273.5$ J

Total heat change:
Q_total = 316.6 + 273.5 = 590.1 J

(ii) Enthalpy change of mixing one mole of trichloromethane with excess ethoxyethane.

ΔH = Q_total / n
n = 0.5 moles of $CHCl_3$
$\Delta H = 590.1 / 0.5$
$\Delta H = 1180.2$ J mol^{-1}

7. (a) State the four colligative properties useful for determination of molecular masses.

1. Relative lowering of vapor pressure
2. Boiling point elevation
3. Freezing point depression

4. Osmotic pressure

(b) Study the following diagram and then answer the subsequent questions.

(i) Give the titles of the locations labeled A, B, C, D, E, and F.

- A: Boiling point of pure solvent
- B: Boiling point of solution
- C: Vapor pressure of pure solvent
- D: Vapor pressure of solution
- E: Freezing point of pure solvent
- F: Freezing point of solution

(ii) Give the names for the difference given by F-E (i.e., F minus E) and D-C (i.e., D minus C).

- F-E: Freezing point depression
- D-C: Boiling point elevation

(c) Ammonium chloride solution was dissolved in water to make a 25% solution. Calculate the temperature at which this solution freezes. The molal boiling point constant for NH_4Cl is -1.86°C kg mol^{-1}.
Step 1: Find the molality of NH_4Cl.
Mass of NH_4Cl = 25 g
Mass of water = 75 g = 0.075 kg
Moles of $NH_4Cl = 25 / (14 + 4 + 35.5) = 25 / 53.5 = 0.467$ mol
Molality = 0.467 / 0.075 = 6.23 m

Step 2: Find freezing point depression.
$\Delta T\_f = i \times K\_f \times m$
i = 2 (since NH_4Cl dissociates into NH_4^+ and Cl^-)
$\Delta T\_f = 2 \times 1.86 \times 6.23$
$\Delta T\_f = 23.2°C$

New freezing point = 0 - 23.2 = -23.2°C

8. (a) 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 99°C, given that the vapor pressure of water at 99°C is 9.749×10^4 Pa.

Step 1: Find the vapor pressure of nitrobenzene.
Total pressure = 1.013×10^5 Pa
Pressure of nitrobenzene = $1.013 \times 10^5 - 9.749 \times 10^4$
$P\_nitrobenzene = 3.81 \times 10^3$ Pa

Step 2: Calculate mass percentage.
% mass = $(P_{nitrobenzene} \times M_{nitrobenzene}) / (P_{water} \times M_{water} + P_{nitrobenzene} \times M_{nitrobenzene}) \times 100$
$= (3.81 \times 10^3 \times 123) / [(9.749 \times 10^4 \times 18) + (3.81 \times 10^3 \times 123)] \times 100$
$= (46863) / (1754820 + 46863) \times 100$
$= (46863 / 1801683) \times 100$
= 2.6%

(c) Show how the equation for the partitioning law of solute "X" dissolved in two immiscible solvents A and B will be represented when solute "X":

(i) Associates in solvent A and remains normal in solvent B.
$K = [X]_B / [X]_A^2$

(ii) Dissociates in solvent A and associates in solvent B.
$K = [X]_B^2 / [X]_A$

(iii) Dissociates in solvent B and remains normal in solvent A.
$K = [X]_B / [X]_A$

(d) Fifty (50) grams of the acid are dissolved in one litre (1000 cm³) of water. The distribution coefficient of the acid between ether and water is 3. A volume of 1000 cm³ of ether is available for use in the extraction process. Two experiments were performed to extract acid from water. In the first experiment, 1000 cm³ of ether was used once, i.e., single extraction. In the second experiment, two extractions were performed, each using 500 cm³ of ether. Compare the amounts of the acid left in the aqueous solution in each case and recommend the best method to extract the acid from water.

Step 1: Understanding the distribution coefficient
The distribution coefficient, K, is given as:
K = [acid] in ether / [acid] in water = 3

This means that the ratio of the concentration of acid in ether to the concentration in water is 3:1 at equilibrium.
Step 2: Single extraction with 1000 cm³ of ether
Let x be the fraction of acid that remains in water after extraction.

Applying the partition law:
$x = (V_w / (K \times V_e + V_w))$

where:
V_w = volume of water = 1000 cm³
V_e = volume of ether used = 1000 cm³
K = 3

$x = (1000 / (3 \times 1000 + 1000))$
$x = (1000 / 4000)$
$x = 0.25$

Amount of acid left in water = 0.25 × 50 g = 12.5 g

Step 3: Double extraction with 500 cm^3 of ether each time
For the first extraction (using 500 cm^3 ether):

$x_1 = (Vw / (K \text{ x } Ve + Vw))$
$x_1 = (1000 / (3 \times 500 + 1000))$
$x_1 = (1000 / 2500)$
$x_1 = 0.4$
Amount of acid left after first extraction = 0.4 × 50 = 20 g
For the second extraction (using 500 cm^3 ether again):

Now, Vw = 1000 cm^3 and the remaining acid = 20 g.

$x_2 = (1000 / (3 \times 500 + 1000))$
$x_2 = (1000 / 2500)$
$x_2 = 0.4$

Amount of acid left after second extraction = 0.4 × 20 = 8 g

Step 4: Comparison and recommendation
- Single extraction with 1000 cm^3 ether leaves 12.5 g of acid in water.
- Double extraction with 500 cm^3 ether each time leaves 8 g of acid in water.

Since double extraction removes more acid from water, it is the better method for extracting the acid effectively.

9. (a) (i) State the law of mass action.

- The law of mass action states that the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants, each raised to the power of their respective stoichiometric coefficients in the balanced chemical equation.

(ii) State the Le Chatelier's principle.

- Le Chatelier's principle states that if an external change is applied to a system at equilibrium, the system will adjust itself to counteract the change and restore a new equilibrium state.

(iii) Define dynamic equilibrium.

- Dynamic equilibrium is a state in a reversible reaction where the rate of the forward reaction is equal to the rate of the backward reaction, and the concentrations of reactants and products remain constant over time.

(iv) State three factors that change the position of the chemical equilibrium.

1. Change in concentration of reactants or products
2. Change in temperature
3. Change in pressure (for gaseous systems)

(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 vapor and 3.0 moles of CO is allowed to come to equilibrium. The equilibrium pressure is 2.0 atm.

(i) Calculate the number of moles of H_2 present at equilibrium.

Let x be the number of moles of H_2 formed at equilibrium. The initial moles of reactants and products are:

$CO = 3.0$, $H_2O = 1.0$, $CO_2 = 0$, $H_2 = 0$

At equilibrium:

$CO = (3.0 - x)$, $H_2O = (1.0 - x)$, $CO_2 = x$, $H_2 = x$

The equilibrium expression for the reaction is:
$Kc = [CO_2][H_2] / [CO][H_2O]$

Substituting the values:
$0.63 = (x * x) / [(3.0 - x)(1.0 - x)]$

Solving for x will give the number of moles of H_2 at equilibrium.

(ii) Calculate the partial pressure of gases at equilibrium mixture.

The partial pressure of each gas at equilibrium is given by:
P_gas = (n_gas / total n) × P_total

Using the total number of moles and solving for each gas will give the respective partial pressures.

(c) The chief reaction used in the contact process is $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 4200$ kJ. On the basis of Le Chatelier's principle, briefly explain three conditions that are available for the maximum yield of $SO_3(g)$.

1. Lowering the temperature: Since the forward reaction is exothermic, decreasing temperature shifts equilibrium to the right, increasing SO_3 yield.
2. Increasing pressure: Since there are fewer moles of gas in the product (2 moles) compared to the reactants (3 moles), increasing pressure favors the forward reaction.
3. Using a catalyst (V_2O_5): A catalyst speeds up the reaction without affecting equilibrium, allowing the reaction to reach equilibrium faster.

10. (a) Use appropriate examples to differentiate between dative and covalent bonds.

- A dative bond (coordinate bond) is formed when one atom donates a lone pair of electrons to another atom, e.g., NH_4^+.
- A covalent bond is formed by the mutual sharing of electrons between atoms, e.g., Cl_2.

(b) With the help of sketches, briefly explain the following concepts:

(i) Two types of hydrogen bonding, giving one example for each.
1. Intermolecular hydrogen bonding - occurs between molecules, e.g., water (H_2O).
2. Intramolecular hydrogen bonding - occurs within the same molecule, e.g., o-nitrophenol.

(ii) Why ortho-nitrophenol has a lower boiling point than para isomer.
- Ortho-nitrophenol has intramolecular hydrogen bonding, reducing intermolecular forces, leading to a lower boiling point compared to para-nitrophenol, which has strong intermolecular hydrogen bonding.

(iii) Ethene has a planar geometry.
- The carbon atoms in ethene are sp^2 hybridized, resulting in a trigonal planar structure with a bond angle of 120°.

(iv) Methane has tetrahedral geometry.
- The carbon atom in methane is sp^3 hybridized, forming a tetrahedral structure with bond angles of 109.5°.

(c) (i) State two conditions that are necessary for the formation of a hydrogen bond.
- The presence of a highly electronegative atom (O, N, or F) in the molecule.
- The presence of a hydrogen atom attached to this electronegative atom.

(ii) State two effects of hydrogen bonding.
- Increased boiling and melting points of compounds.
- Increased solubility of compounds in water.

(iii) How many sigma (σ) and pi (π) bonds are formed between C-C in ethyne?
- Ethyne has one sigma (σ) bond and two pi (π) bonds between carbon atoms.

11. (a) $CH_3CH_2CH_2CH_3$ has a boiling point of -1°C while CH_3CHCH_3 has a boiling point of -12°C.

Briefly explain this observation.
- $CH_3CH_2CH_2CH_3$ (butane) is a straight-chain alkane with stronger van der Waals forces, leading to a higher boiling point. CH_3CHCH_3 (isobutane) is branched, reducing intermolecular interactions and lowering its boiling point.

(b) (i) With one example, state the meaning of "Friedel-Crafts acylation".
- Friedel-Crafts acylation is a reaction in which an acyl chloride or acid anhydride reacts with an aromatic ring in the presence of a Lewis acid catalyst ($AlCl_3$) to form a ketone. Example: Benzene reacts with acetyl chloride (CH_3COCl) to form acetophenone.

(ii) With the aid of illustration, show the reaction mechanism between benzene and nitric acid in the presence of sulfuric acid.
- This involves the generation of the nitronium ion (NO_2^+), which acts as the electrophile in electrophilic aromatic substitution to form nitrobenzene.

(iii) 1,3-dimethylbenzene is oxidized by potassium dichromate(VI) solution. Draw the chemical structure of the product of the reaction.
- The oxidation of 1,3-dimethylbenzene results in the formation of 1,3-benzenedicarboxylic acid (isophthalic acid).

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

(i) $CH_4 + Cl_2$ -----> (UV light) -----> $CH_3Cl + HCl$

(ii) $CH_3\text{-}CH{=}CH_2 + H_2SO_4$ ----------> $CH_3\text{-}CH(OSO_3H)\text{-}CH_3$ (alkyl hydrogen sulfate)
Heat -------> $CH_3\text{-}CH(OH)\text{-}CH_3$ (propan-2-ol)

(iii) $H_3C\text{-}C{\equiv}C\text{-}H + CuCl(aq) + NH_3$ -------> $H_3C\text{-}C{\equiv}C\text{-}Cu + NH_4Cl$

(iv) $CaC_2 + H_2O$ -------> $C_2H_2 + Ca(OH)_2$

12. (a) Give the structural formula of aromatic compounds F to M which are formed in the following reaction scheme.

- The reactions involve halogenation, nitration, oxidation, and substitution of benzene derivatives. The products include brominated, nitro, and oxidized benzene compounds.

(b) What is the product for the chlorination of benzene and methylbenzene in the presence of:
(i) a halogen carrier catalyst
- Benzene undergoes electrophilic substitution with chlorine in the presence of $AlCl_3$ to form chlorobenzene.

(ii) ultra-violet light

- Methylbenzene (toluene) undergoes free radical chlorination under UV light, leading to the formation of benzyl chloride ($C_6H_5CH_2Cl$).

13. (a) With the aid of reaction equations, outline six different applications of haloalkanes in organic synthesis processes. Use R-X as a haloalkane.

1. Formation of Grignard Reagents
   RX + Mg -----> RMgX
   Grignard reagents are used in the synthesis of alcohols, carboxylic acids, and hydrocarbons.

2. Nucleophilic Substitution to Form Alcohols
   RX + NaOH ------> ROH + NaX
   Used in the synthesis of primary, secondary, and tertiary alcohols.

3. Formation of Ethers via Williamson Ether Synthesis
   RX + R'ONa -----> ROR' + NaX
   Used to prepare symmetrical and unsymmetrical ethers.

4. Preparation of Alkanes via Wurtz Reaction
   RX + 2Na + XR -------> R-R + 2NaX
   Useful for extending carbon chains.

5. Synthesis of Amines via Gabriel Amine Synthesis
   RX + NH_3 ---------> RNH_2 + HX
   Important in the formation of primary amines.

6. Elimination Reactions to Form Alkenes
   RX + Base ---------> Alkene + HX
   Used to introduce double bonds in organic molecules.

(b) For each pair of compounds given below, provide a chemical test to distinguish them.

(i) Chlorobenzene and Benzyl chloride
   - Silver Nitrate Test: Benzyl chloride reacts with $AgNO_3$ to form a white precipitate of AgCl, whereas chlorobenzene does not react due to the strong C-Cl bond in the benzene ring.

(ii) $CH_3C=CH_2Br$ and $H_2C=C-CH_3Br$
   - Bromine Water Test: $CH_3C=CH_2Br$ will decolorize bromine water due to the presence of a terminal double bond, whereas $H_2C=C-CH_3Br$ will react slowly.

(c) Silver nitrate solution does not precipitate the chloride in 1-chloropropene, but it does so in 1-chloropropane. Give a reason to account for this.

- In 1-chloropropene, the chlorine is bonded to a sp^2 hybridized carbon, making the C-Cl bond stronger and less susceptible to nucleophilic substitution, preventing AgCl precipitation. In 1-chloropropane, the chlorine is bonded to a sp^3 hybridized carbon, making it more reactive and allowing $AgNO_3$ to form a precipitate.

14. (a) Arrange the following alkyl chlorides in order of decreasing reactivity in an SN_1 reaction:

(i) CH_3Br
(ii) $C(CH_3)_2Br$
(iii) $CH(CH_3)_2Br$
(iv) $CH_3CH_2CH_2Br$

Order of reactivity in SN_1: $C(CH_3)_2Br > CH(CH_3)_2Br > CH_3CH_2CH_2Br > CH_3Br$
- The tertiary alkyl halide ($C(CH_3)_2Br$) is most reactive due to the stability of the carbocation formed.
- The secondary halide ($CH(CH_3)_2Br$) is less reactive than tertiary but more reactive than primary.
- The primary halide ($CH_3CH_2CH_2Br$) is even less reactive.
- Methyl halide (CH_3Br) is the least reactive due to the instability of a methyl carbocation.

(b) Write the mechanism for the following substitution reactions:

(i) $CH_3CH_2OH + HBr$ ---------> $CH_3CH_2Br + H_2O$
- This reaction follows an SN_2 mechanism:
  - Step 1: Protonation of OH group by HBr to form $CH_3CH_2OH_2^+$.
  - Step 2: Br^- attacks $CH_3CH_2OH_2^+$, leading to substitution and formation of CH_3CH_2Br.

(ii) $CH_3SCH_3 + CH_3I$ ----------> $(CH_3)_3S^+ I^-$
- This reaction follows an SN_2 mechanism:
  - Step 1: The nucleophile (CH_3SCH_3) attacks CH_3I from the opposite side of the leaving group.
  - Step 2: The I^- leaves, forming $(CH_3)_3S^+ I^-$.

(c) When phenol is treated with Br_2, a mixture of mono bromo phenol, dibromo phenol, and tribromo phenols are obtained. Write a synthesis mechanism to convert phenol to:

(i) 2-bromophenol
- Phenol + Br_2 (low temperature, in CS_2 or CCl_4) --------> 2-Bromophenol (major) + 4-Bromophenol (minor)

(ii) 4-bromophenol
- Phenol + Br_2 (in acetic acid or glacial acetic acid) ------> 4-Bromophenol (major)

- The reaction conditions control regioselectivity by directing bromine to either the ortho or para position.