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: 2022**

Instructions

1. This paper consists of sections A and B with total of ten questions
2. Each question carries ten marks in section A and fifteen marks in section B.

1. (a) Energy of an electron in hydrogen atom is given by the expression

$E_n = -1.312 \times 10^6 / n^2$ J/mol.

(i) Calculate the amount of energy required to promote an electron from the first energy level to the third energy level.

Solution:

Given formula:
$E_n = -1.312 \times 10^6 / n^2$ J/mol

For n = 1:
$E_1 = -1.312 \times 10^6 / 1^2 = -1.312 \times 10^6$ J/mol

For n = 3:
$E_3 = -1.312 \times 10^6 / 3^2 = -1.312 \times 10^6 / 9$
$E_3 = -1.457 \times 10^5$ J/mol

Energy required to promote the electron:
$\Delta E = E_3 - E_1$
$\Delta E = (-1.457 \times 10^5) - (-1.312 \times 10^6)$
$\Delta E = 1.166 \times 10^6$ J/mol

(ii) Why an electron in its ground state possesses energy less than zero?

Solution:

An electron in its ground state possesses negative energy because it is bound to the nucleus and requires energy to be removed. The negative value represents the stability of the electron within the atom. A free electron, which is not bound to any nucleus, has zero energy. Therefore, the energy being negative indicates that work must be done to remove the electron completely from the atom.

(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 1500 kJ/mol and the atomic radii are 1.60, 0.94 and 1.97Å. Identify the three elements and match the appropriate ionization energy and atomic radius to each configuration.

Solution:

Step 1: Identify the elements

- X: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ corresponds to argon (Ar), a noble gas with a high ionization energy.
- Y: $1s^2\ 2s^2\ 2p^6\ 3s^2$ corresponds to magnesium (Mg), an alkaline earth metal.
- Z: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ corresponds to potassium (K), an alkali metal.

Step 2: Match atomic radius and ionization energy

- Argon (X): Ionization energy = 1500 kJ/mol, Atomic radius = 0.94Å.
- Magnesium (Y): Ionization energy = 740 kJ/mol, Atomic radius = 1.60Å.
- Potassium (Z): Ionization energy = 420 kJ/mol, Atomic radius = 1.97Å.

(ii) Excited sodium atoms may emit radiation with the frequency of $5.09 \times 10^{14}\ s^{-1}$. What is the energy of the photons associated with this radiation?

Solution:

Energy of a photon is given by:
$E = h\nu$

Where:
$h = 6.626 \times 10^{-34}$ J·s (Planck's constant)
$\nu = 5.09 \times 10^{14}\ s^{-1}$

$E = (6.626 \times 10^{-34}) \times (5.09 \times 10^{14})$
$E = 3.37 \times 10^{-19}$ J

(c) Briefly, differentiate the following terms:

(i) Line from continuous spectrum.

Solution:

A line spectrum consists of discrete lines of specific wavelengths emitted or absorbed by atoms, indicating electronic transitions. A continuous spectrum, on the other hand, contains all wavelengths of light without gaps, such as the spectrum of white light.

(ii) Absorption from emission spectrum.

Solution:

An absorption spectrum is formed when atoms absorb specific wavelengths of light, creating dark lines in the spectrum. An emission spectrum is produced when excited atoms release energy at specific wavelengths, forming bright lines against a dark background.

2. (a) Consider the following reaction that takes place in a fixed volume of a container:

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ $\Delta H = -104$ kJ/mol.

How each of the changes affect the quantity of the reactants, products and equilibrium constant (Kc)? Answer appropriately in a tabular form.

Solution:

Change	H_2	Br_2	HBr	Kc Value
Addition of some H_2	-	-	+	No change
Removal of some HBr	+	+	-	No change
Raise in temperature	+	+	-	Decrease
Increase in pressure	-	-	+	No change

(b) When the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ was studied at 25°C, the partial pressures at equilibrium were found to be 1.2 atm for NOCl, 5.0×10^{-2} atm for NO and 0.3 atm for Cl_2. What would be the Kp value for this reaction at 25°C?

Solution:

Kp is given by:

$Kp = (P_{NOCl})^2 / (P_{NO})^2 (P_{Cl_2})$

Substituting the given values:

$Kp = (1.2)^2 / (5.0 \times 10^{-2})^2 (0.3)$

$Kp = 1.44 / (2.5 \times 10^{-3} \times 0.3)$
$Kp = 1.44 / (7.5 \times 10^{-4})$
$Kp = 1920$

3. (a) If the vapour pressure of water at 20°C is 17.5 mmHg and lowering of vapour pressure of a sugar solution is 0.061 mmHg, calculate:

(i) The relative lowering of vapour pressure.

Solution:

Relative lowering of vapour pressure = (P° - P) / P°

= (17.5 - (17.5 - 0.061)) / 17.5
= 0.061 / 17.5
= 3.49×10^{-3}

(ii) The vapour pressure of the solution.

Solution:

$P_{solution}$ = P° - lowering of vapour pressure
= 17.5 - 0.061
= 17.439 mmHg

(iii) The mole fraction of sugar and water.

Solution:

Mole fraction of solute = Relative lowering of vapour pressure
= 3.49×10^{-3}

Mole fraction of water = 1 - 3.49×10^{-3}
= 0.9965

(b) Ethanoic acid had a freezing point of 16.63°C. When 2.5 g of an organic solute was added to 40 g of the acid, the freezing point was lowered to 14.48°C. Calculate the relative molecular mass of the solute.

Solution:

$\Delta T_f = T°_f - T_f$
= 16.63 - 14.48
= 2.15°C

Using the freezing point depression formula:

$m = \Delta T_f / Kf$
m = 2.15 / 3.9
m = 0.5513 mol/kg

Mass of solute = 2.5 g
Mass of solvent = 40 g = 0.04 kg

Moles of solute = m × kg solvent
= 0.5513 × 0.04
= 0.02205 mol

Molar mass = Mass / Moles
= 2.5 / 0.02205
= 113.4 g/mol

3. (c) An aqueous solution freezes at 272.07 K while pure water freezes at 273 K. Calculate the molality and boiling point of this solution (Given Kf for water = 1.86 K/m, Kb = 0.512 K/m).

Solution:

Step 1: Calculate the molality using the freezing point depression formula:

$\Delta Tf = Kf \times m$

where,
$\Delta Tf = 273 - 272.07 = 0.93$ K
Kf = 1.86 K/m

$m = \Delta Tf / Kf$
m = 0.93 / 1.86
m = 0.5 mol/kg

Step 2: Calculate the boiling point elevation:

$\Delta Tb = Kb \times m$

where,
Kb = 0.512 K/m
m = 0.5 mol/kg

$\Delta Tb = 0.512 \times 0.5$
$\Delta Tb = 0.256$ K

Boiling point of solution = $373 + \Delta Tb$
= 373 + 0.256
= 373.26 K

4. (a) (i) Predict whether a chemical bond will be covalent or ionic based on the charge and the relative size of the cations and anions as follows:

Cation/anion	Ionic radius (nm)	Chemical bond
C^{4+}	0.015	Covalent
I^{-}	0.216	Ionic
Na^{+}	0.095	Ionic
F^{-}	0.136	Ionic

(ii) "Intermolecular hydrogen bonding and dative covalent bonding are among the types 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.

Solution:

Intermolecular hydrogen bonding occurs when a hydrogen atom, covalently bonded to a highly electronegative element (such as oxygen, nitrogen, or fluorine), interacts with another electronegative atom from a neighboring molecule.

Example: Water (H_2O) forms hydrogen bonds between the oxygen of one molecule and the hydrogen of another molecule.

Dative covalent bonding (coordinate bonding) occurs when one atom donates both electrons for bond formation.

Example: The ammonium ion (NH_4^+) forms a dative covalent bond when an unshared electron pair on nitrogen is donated to a proton (H^+).

(b) Briefly, comment on 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.

Solution:

Fluorine is the most electronegative element, creating a highly polar H-F bond. The partial positive charge on hydrogen in HF is strongly attracted to the lone pairs of fluorine atoms in neighboring molecules, forming hydrogen bonds. In contrast, chlorine and bromine have lower electronegativities and larger atomic sizes, leading to weaker dipole-dipole interactions and the absence of hydrogen bonding.

(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.

Solution:

Hydrogen chloride (HCl) is a polar molecule with permanent dipole-dipole interactions, which dominate intermolecular forces. When placed together, these dipole forces prevent temporary dipole interactions. However, when HCl is placed with non-polar argon (Ar), the HCl molecules induce a temporary dipole in the Ar atoms, leading to induced dipole interactions.

(c) (i) What is the difference between sp^2 and sp hybridization?

Solution:

sp^2 hybridization occurs when one s orbital and two p orbitals mix, forming three equivalent hybrid orbitals arranged in a trigonal planar geometry with bond angles of 120°. It is commonly found in alkenes and aromatic compounds.

sp hybridization occurs when one s orbital and one p orbital mix, forming two equivalent hybrid orbitals arranged in a linear geometry with bond angles of 180°. It is typically observed in alkynes and molecules with triple bonds.

(ii) Which bond is stronger than the other in each of the following pairs? Give a reason for your choice.

C=O or C-O
C-N or C=O
C-C or C≡C

Solution:

C=O is stronger than C-O because the presence of a double bond increases bond order, reducing bond length and increasing bond strength.

C=O is stronger than C-N because oxygen is more electronegative than nitrogen, creating a stronger bond due to better orbital overlap.

C≡C is stronger than C-C because a triple bond consists of one sigma and two pi bonds, leading to shorter bond length and greater bond energy compared to a single bond.
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 that 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

Solution:
Step 1: Oxidation of propene with cold dilute potassium permanganate ($KMnO_4$) to form propane-1,2-diol.
CH_3-CH=CH_2 + $KMnO_4$ + H_2O -----> CH_3-CHOH-CH_2OH

(ii) Acetone from 2-methyl propene

Solution:
Step 1: Hydration of 2-methylpropene using sulfuric acid and water to form 2-methyl-2-propanol.
$(CH_3)_2C$=CH_2 + H_2O ----> $(CH_3)_2C(OH)$-CH_3

Step 2: Oxidation of 2-methyl-2-propanol using acidified potassium dichromate to form acetone.
$(CH_3)_2C(OH)$-CH_3 + [O] -----> $(CH_3)_2CO$ + H_2O

(iii) Ethanol from propane

Solution:
Step 1: Halogenation of propane using bromine in the presence of UV light to form 1-bromopropane.
$CH_3CH_2CH_3$ + Br_2 -------> $CH_3CH_2CH_2Br$ + HBr

Step 2: Hydrolysis of 1-bromopropane with aqueous KOH to form propanol.
$CH_3CH_2CH_2Br$ + KOH ------> $CH_3CH_2CH_2OH$ + KBr

Step 3: Oxidation of propanol with acidified potassium dichromate to form propanal and further oxidation to ethanol.
$CH_3CH_2CH_2OH$ + [O] ----> CH_3CH_2CHO + H_2O
CH_3CH_2CHO + [O] -----> CH_3CH_2OH

(iv) Ethyne from calcium carbide

Solution:
Step 1: Hydrolysis of calcium carbide with water to produce ethyne.
CaC_2 + $2H_2O$ -----> C_2H_2 + $Ca(OH)_2$

(b) Use Markovnikov's rule to predict the products of the following reactions:
(i) H_3C-C=CH_2 + H_2O ---->

Solution:
According to Markovnikov's rule, the hydroxyl (-OH) group attaches to the more substituted carbon, forming 2-propanol.
H_3C-CH(OH)-CH_3

(ii) $H_3C\text{-}C{=}CH_2$ + HBr ----->

Solution:
The Br^- ion will attach to the more substituted carbon, forming 2-bromopropane.
$H_3C\text{-}CH(Br)\text{-}CH_3$
(iii) $H_3C\text{-}C{=}CH_2$ + HI ---->

Solution:
The iodine atom attaches to the more substituted carbon, forming 2-iodopropane.
$H_3C\text{-}CH(I)\text{-}CH_3$

(c) "Wurtz synthesis is not suitable for preparation of an asymmetrical alkane." Briefly, justify this statement while supporting your answer with a chemical equation.

Solution:
Wurtz synthesis involves the reaction of alkyl halides with sodium metal in dry ether to form alkanes. When two different alkyl halides are used, a mixture of symmetrical and asymmetrical alkanes is obtained, making the process unsuitable for a pure asymmetrical alkane.

Example:
$CH_3Br + C_2H_5Br + 2Na$ -----> $CH_3\text{-}CH_2\text{-}CH_3 + CH_3\text{-}CH_3 + C_2H_5\text{-}C_2H_5$

6. (a) (i) Given 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 (ΔH) for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$.

Solution:
$\Delta H = \Sigma\ \Delta Hf\ (products) - \Sigma\ \Delta Hf\ (reactants)$

$\Delta H = [\Delta Hf\ (CO) + \Delta Hf\ (H_2O)] - [\Delta Hf\ (CO_2) + \Delta Hf\ (H_2)]$

$\Delta H = [-121.31 + (-241.8)] - [-393.5 + 0]$
$\Delta H = -363.11 + 393.5$

$\Delta H = 30.39$ kJ

(ii) What are the four factors affecting the quantity of heat evolved or absorbed during a physical or chemical transformation?

Solution:
1. Nature of the substances involved - Different substances have different enthalpy changes.
2. Mass of the substances - A larger quantity of reactants releases or absorbs more heat.
3. Temperature and pressure conditions - These affect reaction rates and heat transfer.

4. Phase of the reactants and products - Gaseous, liquid, and solid states require different amounts of energy.

(b) Determine the heat of formation of ethyne based on the following information given by the reactions A-D.

A: $C(s) + O_2(g)$ ------> $CO_2(g)$ $\Delta H = -393$ kJ mol^{-1}
B: $H_2(g) + 1/2O_2(g)$ ------> $H_2O(l)$ $\Delta H = -286$ kJ mol^{-1}
C: $6C(s) + 3H_2(g)$ ---------> $C_2H_2(g)$ $\Delta H = +50.2$ kJ mol^{-1}
D: $C_2H_2(g) + 5/2O_2(g)$ ------> $2CO_2(g) + H_2O(l)$ $\Delta H = -1233$ kJ mol^{-1}

Solution:
Using Hess's Law, we combine equations to obtain the formation reaction:

$C(s) + H_2(g)$ -------> $C_2H_2(g)$

Using given enthalpy values:
$\Delta H = \Delta H\_D - [2 \times \Delta H\_A + \Delta H\_B]$

$\Delta H = -1233 - [2(-393) + (-286)]$

$\Delta H = -1233 + 786 + 286$

$\Delta H = -161$ kJ/mol

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 measures of environmental degradation you can address to the community?

Solution:

1. Promotion of afforestation and reforestation to reduce deforestation and maintain ecological balance.
2. Proper waste management practices, including recycling and proper disposal of industrial and domestic waste.
3. Regulation of industrial emissions and use of cleaner production technologies to minimize air and water pollution.
4. Public education and awareness programs on the importance of sustainable environmental conservation.

(b) "Most of the greenhouse gases are produced from anthropogenic activities." Justify this statement by giving two reasons using your answer with appropriate chemical equation in each case.

Solution:
1. Burning fossil fuels releases carbon dioxide (CO_2), a major greenhouse gas.
$C_8H_{18} + O_2$ ---------> $CO_2 + H_2O$

2. Industrial and agricultural activities release methane (CH_4) from livestock farming and landfills.
$CH_4 + O_2$ -----> $CO_2 + H_2O$
(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?

Solution:
1. Formation of sulfur dioxide from combustion of fossil fuels:
$S + O_2$ ------------> SO_2

2. Oxidation of sulfur dioxide to sulfur trioxide:
$2SO_2 + O_2$ --------> $2SO_3$

3. Reaction of sulfur trioxide with water to form sulfuric acid:
$SO_3 + H_2O$ --------> H_2SO_4

4. Formation of nitric acid from nitrogen oxides in the atmosphere:
$2NO_2 + H_2O$ -------> $HNO_3 + HNO_2$

8. (a) (i) While pumping air into a ball, the volume as well as the pressure increase. Does Boyle's law applicable here? Briefly, explain.

Solution:
Boyle's law states that for a fixed amount of gas at constant temperature, the pressure and volume are inversely proportional ($P_1V_1 = P_2V_2$). In this case, as air is pumped into the ball, the amount of gas inside increases, leading to an increase in both volume and pressure. Since the amount of gas is changing rather than keeping it constant, Boyle's law does not strictly apply in this situation.

(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.

Solution:
Hot air is preferred because it is less dense than cold air. According to Charles's law, increasing temperature causes the volume of a gas to expand, reducing its density. Since the buoyant force depends on the density difference between the air inside and outside the balloon, using hot air makes the balloon lighter than the surrounding air, enabling it to rise.

(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.

Solution:

Dalton's law states that the total pressure of a gas mixture is the sum of the partial pressures of its individual gases. However, SO_2 and O_2 can react to form SO_3 under suitable conditions:

$2SO_2 + O_2$ ------> $2SO_3$

Since a chemical reaction alters the number of gas molecules, the final pressure will not simply be the sum of the initial partial pressures of SO_2 and O_2. Therefore, Dalton's law does not strictly apply in this case.
(iv) What would have happened to the gas pressure if the molecular collisions were not elastic?

Solution:
If molecular collisions were not elastic, kinetic energy would be lost with each collision, leading to a gradual decrease in molecular motion. This would cause the gas pressure to drop over time, as pressure depends on the frequency and force of molecular collisions with container walls. Ultimately, the gas would settle without maintaining a uniform pressure.

(b) The density of a gas at 27 °C and 1520 mmHg pressure was found to be 5.46×10^{-3} g/cm³. What will be its density in g/dm³ at s.t.p.?

Solution:
Using the gas law equation:

$P_1V_1/T_1 = P_2V_2/T_2$
Since density (d) is mass per unit volume, the equation can be rewritten as:

$d_1T_1/P_1 = d_2T_2/P_2$

Given data:
$T_1 = 27 + 273 = 300$ K
$P_1 = 1520$ mmHg
$d_1 = 5.46 \times 10^{-3}$ g/cm³
$T_2 = 273$ K (STP)
$P_2 = 760$ mmHg (STP)

Solving for d_2:
$d_2 = (d_1 \times P_2 \times T_1) / (P_1 \times T_2)$
$d_2 = (5.46 \times 10^{-3} \times 760 \times 300) / (1520 \times 273)$
$d_2 = (1.24) / (414.96)$
$d_2 = 3.02 \times 10^{-3}$ g/cm³
Converting to g/dm³:
$d_2 = 3.02$ g/dm³

(c) (i) Relative densities of carbon dioxide and oxygen are 22 and 16, respectively. If 25 cm^3 of carbon dioxide diffuses in 75 seconds, what volume of oxygen gas will diffuse in 96 seconds under similar conditions?
Solution:
Using Graham's law of diffusion:
$V_1/V_2 = \sqrt{(d_2/d_1)} \times t_1/t_2$

where,
$V_1 = 25\ cm^3$
$t_1 = 75\ s$
$d_1 = 22\ (CO_2)$
$d_2 = 16\ (O_2)$
$t_2 = 96\ s$

$V_2 = V_1 \times \sqrt{(d_2/d_1)} \times t_2/t_1$
$V_2 = 25 \times \sqrt{(16/22)} \times (96/75)$
$V_2 = 25 \times \sqrt{0.727} \times 1.28$
$V_2 = 25 \times 0.853 \times 1.28$
$V_2 = 27.3\ cm^3$
(ii) What are the two significances of Graham's law of diffusion in our daily life?

Solution:
1. Gas leakage detection: Graham's law explains how gases like LPG and natural gas diffuse rapidly, allowing people to detect leaks through their smell.
2. Respiration process: Oxygen and carbon dioxide diffuse across the alveoli in the lungs, enabling efficient gas exchange necessary for breathing.

9. (a) Briefly, explain five uses of metal oxides in daily life.

Solution:

1. Construction industry: Metal oxides such as calcium oxide (CaO) are used in cement and mortar production.
2. Electronics and semiconductors: Silicon dioxide (SiO_2) is used in making microchips and electronic components.
3. Pigments and paints: Titanium dioxide (TiO_2) is widely used in white paints, cosmetics, and sunscreens.
4. Catalysts in chemical reactions: Metal oxides like vanadium(V) oxide (V_2O_5) are used in industrial catalysis, such as the production of sulfuric acid.
5. Medical applications: Zinc oxide (ZnO) is used in skin ointments and sunscreens due to its antibacterial and UV-blocking properties.

(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 a crucible, a black solid S, brown fumes of gas T and a gas that relighted a glowing splint were formed.

(i) Identify solids P and S, and gases R and T.

Solution:

- Solid P is copper(II) carbonate ($CuCO_3$), which is green.
- Solution Q is copper(II) nitrate ($Cu(NO_3)_2$), which is blue.
- Gas R is carbon dioxide (CO_2), which forms a white precipitate with lime water.
- Solid S is copper(II) oxide (CuO), which is black.
- Gas T is nitrogen dioxide (NO_2), which is brown.
- The gas that relights a glowing splint is oxygen (O_2).

(ii) Write an equation for the reaction between solid P and dilute nitric acid.

$CuCO_3(s) + 2HNO_3(aq)$ ------> $Cu(NO_3)_2(aq) + CO_2(g) + H_2O(l)$

(c) What is the importance of the following metal compounds in everyday life?

(i) Lime stone
Solution:
Limestone ($CaCO_3$) is used in cement and concrete production, water purification, and as a raw material for producing quicklime (CaO), which is used in agriculture to neutralize acidic soils.

(ii) Plaster of Paris
Solution:

Plaster of Paris ($CaSO_4 \cdot \frac{1}{2}H_2O$) is used in making sculptures, moldings, orthopedic casts, and building materials for wall finishing due to its ability to harden upon mixing with water.
10. (a) Briefly explain the following concepts:

(i) Concentrated sulphuric acid is necessary for nitration of benzene.

Solution:
Concentrated sulfuric acid acts as a catalyst in nitration by generating the nitronium ion (NO_2^+), the active electrophile required for the reaction. It protonates nitric acid (HNO_3), leading to the formation of NO_2^+, which then reacts with benzene.

$HNO_3 + H_2SO_4$ -------> $NO_2^+ + HSO_4^- + H_2O$

(ii) Bromination of benzene takes place in the presence of Lewis acid, while that of hydroxybenzene does not require the presence of Lewis acid.

Solution:
Benzene is less reactive than hydroxybenzene (phenol) and requires a Lewis acid such as $FeBr_3$ to polarize the bromine molecule, making it more electrophilic. However, hydroxybenzene has an electron-donating -OH group that increases electron density on the benzene ring, allowing bromination to occur without a catalyst.

(iii) Despite chlorine atom being an electron withdrawing group, it directs an incoming group to the ortho or para positions in electrophilic aromatic substitution reactions.

Solution:
Chlorine has lone pairs that participate in resonance, donating electron density to the benzene ring at the ortho and para positions. This stabilizes the intermediate carbocation in electrophilic substitution, favoring these positions despite chlorine's overall electron-withdrawing inductive effect.

(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

Solution:
Bromine water test:
- Benzene does not decolorize bromine water in the absence of a catalyst.
- Ethane undergoes free radical substitution in the presence of UV light, leading to bromine decolorization.

$C_2H_6 + Br_2$ ------> $C_2H_5Br + HBr$ (in presence of UV light)

(ii) 3-chloro-2-methylpent-2-ene and 1-chloropropane

Solution:
Reaction with bromine water:

- 3-chloro-2-methylpent-2-ene decolorizes bromine water due to the presence of a double bond.
- 1-chloropropane does not react with bromine water.

$CH_3C(Cl)=CHCH_2CH_3 + Br_2$ -----> $CH_3C(Br)\text{-}CH(Br)\text{-}CH_2CH_3$

(iii) Bromobenzene and bromomethane
Solution:

Reaction with aqueous NaOH:

- Bromobenzene does not react readily with aqueous NaOH due to the strong C-Br bond in the benzene ring.
- Bromomethane undergoes nucleophilic substitution to form methanol.

CH_3Br + NaOH-----> CH_3OH + NaBr

(c) Briefly explain the following concepts:

(i) $(CH_3)_2CHBr$ undergoes SN1 mechanism, while $CH_3CH_2CH_2Br$ undergoes SN2 mechanism when they react with aqueous alkalis.

Solution:
- $(CH_3)_2CHBr$ is a secondary halide, which forms a stable carbocation in an SN1 reaction due to inductive and hyperconjugation effects.
- $CH_3CH_2CH_2Br$ is a primary halide, which favors SN2 since the steric hindrance is low, allowing direct nucleophilic attack in a single-step mechanism.

(ii) Haloalkanes undergo nucleophilic substitution reactions, while halobenzenes undergo electrophilic substitution reactions.

Solution:
- Haloalkanes have a polar C-X bond that allows nucleophiles to attack the carbon, replacing the halide in nucleophilic substitution.
- Halobenzenes undergo electrophilic substitution because the benzene ring is electron-rich and does not easily undergo nucleophilic attack due to resonance stabilization of the C-X bond.

(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?

Solution:
- Hydrocarbon K gives a monocarboxylic acid, suggesting it is an alkylbenzene with a single alkyl group, likely ethylbenzene ($C_6H_5CH_2CH_3$), which oxidizes to benzoic acid.
- Hydrocarbon L forms a tricarboxylic acid upon oxidation, which suggests the presence of three methyl groups, likely 1,2,3-trimethylbenzene (mesitylene, $C_6H_3(CH_3)_3$), which oxidizes to trimesic acid (benzene-1,2,3-tricarboxylic acid).