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: 2017**

Instructions

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

2. Each question carries ten marks

1. (a) Distinguish between the following:

(i) Isotopes and isotopy.
Isotopes are atoms of the same element that have the same atomic number but different mass numbers due to differences in the number of neutrons. For example, carbon has isotopes such as carbon-12, carbon-13, and carbon-14.
Isotopy refers to the phenomenon of the existence of isotopes of an element. It describes the property of elements having atoms with the same number of protons but different numbers of neutrons.

(ii) Azimuthal quantum number and magnetic quantum number.
The azimuthal quantum number (l) defines the shape of an orbital and the subshell to which an electron belongs. It can take values from 0 to (n-1) for a given principal quantum number (n). For example, for n = 3, the possible values of l are 0, 1, and 2, corresponding to the s, p, and d subshells, respectively.
The magnetic quantum number (m_l) describes the orientation of an orbital in space. It depends on the azimuthal quantum number and can have values ranging from -l to +l, including zero. For instance, if l = 1 (p-orbital), the possible values of m_l are -1, 0, and +1, representing three different orientations in space.

(iii) Atomic mass unit and relative atomic mass.
An atomic mass unit (amu) is defined as one-twelfth the mass of a carbon-12 atom, approximately equal to 1.6605×10^{-27} kg. It is a fundamental unit used to express atomic and molecular masses.
Relative atomic mass (Ar) is the weighted average mass of all the isotopes of an element compared to one-twelfth of the mass of a carbon-12 atom. It takes into account the natural abundance of each isotope.

(b) The mass spectrographic measurements of an element X whose atomic number is 31 indicated peaks at 79.21, 11.2, and 9.59. The isotopic masses are 69, 70, and 71 atomic mass unit (a.m.u) respectively.

(i) Write the conventional symbols for the three isotopes.
The three isotopes of element X (Gallium, atomic number 31) are:
$^{69}_{31}Ga$, $^{70}_{31}Ga$, and $^{71}_{31}Ga$.

(ii) Calculate the relative atomic mass of X.
Relative atomic mass (Ar) is given by:

Ar = (isotopic mass × relative abundance) / 100
Ar = (69 × 79.21 + 70 × 11.2 + 71 × 9.59) / 100
Ar = (5465.49 + 784 + 681.89) / 100
Ar = 6923.38 / 100
Ar = 69.23

(iii) Explain why atomic weights of elements are not whole numbers.
Atomic weights are not whole numbers because they are calculated as the weighted average of the masses of all naturally occurring isotopes of an element. Since different isotopes have different masses and varying natural abundances, the average atomic weight is usually a decimal value.

(c) The mass number of two atoms, A and B, with the same atomic number, are 235 and 238, respectively. If A contains 143 neutrons in its nucleus, find the number of neutrons and electrons in B.

Number of neutrons in B = Mass number - Atomic number
= 238 - (235 - 143)
= 238 - 92
= 146

Since atomic number remains the same, the number of electrons in B = 92.

2. (a) Define the following:

(i) Dative bonding.
Dative bonding, also known as coordinate bonding, is a type of covalent bond where both electrons in the bond are donated by one atom. This occurs when an electron-deficient species accepts a lone pair from an electron-rich donor. An example is the bonding in the ammonium ion (NH_4^+), where a nitrogen atom donates a lone pair to a proton (H^+).

(ii) Ionic bonding.
Ionic bonding is the electrostatic force of attraction between oppositely charged ions formed by the complete transfer of electrons from one atom to another. This bond typically occurs between a metal and a non-metal, such as in sodium chloride (NaCl), where sodium donates an electron to chlorine, forming Na^+ and Cl^- ions.

(iii) Valence electrons.
Valence electrons are the outermost electrons in an atom that participate in chemical bonding. These electrons determine the reactivity and chemical properties of an element. For example, carbon has four valence electrons, which allow it to form covalent bonds with other atoms.

(b) Summarize three major ideas of the Valence Shell Electron Pair Repulsion (VSEPR) theory.

i. Electron pairs around a central atom repel each other and arrange themselves as far apart as possible to minimize repulsion.
ii. The shape of a molecule is determined by the number of bonding and lone electron pairs around the central atom.
iii. Lone pairs repel more strongly than bonding pairs, affecting bond angles and molecular geometry.

(c) Outline four differences between sigma and pi bonds.

i. Sigma bonds (σ) form by the head-on overlap of atomic orbitals, while pi bonds (π) form by the side-on overlap of p orbitals.
ii. Sigma bonds allow free rotation of bonded atoms, whereas pi bonds restrict rotation.

iii. Sigma bonds are stronger than pi bonds due to greater orbital overlap.
iv. A single bond consists of one sigma bond, while double and triple bonds contain one sigma bond and one or two pi bonds, respectively.

(d) Determine the name of a geometrical structure and one example of the molecule formed from the following hybridized orbitals.

(i) Sp^3
Geometrical structure: Tetrahedral
Example: Methane (CH_4)

(ii) Sp^2
Geometrical structure: Trigonal planar
Example: Ethene (C_2H_4)

(iii) Sp
Geometrical structure: Linear
Example: Carbon dioxide (CO_2)

3. (a) (i) Write two similarities between diffusion and effusion.

i. Both processes involve the movement of gas molecules from a region of higher concentration to a region of lower concentration.
ii. Both depend on the kinetic energy of gas molecules and follow Graham's law, which states that the rate of diffusion or effusion is inversely proportional to the square root of the molar mass of the gas.

(ii) The rate of effusion of an unknown gas was measured to be 24.0 mL/min. Under the same conditions, the measured rate of effusion of pure methane was 47.8 mL/min. What is the molar mass of the unknown gas?

Using Graham's law of effusion:

(rate of effusion of gas 1 / rate of effusion of gas 2) = $\sqrt{}$(molar mass of gas 2 / molar mass of gas 1)

Let M be the molar mass of the unknown gas. Given:
Rate of unknown gas = 24.0 mL/min
Rate of methane (CH_4) = 47.8 mL/min
Molar mass of CH_4 = 16 g/mol

$(24.0 / 47.8) = \sqrt{(16 / M)}$

Squaring both sides:

$(24.0 / 47.8)^2 = 16 / M$
$0.252 = 16 / M$

Solving for M:

$M = 16 / 0.252$
$M = 63.49$ g/mol

(b) Using the kinetic theory of gases, state four properties of an ideal gas.

i. Gas molecules are in constant, random motion and collide elastically with each other and with the walls of the container.
ii. The volume of individual gas molecules is negligible compared to the total volume of the gas.
iii. There are no intermolecular forces between gas molecules.
iv. The average kinetic energy of gas molecules is directly proportional to the absolute temperature (Kelvin).

(c) A sample of ammonia gas with a volume of 3.5 dm^3 at a pressure of 1.68 atm was compressed to a volume of 1.35 dm^3 at constant temperature.

(i) Calculate the final pressure of the gas.

Using Boyle's Law:

$P_1V_1 = P_2V_2$

Given:
$P_1 = 1.68$ atm
$V_1 = 3.5\ dm^3$
$V_2 = 1.35\ dm^3$
Solving for P_2:

$P_2 = (P_1V_1) / V_2$
$P_2 = (1.68 \times 3.5) / 1.35$
$P_2 = 5.88 / 1.35$
$P_2 = 4.36$ atm

(ii) Name and state the governing gas law in question 3(c)(i).

Boyle's Law: It states that the pressure of a gas is inversely proportional to its volume at constant temperature, expressed mathematically as $P_1V_1 = P_2V_2$.

4. (a) Define the following:

(i) Relative density of a gas.
Relative density of a gas is the ratio of the density of a gas to the density of a reference gas, usually hydrogen or air, under the same conditions of temperature and pressure. It is a dimensionless quantity.

(ii) Normal density of a gas.
Normal density of a gas refers to the mass per unit volume of the gas measured at standard temperature and pressure (STP), usually expressed in g/L or kg/m^3.

(b) Show that the relative molecular mass of a gas is twice its relative vapour density.

Relative vapour density (RVD) is given by:
RVD = (Mass of a certain volume of gas) / (Mass of an equal volume of hydrogen)
Since the molar mass of hydrogen is 2 g/mol, the molar mass (M) of any gas can be related to its relative vapour density as follows:

$M = 2 \times RVD$

This shows that the relative molecular mass of a gas is twice its relative vapour density.

(c) (i) A determination of the density of ethanoic acid vapour at 1 atm pressure and 400 K gave a result of $2.74\ g/dm^3$. Assuming ideal condition, calculate the apparent molecular weight of ethanoic acid under these conditions.

Using the ideal gas equation:

$PV = nRT$
Since density (d) = m/V and molar mass (M) = m/n, we can rearrange as:

$M = (dRT) / P$

Given:
$d = 2.74\ g/dm^3 = 2.74\ g/L$
$R = 0.0821\ L\ atm\ K^{-1}\ mol^{-1}$
$T = 400\ K$
$P = 1\ atm$

$M = (2.74 \times 0.0821 \times 400) / 1$
$M = (89.752) / 1$
$M = 89.75\ g/mol$
(ii) What can you deduce from your results in 4(c)(i)? Briefly explain.

The calculated molecular weight of ethanoic acid (89.75 g/mol) is approximately twice its theoretical molar mass (60 g/mol). This suggests that ethanoic acid exists as a dimer ($C_2H_4O_4$) in the vapour phase due to hydrogen bonding between molecules.

(d) A 0.0721 g of water vaporised at 150°C and 755 mmHg pressure occupied a volume of 140 cm^3. Show that the relative molecular mass of water vapour proves the formula for steam.

Using the ideal gas equation:

$M = (dRT) / P$

First, convert given values:
$P = 755$ mmHg $= (755 / 760)$ atm $= 0.9934$ atm
$V = 140\ cm^3 = 0.140$ L
$T = 150°C = 423$ K
$R = 0.0821$ L atm K^{-1} mol^{-1}

Using: $M = (mRT) / PV$

$M = (0.0721 \times 0.0821 \times 423) / (0.9934 \times 0.140)$
$M = (2.506) / (0.1391)$
$M = 18.02$ g/mol

Since the calculated molar mass is approximately 18 g/mol, it confirms that the molecular formula of steam is H_2O.
5. (a) (i) Give the meaning of osmotic pressure of a solution.

Osmotic pressure is the pressure required to prevent the flow of solvent molecules into a solution through a semipermeable membrane. It is a colligative property and depends on the concentration of solute particles in the solution rather than their identity.

(ii) Briefly explain in terms of vapour pressure why the freezing point of a solution is lower than that of a pure solvent.

When a solute is added to a solvent, the vapour pressure of the solution decreases because fewer solvent molecules are available at the surface to escape into the vapour phase. Since freezing occurs when the vapour pressure of the liquid equals the vapour pressure of the solid, the decreased vapour pressure causes the freezing point to drop, resulting in freezing point depression.

(b) When water and ice are mixed, the temperature of the mixture is 0°C, but, if methanol (CH_3OH) and ice are mixed, a temperature of +10°C is readily attained. Explain why the two mixtures show such different temperature behaviours.

When water and ice are mixed, the system maintains equilibrium at 0°C due to the latent heat of fusion. However, when methanol and ice are mixed, methanol has a lower freezing point and higher solubility in ice, leading to partial dissolution and exothermic interactions. This results in a higher equilibrium temperature of +10°C.

(c) Calculate the molar mass of Y given that a solution of 60 g of Y in 1 dm^3 of water exerts an osmotic pressure of $4.31 \times 10^3\ Nm^{-2}$ at 25°C.

Using the osmotic pressure equation:

$\Pi = cRT$

Where:
$\Pi = 4.31 \times 10^3\ N/m^2$
$R = 8.314\ J\ mol^{-1}\ K^{-1}$
$T = 25°C = 298\ K$
$c = n/V = (60/M)\ mol\ dm^{-3}$

Rearranging for M:

$M = (60 \times 8.314 \times 298) / (4.31 \times 10^3 \times 1)$

$M = (148711.2) / (4310)$
$M = 34.52\ g/mol$

(d) A 0.003 kg of acetic acid (CH_3COOH) is added to 500 cm^3 of water. If 23% of the acid is dissociated, what will be the depression in freezing point? (Kf for water = 1.86 °Ckg/mol, density of water = 0.997 g/cm^3).

First, calculate the number of moles of acetic acid:

Molar mass of CH_3COOH = 60 g/mol
Mass = 0.003 kg = 3 g

Moles of acetic acid = 3 / 60 = 0.05 mol
Since 23% of the acid dissociates, the van't Hoff factor (i) is:
$i = 1 + \alpha$
$i = 1 + 0.23$
$i = 1.23$
Using the freezing point depression formula:

$\Delta T = i \times K_f \times m$

Where:
m = molality = (0.05 mol) / (0.5 kg) = 0.1 mol/kg
K_f = 1.86 °Ckg/mol
i = 1.23

$\Delta T = 1.23 \times 1.86 \times 0.1$
$\Delta T = 0.229$ °C

The freezing point depression is 0.229°C.

6. (a) (i) Define vapour pressure.

Vapour pressure is the pressure exerted by a vapour in equilibrium with its liquid or solid phase at a given temperature. It represents the tendency of molecules to escape from the liquid phase into the gaseous phase.

(ii) Using Raoult's law of vapour pressure, show that the lowering of vapour pressure is proportional to the mole fraction of the solute.

Raoult's law states that the partial vapour pressure of a component in a solution is proportional to its mole fraction:

$P_1 = X_1 P_1^0$

Where:
P_1 = Vapour pressure of the solvent in the solution
X_1 = Mole fraction of the solvent
P_1^0 = Vapour pressure of the pure solvent

The relative lowering of vapour pressure is given by:

$(P_1^0 - P_1) / P_1^0 = X_2$

Since X_2 (mole fraction of solute) is directly proportional to the number of solute particles, this equation shows that vapour pressure lowering is proportional to the mole fraction of the solute.

(b) Briefly explain why the solution becomes ideal when it is made more dilute.

In an ideal solution, intermolecular forces between solute-solvent, solute-solute, and solvent-solvent molecules are nearly identical. As a solution becomes more dilute, the solute molecules are widely separated, reducing their interactions, and making the behaviour of the solution closer to that of an ideal solution.

(c) Two liquids A and B form an ideal solution when mixed. At 298 K, the vapour pressure of pure A and B for a mixture of 1 mole of A and 3 moles of B are 32 kPa and 16 kPa, respectively. Calculate:

(i) The vapour pressure of the mixture.

Using Raoult's law:
$P = (X_a P_a^o) + (X\_b P\_b^o)$

Where:
X_a = mole fraction of A = 1 / (1 + 3) = 1/4 = 0.25
X_b = mole fraction of B = 3 / (1 + 3) = 3/4 = 0.75
P_a^o = 32 kPa
P_b^o = 16 kPa

$P = (0.25 \times 32) + (0.75 \times 16)$
$P = 8 + 12$
P = 20 kPa

(ii) The mole fraction of A in the vapour which is in equilibrium with the mixture.

Mole fraction of A in vapour phase (Y_a) is given by:

$Y_a = (X_a P_a^o) / P\_total$

$Y_a = (0.25 \times 32) / 20$
$Y_a = 8 / 20$
$Y_a = 0.4$

Thus, the mole fraction of A in the vapour is 0.4.

Solution

7. (a) (i) Briefly explain the principle of solvent extraction.

Solvent extraction is a separation technique based on the differential solubility of a compound in two immiscible liquids, usually water and an organic solvent. The principle involves dissolving the desired solute preferentially in one of the phases, followed by phase separation to isolate the solute. The efficiency depends on the partition coefficient, which determines the solute distribution between the two solvents.

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

Fractional distillation separates components of a mixture based on differences in their boiling points using a fractionating column, which provides multiple condensation-evaporation cycles, improving separation efficiency. It is commonly used for separating liquid mixtures like crude oil components.

Steam distillation is used for separating temperature-sensitive substances, such as essential oils, by introducing steam into the mixture. The steam reduces the partial pressure of the components, allowing them to vaporize at lower temperatures, preventing decomposition.

Key Differences:
- Fractional distillation relies on boiling point differences, whereas steam distillation exploits the interaction with steam.
- Fractional distillation requires a fractionating column, while steam distillation involves direct steam injection.
- Steam distillation is ideal for heat-sensitive compounds, while fractional distillation is used for complex liquid mixtures.

(b) Steam distillation of a mixture of an organic compound B and water at 98°C and pressure of 101320 Pa yielded a distillate containing 31.6% by volume of B. The vapour pressure of pure water at this temperature is 94260 Pa. The densities of B and water are 0.961 g/cm³ and 1.000 g/cm³, respectively. Calculate the relative molecular mass of B.

Step 1: Calculate the vapour pressure of B in the mixture
Total pressure = Vapour pressure of water + Vapour pressure of B

101320 Pa = 94260 Pa + P_B

P_B = 101320 - 94260
P_B = 7050 Pa

Step 2: Calculate the mass of B in the distillate
Let V be the total volume of distillate.
Volume of B = 31.6% of V = 0.316V
Volume of water = 68.4% of V = 0.684V

Mass of B = (Density of B) × (Volume of B)
Mass of B = (0.961 g/cm³) × (0.316V cm³)
Mass of B = 0.3036V g

Mass of water = (Density of water) × (Volume of water)
Mass of water = (1.000 g/cm³) × (0.684V cm³)
Mass of water = 0.684V g

Step 3: Use Dalton's law to determine the molar mass of B

Since the vapour pressure ratio is equal to the mole ratio in the gaseous phase,

(moles of B / moles of water) = (P_B / P_H_2O)

Let M_B be the molar mass of B and M_H_2O = 18 g/mol.

$(0.3036V / M\_B) / (0.684V / 18) = (7050 / 94260)$

$(0.3036 / M\_B) / (0.038) = 0.0748$

$0.3036 / M\_B = 0.0748 \times 0.038$

$0.3036 / M\_B = 0.00284$

$M\_B = 0.3036 / 0.00284$

M_B = 106.9 g/mol

The relative molecular mass of B is approximately 107 g/mol.

8. (a) Define the following:

(i) Standard enthalpy change of neutralization.
Standard enthalpy change of neutralization is the enthalpy change that occurs when one mole of hydrogen ions (H^+) from an acid reacts with one mole of hydroxide ions (OH^-) from a base to form one mole of water under standard conditions (298 K, 1 atm, 1 mol/dm^3 concentration). It is usually exothermic, with values around -57 kJ/mol for strong acid-base reactions.

(ii) Heat of solution.
Heat of solution (enthalpy of solution) is the enthalpy change when one mole of a substance dissolves in a large excess of solvent to form an infinitely dilute solution under standard conditions. It can be exothermic or endothermic, depending on solute-solvent interactions.

(iii) Bond energy.
Bond energy is the amount of energy required to break one mole of a specific chemical bond in a gaseous molecule under standard conditions. It is a measure of bond strength and is expressed in kJ/mol. For example, the bond energy of the H-H bond in H_2 is 436 kJ/mol.

(iv) Standard enthalpy change of combustion.
Standard enthalpy change of combustion is the enthalpy change when one mole of a substance is completely burned in oxygen under standard conditions, with all reactants and products in their standard states. It is always exothermic. For example, the standard enthalpy of combustion of methane is -890 kJ/mol.

(b) Differentiate between:

(i) Lattice energy and energy of reaction.
Lattice energy is the energy released when one mole of an ionic solid is formed from its gaseous ions. It is always exothermic and depends on ionic charge and size.
Energy of reaction refers to the overall enthalpy change during a chemical reaction, which can be exothermic or endothermic depending on bond formation and breaking.

(ii) Standard molar enthalpy change of dissolution and heat of combustion.
Standard molar enthalpy change of dissolution refers to the heat change when one mole of a solute dissolves in a solvent under standard conditions, whereas heat of combustion is the energy released when one mole of a substance burns completely in oxygen. The former can be endothermic or exothermic, while the latter is always exothermic.

(c) Given the standard enthalpy change of combustion of hydrogen, $\Delta H^o = -286$ kJ/mol; carbon, $\Delta H^o = -394$ kJ/mol; methane, $\Delta H^o = -890$ kJ/mol; ethane, $\Delta H^o = -1390$ kJ/mol and heat of formation of CH_3CH_2OH is -276 kJ/mol, calculate in kJ/mol the enthalpy change:

(i) of formation of methane.

Using the standard enthalpy of combustion equation:

$CH_4 + 2O_2$ -----> $CO_2 + 2H_2O$
$\Delta H^o = -890$ kJ/mol

Using the formation reaction:

$\Delta H^o\_f (CH_4) = \Delta H^o\_c (C) + 2\Delta H^o\_c (H_2) - \Delta H^o\_c (CH_4)$

$= (-394) + 2(-286) - (-890)$
$= -394 - 572 + 890$
$= -76$ kJ/mol

(ii) of formation of ethane.

$2C + 3H_2 \rightarrow C_2H_6$
$\Delta H\_f^o = \Delta H\_c^o(C) + (3/2)\Delta H\_c^o(H_2) - \Delta H\_c^o(C_2H_6)$

$= 2(-394) + 3(-286) - (-1390)$
$= -788 - 858 + 1390$
$= -256$ kJ/mol

(iii) for the reaction $CH_2{=}CH_2(g) + H_2O(g)$ ----> $CH_3CH_2OH(g)$

$\Delta H = \Delta H\_f (CH_3CH_2OH) - [\Delta H\_f (CH_2{=}CH_2) + \Delta H\_f (H_2O)]$

Since ΔH_f of ethene = +52 kJ/mol and ΔH_f of $H_2O(g)$ = -242 kJ/mol,

$\Delta H = (-276) - [(+52) + (-242)]$
$\Delta H = -276 - (-190)$
$\Delta H = -86$ kJ/mol

(iv) of combustion of 4.48 dm³ of ethane.

Molar volume of gas at STP = 22.4 dm³
Moles of ethane = 4.48 / 22.4 = 0.2 mol

Enthalpy of combustion of ethane = -1390 kJ/mol

Total energy released = 0.2 × (-1390)
= -278 kJ

9. (a) Study carefully the information in the following table and then answer the questions that follow.

Process	ΔH_{298} (kJ mol⁻¹)
$Na(s) \text{ -----> } Na(g)$	+108
$\frac{1}{2} Cl_2(g) \text{ --> } Cl(g)$	+121
$Na(g) \text{ -----> } Na^+(g) + e$	+496
$Cl(g) + e \text{ ---> } Cl^-(g)$	-349
$NaCl(s) \text{ ----> } Na^+(g) + Cl^-(g)$	+787
$NaCl(s) + H_2O(l) \text{ ----> } Na^+(aq) + Cl^-(aq)$	+4.0

(i) Calculate the enthalpy change for the process $2Cl(g) \text{ ------> } Cl_2(g)$.

The enthalpy change for $\frac{1}{2} Cl_2(g) \text{ -----> } Cl(g)$ is +121 kJ/mol.
For $Cl_2(g) \text{ ------> } 2Cl(g)$, $\Delta H = 2 \times 121 = +242$ kJ/mol.
Reversing this reaction:
$2Cl(g) \rightarrow Cl_2(g)$, $\Delta H = -242$ kJ/mol.

(ii) Calculate the standard molar enthalpy change for the process:

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

Using Hess's law:

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$

= (+108) + (+121) + (+496) + (-349)
= 376 kJ/mol

(iii) Compare the difference between enthalpy change for the processes:

$NaCl(s) \text{ -----> } Na^+(g) + Cl^-(g)$ and $NaCl(s) + H_2O(l) \rightarrow Na^+(aq) + Cl^-(aq)$.

The first process represents the lattice energy of NaCl, which is the energy required to separate one mole of solid NaCl into its gaseous ions. This is a highly endothermic process (+787 kJ/mol).

The second process represents the dissolution of NaCl in water, which is nearly thermoneutral (+4 kJ/mol), indicating that hydration energy almost compensates for lattice energy, leading to a minor enthalpy change.

9. (b) Magnesium will displace copper from copper (II) sulfate solution according to the equation:
$CuSO_4(aq) + Mg(s) \text{ ---------> } Cu(s) + MgSO_4(aq)$.

When an excess of magnesium was added to 100 cm^3 of 0.1 mol dm^{-3} copper(II) sulfate, the temperature increased by 46.3°C. It is known that the density and specific heat capacity of the solution are 1.0 g cm^{-3} and 4.18 J g^{-1} $°C^{-1}$, respectively.

(i) Calculate the molar enthalpy change for the reaction.

Heat absorbed by solution (q) = $mc\Delta T$
Where:
$m = 100\ cm^3 \times 1.0\ g/cm^3 = 100\ g$
$c = 4.18\ J/g°C$
$\Delta T = 46.3°C$

$q = (100 \times 4.18 \times 46.3)$
$q = 19347.4\ J$
$q = 19.35\ kJ$

Moles of $CuSO_4 = (0.1\ mol/dm^3 \times 0.1\ dm^3) = 0.01\ mol$

Molar enthalpy change = q / moles
$\Delta H = 19.35\ kJ / 0.01\ mol$
$\Delta H = -1935\ kJ/mol$

(ii) Minimum quantity of magnesium required.

Reaction: $Mg + CuSO_4 \text{ --------> } Cu + MgSO_4$

1 mol Mg reacts with 1 mol $CuSO_4$.

Moles of $CuSO_4$ = 0.01 mol, so moles of Mg required = 0.01 mol.

Mass of Mg = 0.01 mol × 24.3 g/mol = 0.243 g.

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

Moles of Mg = 0.8 g / 24.3 g/mol = 0.0329 mol.

Since $CuSO_4$ is limiting, we use 0.01 mol $CuSO_4$.

Heat released = 19.35 kJ.

Using $q = mc\Delta T$:

$\Delta T = q / (mc)$
$\Delta T = (19.35 \times 10^3) / (100 \times 4.18)$
$\Delta T = 46.3°C$.

Since the reaction depends on $CuSO_4$, ΔT remains the same.

10. (a) Differentiate between the following:

(i) Equilibrium constant, Kc, and rate constant, k.

The equilibrium constant (Kc) is a dimensionless quantity that expresses the ratio of the concentrations of products to reactants at equilibrium for a reversible reaction at a given temperature. It determines the extent of a reaction but does not provide information about the speed of the reaction.

The rate constant (k) is a proportionality constant in the rate equation of a reaction that relates the reaction rate to the concentration of reactants. It depends on temperature and activation energy but does not indicate the final equilibrium position.

(ii) Equilibrium position and rate of reaction.

The equilibrium position refers to the relative concentrations of reactants and products when a reversible reaction reaches a state where forward and reverse reaction rates are equal. It is determined by the equilibrium constant (Kc) and can shift with changes in conditions such as pressure, temperature, and concentration.

The rate of reaction measures how fast reactants are converted into products. It depends on factors like temperature, concentration, catalysts, and surface area but does not determine the final composition at equilibrium.

(b) Consider the following reversible equilibrium:

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

(i) Write down the Kc and Kp expressions.

For equilibrium constant Kc:

$Kc = [CO_2]^4 / ([C_2H_6]^2 [O_2]^7)$

Since $H_2O(l)$ is a pure liquid, it is not included in the expression.

For equilibrium constant Kp:

$Kp = (P\_CO_2)^4 / (P\_C_2H_6)^2 (P\_O_2)^7$

(ii) Derive the relationship between Kc and Kp.

The general relationship between Kp and Kc is given by:

$Kp = Kc (RT)^\wedge(\Delta n)$

Where:
$R = 0.0821$ L atm K^{-1} mol^{-1}
T = Temperature in Kelvin
Δn = (Sum of moles of gaseous products) - (Sum of moles of gaseous reactants)

For the given reaction:

$\Delta n = (4 - 2) + (0 - 7) = -5$

Thus, $Kp = Kc (RT)^{-5}$.
(c) A 7.52 cm^3 of a gas H was mixed with 7.0 cm^3 of a gas Q in a one-liter flask at 298 K. At equilibrium, 10.93 cm^3 of gas HQ was formed. Calculate the equilibrium constant, Kc, for the reaction:

$H_2(g) + Q_2(g) \rightleftharpoons 2HQ(g)$.

Initial moles:
$H_2 = 7.52\ cm^3$, $Q_2 = 7.0\ cm^3$, $HQ = 0\ cm^3$.

Change in moles:
H_2 = -5.47 cm^3, Q_2 = -5.47 cm^3, HQ = +10.93 cm^3.

Equilibrium moles:
H_2 = (7.52 - 5.47) = 2.05 cm^3,
Q_2 = (7.0 - 5.47) = 1.53 cm^3,
HQ = 10.93 cm^3.

$Kc = [HQ]^2 / ([H_2] [Q_2])$

$Kc = (10.93)^2 / (2.05 \times 1.53)$

$Kc = 119.49 / 3.1365$

$Kc = 38.1$

Thus, the equilibrium constant Kc = 38.1.

11. (a) Using one appropriate example in each case, briefly explain the meaning of the following terms:

(i) Homologous series.

A homologous series is a group of organic compounds that have the same functional group and general formula, but differ by a CH_2 unit between consecutive members. They exhibit similar chemical properties and show a gradual change in physical properties.

Example: Alkanes (CH_4, C_2H_6, C_3H_8).

(ii) Functional group.

A functional group is a specific atom or group of atoms within a molecule that determines its chemical properties and reactivity.

Example: Hydroxyl (-OH) group in alcohols like ethanol (C_2H_5OH).

(iii) Unsaturated hydrocarbon.

An unsaturated hydrocarbon is an organic compound that contains one or more double or triple bonds between carbon atoms.

Example: Ethene (C_2H_4) has a C=C double bond.

(iv) Alkyl group.

An alkyl group is a hydrocarbon fragment derived from an alkane by removing one hydrogen atom, making it reactive and capable of forming bonds with other atoms.

Example: Methyl ($-CH_3$) in methane (CH_4).

(b) Write the formula of the following alkyl groups:

(i) Methyl group: CH_3^-
(ii) Butyl group: $C_4H_9^-$
(iii) Ethyl group: $C_2H_5^-$
(iv) Propyl group: $C_3H_7^-$

(c) Complete the following reactions:

(i) $CaC_2(s) + 2H_2O(l)$ ------> $C_2H_2(g) + Ca(OH)_2(aq)$
(ii) CH_3CH_2OH -----> (Conc. H_2SO_4, Heat)----> $CH_2{=}CH_2 + H_2O$
(iii) $CH_3CH_2Cl + KOH$ ------> (Heat)------> $CH_3CH_2OH + KCl$
(iv) $CH_3CH{=}CH_2 + H_2O$ -----> (H^+)-------> $CH_3CH(OH)CH_3$

12. (a) Define the following terms:

(i) Resonance energy.

Resonance energy is the difference in energy between the actual structure of a molecule (resonance hybrid) and the most stable hypothetical resonance structure. It represents the extra stability gained due to electron delocalization. For example, benzene has a resonance energy of approximately 150 kJ/mol, making it more stable than a hypothetical cyclohexatriene structure.

(ii) Aromatic compound.

An aromatic compound is an organic molecule that contains a conjugated pi-electron system following Hückel's rule ($4n + 2$ π-electrons) and exhibits delocalized electron stability. Example: Benzene (C_6H_6), which has a delocalized electron cloud over its six carbon atoms.

(b) Briefly explain why methyl benzene (toluene) is more reactive than benzene.

Methyl benzene (toluene) is more reactive than benzene because the methyl group ($-CH_3$) is an electron-donating group via the +I effect (inductive effect) and hyperconjugation. This increases the electron density in the benzene ring, particularly at the ortho and para positions, making electrophilic substitution reactions occur more readily.

(c) Write equations to show what will happen when methyl benzene is:

(i) Treated with chloromethane (CH_3Cl) in presence of aluminium chloride ($AlCl_3$).

This is a Friedel-Crafts alkylation reaction:

$C_6H_5CH_3 + CH_3Cl$ ---->($AlCl_3$)-----> $C_6H_4(CH_3)_2 + HCl$

(ii) Treated with chlorine in presence of ultraviolet (UV) light.

This results in free radical substitution at the methyl group:

$C_6H_5CH_3 + Cl_2$ ---->(UV) --->$C_6H_5CH_2Cl + HCl$

(iii) Refluxed with potassium manganate (VII) ($KMnO_4$) in the presence of an acid.

Oxidation of the methyl group to a carboxyl group:

$C_6H_5CH_3 + 3[O]$ ----->($KMnO_4$, H^+) ------> $C_6H_5COOH + H_2O$

(iv) Burnt in excess oxygen.

Complete combustion:

$C_6H_5CH_3 + 9O_2$ ----> $7CO_2 + 4H_2O$

(d) Indicate in the following aromatic compounds, which substituent group entered first. Give reason(s) for your answer.

(i) The CH_3 (methyl) group is the first substituent. Methyl is an electron-donating group, directing new substitutions to ortho and para positions.

(ii) The OH (hydroxyl) group entered first because it strongly activates the benzene ring via electron donation through resonance, making electrophilic substitution favor ortho and para positions.

(iii) The NO_2 (nitro) group entered first as it is an electron-withdrawing group, deactivating the ring and directing new substitutions to the meta position.

Solution

14. (a) State Markovnikov's rule.

Markovnikov's rule states that during the addition of a hydrogen halide (HX) or water (H_2O) to an asymmetric alkene, the hydrogen atom attaches to the carbon with more hydrogen atoms (the less substituted carbon), while the halide or hydroxyl group attaches to the more substituted carbon. This occurs due to the formation of a more stable carbocation intermediate.

Example: Addition of HBr to propene:

$CH_3\text{-}CH=CH_2 + HBr$ ----> $CH_3\text{-}CHBr\text{-}CH_3$

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

(i) Br_2 (Bromine).

Phenylethene reacts with bromine in two possible ways:
- Electrophilic addition to the double bond (side chain reaction):

$C_6H_5CH{=}CH_2 + Br_2$ ----> $C_6H_5CHBr\text{-}CH_2Br$

- Electrophilic substitution on the benzene ring under specific conditions:

$C_6H_5CH{=}CH_2 + Br_2$ ----> $Br\text{-}C_6H_4\text{-}CH{=}CH_2 + HBr$

(ii) H_2 (Pt) at 25°C.

Selective hydrogenation of the alkene (side chain reaction):

$C_6H_5CH{=}CH_2 + H_2$ ----> $C_6H_5CH_2CH_3$

(iii) H_2 (Pt) at 200°C.

Complete hydrogenation of both the alkene and the aromatic ring:

$C_6H_6CH{=}CH_2 + 3H_2$ ----> $C_6H_{12}CH_2CH_3$

(c) Complete the following reactions:

(i) Nitration of benzene with concentrated nitric acid and sulfuric acid:

$C_6H_6 + HNO_3$ ----> (Conc. H_2SO_4, 50°C) $C_6H_5NO_2 + H_2O$

(ii) Friedel-Crafts alkylation with methyl chloride (CH_3Cl) and $AlCl_3$:

$C_6H_6 + CH_3Cl$ ----> ($AlCl_3$) $C_6H_5CH_3 + HCl$

(iii) Hydrogenation of benzene with nickel catalyst at 200°C:

$C_6H_6 + 3H_2$ ----> (Ni, 200°C) C_6H_{12}

(d) Arrange the following set of compounds in order of decreasing relative reactivity to an electrophile E^+:

(i) Chlorobenzene, 2,4-dinitrobenzene, 4-nitrochlorobenzene.

Reactivity order: Chlorobenzene > 4-nitrochlorobenzene > 2,4-dinitrobenzene

Explanation: The presence of nitro ($-NO_2$) groups deactivates the benzene ring by withdrawing electron density via resonance and induction, making it less reactive toward electrophilic substitution.

(ii) Methylbenzene, 4-nitromethylbenzene, 2,4-dinitromethylbenzene.

Reactivity order: Methylbenzene > 4-nitromethylbenzene > 2,4-dinitromethylbenzene

Explanation: The methyl ($-CH_3$) group is an electron-donating group that activates the benzene ring, while the nitro ($-NO_2$) groups deactivate it. The more nitro groups present, the lower the reactivity toward electrophilic substitution.