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: 2016**

Instructions

1. This paper consists of sections A and B with total of fourteen questions

2. Each question carries ten marks in section A and fifteen marks in section B.

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1. (a) State the following:

(i) Postulates of Bohr's atomic model:

Bohr's atomic model was based on the following postulates:

- Electrons revolve around the nucleus in fixed circular orbits without radiating energy.
- Each orbit corresponds to a definite energy level, and an electron remains in an orbit as long as it does not absorb or emit energy.
- Energy is absorbed or emitted only when an electron moves from one orbit to another.
- The angular momentum of an electron is quantized and is given by $mvr = nh/2\pi$, where n is a positive integer.

(ii) Shortcomings of Bohr's atomic model:

- It could not explain the spectra of atoms with more than one electron.
- It did not account for the splitting of spectral lines in the presence of an electric or magnetic field (Stark and Zeeman effects).
- It could not explain why certain orbits are preferred over others.
- It did not consider the wave nature of electrons as proposed in quantum mechanics.

(b) An electromagnetic radiation of wavelength 2420 Å is sufficient to ionize sodium. Calculate the ionization energy of sodium atom in kJmol^{-1}.

Given:

Wavelength (λ) = 2420 Å = 2420×10^{-10} m

Energy of radiation is given by $E = hc/\lambda$

where $h = 6.626 \times 10^{-34}$ J.s, $c = 3.0 \times 10^{8}$ m/s

$E = (6.626 \times 10^{-34} \times 3.0 \times 10^{8}) / (2420 \times 10^{-10})$

$E = 8.22 \times 10^{-19}$ J per photon

To find the ionization energy per mole, multiply by Avogadro's number (6.022×10^{23} mol^{-1}):

Ionization energy = $(8.22 \times 10^{-19} \times 6.022 \times 10^{23}) / 1000$

Ionization energy = 494 kJmol^{-1}

(c) Calculate the wave number of the longest wavelength transition in Balmer series of hydrogen.

Wave number ($\bar{v}$) is given by Rydberg equation:

$\bar{v} = R\_H (1/n_1^2 - 1/n_2^2)$

For the longest wavelength in the Balmer series, $n_1 = 2$, $n_2 = 3$:

$\bar{v} = (1.097 \times 10^{7}\ \text{m}^{-1}) (1/2^2 - 1/3^2)$

$\bar{v} = (1.097 \times 10^{7}) (1/4 - 1/9)$

$\bar{v} = (1.097 \times 10^{7}) (5/36)$

$\bar{v} = 1.52 \times 10^{6}\ \text{m}^{-1}$

2. (a) Define the following:

(i) Principal quantum number: It represents the main energy level of an electron in an atom. It is denoted by n and determines the size of the orbital.

(ii) Azimuthal quantum number: It represents the shape of an orbital and is denoted by l. It depends on the principal quantum number and can have values from 0 to (n-1).

(b) Given the quantum number, $n = 3$, answer the following questions:

(i) List all possible orbitals present in this quantum energy.

For $n = 3$, possible values of l are 0, 1, and 2. This corresponds to the orbitals:

- $l = 0 \rightarrow 3s$
- $l = 1 \rightarrow 3p$
- $l = 2 \rightarrow 3d$

(ii) Write possible values of m_l and m_s for this quantum number.

For $l = 0$ (3s): $m_l = 0$

For $l = 1$ (3p): $m_l = -1, 0, +1$

For $l = 2$ (3d): $m_l = -2, -1, 0, +1, +2$

For all orbitals, $m_s = \pm 1/2$

(c) The mass spectrum of an element enables the relative abundance of each isotope of the element to be determined. Data relating to mass spectrum of an element X whose atomic number is 15 is indicated in the table below. Study the data and answer the questions that follow:

Mass Number of Isotopes	Relative Abundance
79	50.5%
81	49.5%

(i) Define the term isotope.

Isotopes are atoms of the same element that have the same number of protons but different numbers of neutrons, leading to different mass numbers.

(ii) Write the conventional symbols for the two isotopes of element X.

^{79}X and ^{81}X

(iii) Calculate the relative atomic mass of X to three significant figures.

Relative atomic mass = $(79 \times 50.5 + 81 \times 49.5) / 100$

$= (3989.5 + 4009.5) / 100$

$= 79.99 \approx 80.0$

3. (a) Give reasons for the following observations:

(i) Both sodium and hydrogen occur in group IA of the periodic table, yet the melting point of sodium chloride is 800°C while that of HCl is -114°C.

Sodium chloride has a high melting point due to its strong ionic bonds between Na^+ and Cl^-. HCl, however, has weak van der Waals forces and dipole-dipole interactions, making it a gas at room temperature with a low melting point.

(ii) Sodium chloride is soluble in water but not in benzene.
Sodium chloride dissolves in water because water is polar and can stabilize Na^+ and Cl^- ions. Benzene is nonpolar and cannot dissolve ionic compounds.

(iii) Although both oxygen and sulphur are in the same group of the periodic table, the hydride of oxygen (H_2O) is a liquid but the hydride of sulphur (H_2S) is a gas at room temperature.
H_2O forms strong hydrogen bonds, leading to a higher boiling point, while H_2S has only weak dipole-dipole interactions, making it a gas at room temperature.

(b) (i) Study the following compounds: hydrogen sulphide (H_2S), ammonia (NH_3), hydrogen fluoride (HF), chloroform ($CHCl_3$), and ethanoic acid (CH_3COOH). With reasons, describe the compounds which contain and those which do not contain hydrogen bonds.
Compounds containing hydrogen bonds: NH_3, HF, CH_3COOH
Compounds without hydrogen bonds: H_2S, $CHCl_3$
NH_3, HF, and CH_3COOH contain highly electronegative elements (N, F, O) bonded to hydrogen, allowing hydrogen bonding. H_2S and $CHCl_3$ lack strong hydrogen bonding.

(ii) Briefly explain why dimethyl ether is more volatile than ethanol although their molecular weights are the same.
Ethanol has hydrogen bonding, which increases intermolecular attraction, leading to a higher boiling point. Dimethyl ether lacks hydrogen bonding, making it more volatile.

4. (a) State why it was necessary to modify the ideal gas equation and show how the modified equation looks like. Define all symbols in the equation.
The ideal gas equation assumes gases have no intermolecular forces and occupy no volume, which is inaccurate. The Van der Waals equation corrects this:
$(P + a(n/V)^2)(V - nb) = nRT$
P = pressure, V = volume, n = number of moles, R = gas constant, T = temperature, a and b are constants correcting for intermolecular forces and molecular volume.

4. (b) Briefly explain why beyond certain temperatures gases cannot be liquefied.

When a gas is heated beyond its critical temperature, the kinetic energy of its molecules becomes too high for intermolecular forces to bring them together into a liquid phase. At this temperature, even under high pressure, the gas cannot condense into a liquid, meaning liquefaction is impossible.

(c) One mole of diethyl ether occupies 1.5 litres at 227°C. Calculate the pressure if the Van der Waals constants for diethyl ether are:
$a = 17.38\ \text{atm} \cdot \text{litre}^2\text{mol}^{-2}$

b = 0.134 litre mol^{-1}

Given:
$V = 1.5$ L
$T = 227°C = 227 + 273 = 500$ K
$n = 1$ mole
$R = 0.0821\ atm \cdot L \cdot mol^{-1} \cdot K^{-1}$

Using Van der Waals equation:

$(P + a(n/V)^2)(V - nb) = nRT$

$(P + (17.38 \times 1^2 / 1.5^2))(1.5 - (1 \times 0.134)) = 1 \times 0.0821 \times 500$

$(P + (17.38 / 2.25))(1.5 - 0.134) = 41.05$

$(P + 7.73) \times 1.366 = 41.05$

$P + 7.73 = 41.05 / 1.366$

$P = (41.05 / 1.366) - 7.73$

$P = 30.06$ atm

5. (a) Define the following terms with reference to gases:

(i) Critical temperature: The highest temperature at which a substance can exist as a liquid. Above this temperature, no amount of pressure can liquefy the gas.

(ii) Critical volume: The volume occupied by one mole of a gas at its critical temperature and pressure.

(iii) Critical pressure: The minimum pressure required to liquefy a gas at its critical temperature.

(b) From the 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 (Mr), and the gas constant, R.

The ideal gas equation is given by:

$PV = nRT$

Since n = mass (m) / molar mass (Mr), we substitute:

$P \times V = (m / Mr) \times R \times T$

Rearrange for m/V, which is density (ρ):

$\rho = (P \times Mr) / (R \times T)$

(c) A certain dry gas is composed of 21 percent by volume of oxygen, 1 percent of argon, and 78 percent of nitrogen. Find its density in gdm^{-3} at 20°C and 98.65 kNm^{-2} pressure.

Molar masses:
$O_2 = 32\ gmol^{-1}$, $Ar = 40\ gmol^{-1}$, $N_2 = 28\ gmol^{-1}$

Average molar mass (Mr) = $(0.21 \times 32) + (0.01 \times 40) + (0.78 \times 28)$
$= 6.72 + 0.40 + 21.84$
$= 28.96\ gmol^{-1}$

Convert pressure:
$98.65\ kNm^{-2} = 98.65 \times 10^3\ Nm^{-2} = 98.65 \times 10^3\ Pa$

Using $\rho = (P \times Mr) / (R \times T)$, with $R = 8.314\ Jmol^{-1}K^{-1}$ and $T = 20 + 273 = 293\ K$:

$\rho = (98.65 \times 10^3 \times 28.96) / (8.314 \times 293)$
$\rho = (2.855 \times 10^6) / 2437.9$
$\rho = 1.171\ gdm^{-3}$

6. (a) Give two differences between osmosis and diffusion.

Osmosis involves the movement of solvent molecules through a semipermeable membrane, while diffusion is the movement of molecules from a high concentration to a low concentration without a membrane.

Osmosis occurs only in liquids, whereas diffusion can occur in gases, liquids, or solids.

(b) When 15 g of glucose ($C_6H_{12}O_6$) was dissolved in 50 g of a certain solvent with a relative molecular mass of 180 g, the freezing point was depressed by 8.0°C. Using these data, calculate the freezing point depression constant for the solvent.

$\Delta T_f = K_f \times$ (moles of solute / kg of solvent)

Moles of glucose = 15 / 180 = 0.0833 mol

Mass of solvent = 50 g = 0.050 kg

$8.0 = K_f \times (0.0833 / 0.050)$

$K_f = 8.0 \times (0.050 / 0.0833)$

$K_f = 4.8$ °C kg mol^{-1}

(c) An aqueous solution of sugar containing 19.15 g of sugar per dm^3 has osmotic pressure of 136,300 Nm^{-2} at 20°C. Calculate the relative molecular mass of sugar.

Using the osmotic pressure equation:

$\pi = (n/V)\ RT$

where $\pi = 136300$ Pa, $V = 1$ dm^3 $= 0.001$ m^3, $R = 8.314$ Jmol^{-1}K^{-1}, and $T = 293$ K

n = mass / molar mass (M), so

$\pi = (\text{mass} / M \times V) \times RT$

Rearrange for M:
$M = (\text{mass} \times R \times T) / (\pi \times V)$

$M = (19.15 \times 8.314 \times 293) / (136300 \times 1)$
$M = (46621.8) / 136300$

$M = 342$ gmol^{-1}

7. (a) Give a brief molecular explanation of positive and negative deviations from Raoult's law for non-ideal binary solutions.

Positive deviation occurs when intermolecular forces between different components of the mixture are weaker than those in the pure components. This leads to higher vapour pressure than expected because molecules escape easily. An example is ethanol and acetone.

Negative deviation occurs when intermolecular forces between different components of the mixture are stronger than in the pure components, leading to lower vapour pressure than expected. An example is water and nitric acid due to strong hydrogen bonding.

(b) What vapour pressure lowering difference(s), if any, would you expect for 1 M aqueous solutions of
(i) $CaCl_2$
(ii) KBr
(iii) Na_3PO_4
Justify your answer.

Vapour pressure lowering is related to the number of particles in solution (colligative property).

(i) $CaCl_2$ dissociates into three ions (Ca^{2+} and $2Cl^-$), so it lowers vapour pressure significantly.
(ii) KBr dissociates into two ions (K^+ and Br^-), lowering vapour pressure moderately.
(iii) Na_3PO_4 dissociates into four ions ($3Na^+$ and PO_4^{3-}), lowering vapour pressure the most.

Thus, the order of vapour pressure lowering is $Na_3PO_4 > CaCl_2 > KBr$.

(c) Benzene (C_6H_6) and toluene ($C_6H_5CH_3$) form an ideal solution. At 333 K, the vapour pressure of pure benzene is 53.3 kPa while that of pure toluene is 26.7 kPa. If a solution is prepared by mixing two moles of benzene and three moles of toluene:

(i) Find the partial pressure of each component in the vapour phase in equilibrium with this solution at 333 K.

Mole fractions:
X_benzene = 2 / (2 + 3) = 2/5 = 0.4
X_toluene = 3 / (2 + 3) = 3/5 = 0.6

Partial pressures:
P_benzene = X_benzene × P°_benzene = 0.4 × 53.3 = 21.32 kPa
P_toluene = X_toluene × P°_toluene = 0.6 × 26.7 = 16.02 kPa

(ii) Calculate the total vapour pressure of the solution.

P_total = P_benzene + P_toluene
P_total = 21.32 + 16.02
P_total = 37.34 kPa

(iii) Explain which substance will be collected from the top of the distillation column, if a mixture of benzene and toluene is distilled.

Benzene has a higher vapour pressure and lower boiling point, so it will be collected at the top of the distillation column as it evaporates more readily.

8. (a) Pure ethanol (C_2H_5OH) boils at 78.3°C and at a pressure of 760 mmHg. When 2.51 g of an organic compound M (Mwt = 146 g) is dissolved in 100 g of ethanol, the solution boils at 85.9°C and 770 mmHg.

(i) Explain why the boiling point of ethanol was raised.

The addition of a non-volatile solute lowers the vapour pressure of the solvent, requiring a higher temperature for the solution to reach the atmospheric pressure, thus raising the boiling point (boiling point elevation).

(ii) Calculate the molal boiling point constant, K_b, for ethanol.

$\Delta T_b = K_b \times m$

where m = moles of solute / kg of solvent
= (2.51 / 146) / (100 / 1000)
= (0.0172) / (0.1)
= 0.172 m

$\Delta T_b = 85.9 - 78.3 = 7.6°C$

$K_b = 7.6 / 0.172$
$K_b = 44.2$ °C kg mol^{-1}

(b) A solution was prepared by dissolving 2.40 g of biphenyl ($C_{12}H_{10}$) in 75.00 g of benzene. Calculate the boiling point of the solution given that K_b = 2.53 °C/m, K_f = 5.12 °C/m; boiling point of pure benzene = 80.1°C and freezing point of pure benzene = 5.5°C.

Moles of biphenyl = 2.40 / 154 = 0.0156 mol
Molality = 0.0156 / (75/1000) = 0.208 m

$\Delta T_b = K_b \times$ molality
= 2.53 × 0.208
= 0.526°C

Boiling point = 80.1 + 0.526
= 80.6°C

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

At equilibrium, the forward and reverse reactions occur at the same rate, meaning reactants and products are formed continuously but in equal amounts, maintaining a constant concentration.

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

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

At equilibrium, molecules of H_2 and I_2 react to form HI at the same rate as HI decomposes into H_2 and I_2, maintaining constant concentrations.

(b) (i) Mention the four common stresses explained by Le Chatelier's principle to help maximize the yield of ammonia gas in the Haber process.

- Change in concentration
- Change in pressure
- Change in temperature
- Addition of a catalyst

(ii) The equation for production of ammonia gas is:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92.6$ kJ

From the given equation, explain how maximum yield of ammonia can be achieved.

- Increasing pressure shifts equilibrium to the side with fewer gas molecules (right side), increasing ammonia yield.
- Lowering temperature favors the exothermic reaction, increasing yield.
- Removing ammonia as it forms shifts equilibrium forward.
- Using a catalyst like iron speeds up the reaction without shifting equilibrium.

10. (a) State the following:

(i) Heat of reaction: The energy change during a chemical reaction, measured as the difference between reactants and products.

(ii) Exothermic reaction: A reaction that releases heat, making the surroundings warmer (e.g., combustion of methane).

(iii) Endothermic reaction: A reaction that absorbs heat, making the surroundings cooler (e.g., dissolution of ammonium nitrate).

(b) 1.5 g of ammonium nitrate (NH_4NO_3) was added to 35.0 g of water in a plastic beaker and stirred until the salt dissolved. The temperature of the solution dropped from 22.7°C to 19.4°C.

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

Since heat is absorbed from the surroundings (temperature decreases), the process is endothermic.

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

$q = m \times C \times \Delta T$

$= (35 \times 4.184 \times (19.4 - 22.7))$
$= (35 \times 4.184 \times -3.3)$
$= -483.8$ J
$= -0.484$ kJ

Moles of $NH_4NO_3 = 1.5 / 80 = 0.01875$ mol

$\Delta H = q / n$
$= -0.484 / 0.01875$
$= -25.8$ kJ/mol

11. (a) Briefly explain the following terms and give an example of a family of organic compounds in each case:

(i) Hydrocarbon: A hydrocarbon is an organic compound composed entirely of carbon and hydrogen atoms. They can be alkanes, alkenes, or alkynes.
Example: Methane (CH_4), which belongs to the alkane family.

(ii) Saturated hydrocarbon: A hydrocarbon in which all carbon-carbon bonds are single bonds, meaning they contain the maximum number of hydrogen atoms.
Example: Ethane (C_2H_6), which is an alkane.

(iii) Unsaturated hydrocarbon: A hydrocarbon that contains one or more double or triple bonds between carbon atoms.
Example: Ethene (C_2H_4), which is an alkene.

(b) 10 cm^3 of a gaseous hydrocarbon Q required 45 cm^3 of oxygen for complete combustion. Q reacts with 1 mole of bromine gas to form a brominated compound of relative molecular mass 186, which contains 79.2 percent bromine.

(i) Determine the molecular formula of Q.

Combustion reaction of a hydrocarbon follows:
$C_xH_\gamma + O_2 \rightarrow CO_2 + H_2O$

From the volume ratio,
1 volume of Q reacts with 4.5 volumes of O_2, suggesting the formula C_4H_{10} or C_4H_8.

To confirm, we use bromine reaction and molecular mass.

Given mass fraction of bromine:
Mass of bromine in compound = 79.2 percent of 186
= 0.792 × 186
= 147.31 g

Since each molecule contains one bromine atom (atomic mass 80 g/mol),
Number of bromine atoms = 147.31 / 80 ≈ 2

This suggests the molecular formula of Q is C_4H_8.

(ii) Give the structural formula of Q.

Since Q reacts with bromine and is C_4H_8, it is an alkene. The simplest structure satisfying these conditions is butene:

$H_2C=CH-CH_2-CH_3$ (1-butene) or
$CH_3-CH=CH-CH_3$ (2-butene)

Thus, the structural formula of Q is either 1-butene or 2-butene.

12. (a) Define the following:

(i) Isomers: Compounds with the same molecular formula but different structural arrangements or spatial orientations.
(ii) Isomerism: The phenomenon where compounds have the same molecular formula but different structures, leading to different physical and chemical properties.

(b) Write the structural formulae of the following:

(i) 3-methyl-1-pentene:

$CH_2=CH-CH(CH_3)-CH_2-CH_3$

(ii) 2-methyl-2-pentene:

$CH_3-C(CH_3)=CH-CH_2-CH_3$

(iii) 2,2-dimethylpentane:

CH_3-$C(CH_3)_2$-CH_2-CH_2-CH_3

(iv) 4-methylpent-2-yne:

CH_3-C≡C-$CH(CH_3)$-CH_3

(c) Identify a simple chemical test that can be used to distinguish between the following compounds.

(i) 1-butyne and 2-butyne: Use ammoniacal silver nitrate (Tollen's reagent). 1-butyne gives a white precipitate, while 2-butyne does not react.
(ii) Butane and butene: Use bromine water. Butene decolorizes bromine water, while butane does not react.

13. (a) (i) Outline the stages in the formation of chloromethane from methane and chlorine at 450°C.

1. Initiation: Cl_2 -----> 2Cl• (formation of chlorine radicals by UV light or heat)
2. Propagation:
   CH_4 + Cl• -----> CH_3• + HCl
   CH_3• + Cl_2 ----> CH_3Cl + Cl•
3. Termination: Radicals recombine to stop the reaction:
   CH_3• + Cl• ----> CH_3Cl

(ii) Give a reason why the chloromethane obtained in (a) (i) is not pure.

Multiple substitution reactions occur, leading to dichloromethane, trichloromethane, and tetrachloromethane as by-products.

(b) Bromolalkanes may react with alcoholic potassium hydroxide solution to form alkenes.

(i) What type of organic reaction is this reaction?

Elimination (dehydrohalogenation) reaction.

(ii) Write an equation for the reaction of 1-bromobutane with alcoholic potassium hydroxide.

$CH_3CH_2CH_2CH_2Br$ + KOH(alc) -----> CH_3CH=$CHCH_3$ + HBr

(iii) Draw the structural formula of the alkene obtained by reaction between 2-bromobutane and alcoholic potassium hydroxide.

CH_3-CH=CH-CH_3 (but-2-ene)

14. (a) Briefly explain the following:

(i) The C-C bonds are all equal and intermediate in length between a single and a double bond in benzene.

Benzene has delocalized π-electrons forming a resonance structure, making all C-C bonds of equal length (1.39 Å), intermediate between single (1.54 Å) and double bonds (1.34 Å).

(ii) Dry ether is necessary in the preparation and use of the Grignard reagent.

Grignard reagents are highly reactive with water and oxygen. Dry ether prevents hydrolysis of RMgX, ensuring stability and reactivity.

(b) The chlorination of methyl benzene and 1,1-dimethylethyl benzene yield the following isomers:

For methyl benzene:
Position 2 (60%), Position 3 (0.5%), Position 4 (39.5%)

For 1,1-dimethylethyl benzene:
Position 2 (22%), Position 3 (8%), Position 4 (70%)

The different product ratio is due to steric hindrance and electronic effects. In methyl benzene, positions 2 and 4 are favored due to electron-donating resonance effects of the methyl group. In 1,1-dimethylethyl benzene, the bulky tert-butyl group hinders ortho substitution, making para substitution (position 4) more dominant.