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: 2001**

Instructions

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

2. Each question carries ten marks.

1. (a) State the rules which govern the pairing of electrons in orbitals of an atom which is in ground state.

The rules governing electron pairing in atomic orbitals are:

1. Aufbau Principle – Electrons fill orbitals in order of increasing energy, starting from the lowest available orbital.
2. Hund's Rule – Electrons occupy degenerate orbitals singly with parallel spins before pairing occurs to minimize electron repulsion.
3. Pauli Exclusion Principle – No two electrons in an atom can have the same set of four quantum numbers, meaning an orbital can hold a maximum of two electrons with opposite spins.

(b) Give the name of a geometrical structure and one example of the molecule formed from the following hybridized atomic orbitals.

(i) sp^3 hybridized orbitals

Geometrical Structure: Tetrahedral
Example: Methane (CH_4)

(ii) sp^2 hybridized orbitals

Geometrical Structure: Trigonal Planar
Example: Ethene (C_2H_4)

(iii) dsp^3 hybridized orbitals

Geometrical Structure: Trigonal Bipyramidal
Example: Phosphorus Pentachloride (PCl_5)

(c) Calculate the energy associated with an electron moving in an orbital of principle quantum number n = 2.

Energy of an electron in an orbital is given by:

$E = -13.6 \text{ eV} / n^2$

For n = 2,

$E = -13.6 / 2^2$
$E = -13.6 / 4$
$E = -3.4 \text{ eV}$

2. (a) State

(i) Avogadro's law

Avogadro's law states that equal volumes of gases at the same temperature and pressure contain the same number of molecules.

(ii) Dalton's law of partial pressure

Dalton's law states that the total pressure exerted by a mixture of gases in a container is equal to the sum of the partial pressures of the individual gases.

$P\_total = P_1 + P_2 + P_3 + \ldots$

(b) A 15.5-litre sample of 0.75 mole oxygen gas at a pressure of 1 atmosphere and a temperature of 25°C was completely converted to ozone (O_3) at the same temperature and pressure. What was the volume of ozone?

From the equation:

$3O_2(g) \text{ ----> } 2O_3(g)$

Using the mole ratio,

$0.75 \text{ mol } O_2 \times (2 \text{ mol } O_3 / 3 \text{ mol } O_2) = 0.5 \text{ mol } O_3$

Since 1 mole of gas at given temperature and pressure occupies the same volume,

Volume of ozone = (0.5 mol / 0.75 mol) × 15.5 L
= 10.33 L

(c) A mixture of helium and oxygen is used in diving tanks instead of nitrogen, which at elevated pressures dissolves in blood producing an agonizing condition called "the bends".

For a particular dive, 40 litres of oxygen at 25°C and 1.0 atmosphere were pumped along with 12 litres of helium at 25°C and 1.0 atmosphere into a tank with a volume of 5.0 litres. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.

Using Boyle's Law:

$P_1V_1 = P_2V_2$

For oxygen:

(1.0 atm) (40 L) = P_2 (5 L)
P_2 = 8 atm

For helium:

(1.0 atm) (12 L) = P_2 (5 L)
P_2 = 2.4 atm

Total pressure = 8 + 2.4 = 10.4 atm

3. (a) 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 concentrations of the reactants, each raised to the power of their stoichiometric coefficients in the balanced chemical equation.

(b) Distinguish between equilibrium constant and reaction quotient.

Equilibrium constant (K) is the ratio of the concentration of products to reactants at equilibrium, while reaction quotient (Q) is the same ratio at any point in time before equilibrium is reached.

(c) A 4-litre flask was filled with 2.0 moles of gaseous SO_2 and 2.0 moles of gaseous NO_2 and heated. After equilibrium was reached, it was found that 1.2 moles of gaseous NO was present. Assume that the reaction

$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

occurs under these conditions. Calculate the value of Kc and Kp for this reaction.

Using the ICE table method, determine equilibrium concentrations, then apply:

$Kc = [SO_3][NO] / [SO_2][NO_2]$

Kp is calculated using the relation:

$Kp = Kc (RT)^{\Delta n}$

where Δn is the change in the number of moles of gas.

4. (a) What is meant by

(i) Oxidation state

Oxidation state is the charge an atom would have if all bonds were ionic.

(ii) Reducing agent

A reducing agent is a substance that donates electrons in a redox reaction and gets oxidized itself.

(iii) Oxidation

Oxidation is the process of losing electrons, increasing oxidation state.

(iv) Reduction

Reduction is the process of gaining electrons, decreasing oxidation state.

(b) Which of the following equations represent redox reactions?

(i) $H_2(g) + Cl_2(g)$ ---> $2HCl(g)$ ✅
(ii) $NaOH(aq) + H_2SO_4(aq)$ ----> $NaHSO_4(aq) + H_2O(l)$ ❌ (acid-base reaction)
(iii) $BaCl_2(aq) + H_2SO_4(aq)$ ----> $BaSO_4(s) + 2HCl(aq)$ ❌ (precipitation reaction)
(iv) $Cl_2(aq) + 3I^-(aq) + 3H^+(aq)$ -----> $Cl^-(aq) + I_3^-(aq) + 3H_2O(l)$ ✅
(v) $2Cu^{2+}(aq) + 4I^-(aq)$ ----> $2CuI(s) + I_2(aq)$ ✅

(c) Write a balanced equation for the reaction between

(i) Acidified dichromate (VI) ions and sulphur dioxide solution

$Cr_2O_7^{2-} + SO_2 + H^+$ ------> $Cr^{3+} + SO_4^{2-} + H_2O$

(ii) Manganate(VII) ions and iron (II) ions in acid solution
$MnO_4^- + Fe^{2+} + H^+$ ---> $Mn^{2+} + Fe^{3+} + H_2O$

5. (a) Define the term transition metals.

Transition metals are elements that have partially filled d-orbitals and can exhibit multiple oxidation states in their compounds.

(b) Write the electronic configurations of Cr^{3+} and Cu.

Cr^{3+}: [Ar] $3d^3$
Cu: [Ar] $3d^{10}$ $4s^1$

(c) Explain in terms of their electronic configurations why Cr and Cu are said to violate the Aufbau principle.

Chromium and copper do not follow the expected filling order due to the stability provided by half-filled and fully-filled d orbitals.

(d) (i) Give the formula of a compound or ion containing chromium in an oxidation state of +6.

$K_2Cr_2O_7$ (Potassium dichromate)

(ii) Give the formula of the chromium complex dichlorobis (ethylenediamine) chromium (III) nitrate.

$[Cr(en)_2Cl_2]NO_3$

(iii) In (ii) above, which ligand is anionic and neutral?
Anionic: Cl^-
Neutral: en (ethylenediamine)

6. (a) Distinguish between solubility and solubility product of a given solid substance.

Solubility refers to the amount of a solute that dissolves in a solvent at equilibrium, whereas solubility product (Ksp) is the equilibrium constant for the dissolution of a sparingly soluble compound.
6. (b) A solution is prepared by mixing 150.0 ml of 1.00×10^{-2} M $Mg(NO_3)_2$ and 250.0 ml of 1.00×10^{-4} M NaF. Calculate the concentrations of Mg^{2+} and F^- at equilibrium with solid MgF_2. (Ksp = 6.4×10^{-9} mol² dm⁻⁶ at 298 K)

Step 1: Determine initial concentrations after mixing

Since different volumes are mixed, the new concentrations must be calculated using dilution:

Total volume = 150.0 ml + 250.0 ml = 400.0 ml = 0.400 dm^3

New concentration of Mg^{2+}:

$C(Mg^{2+}) = (1.00 \times 10^{-2}\ M \times 150.0\ ml) / 400.0\ ml$
$= (1.50 \times 10^{-3}\ M)$

New concentration of F^-:

$C(F^-) = (1.00 \times 10^{-4}\ M \times 250.0\ ml) / 400.0\ ml$
$= (6.25 \times 10^{-5}\ M)$

Step 2: Establish equilibrium conditions

The solubility equilibrium for MgF_2 is:

$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$

Let s be the solubility of MgF_2 in mol dm^{-3}.

At equilibrium:
$[Mg^{2+}] = (1.50 \times 10^{-3}) + s$
$[F^-] = (6.25 \times 10^{-5}) + 2s$

Step 3: Apply solubility product expression

$Ksp = [Mg^{2+}] [F^-]^2$
$6.4 \times 10^{-9} = (1.50 \times 10^{-3} + s) (6.25 \times 10^{-5} + 2s)^2$

Since s is small compared to the initial concentrations, an approximation can be made:

$6.4 \times 10^{-9} \approx (1.50 \times 10^{-3}) (6.25 \times 10^{-5})^2$

Step 4: Solve for equilibrium concentrations

$6.4 \times 10^{-9} = (1.50 \times 10^{-3}) (3.91 \times 10^{-9})$
$6.4 \times 10^{-9} / 1.50 \times 10^{-3} = 3.91 \times 10^{-9}$
$s \approx 4.27 \times 10^{-6}$ M

Final equilibrium concentrations:

$[Mg^{2+}] \approx 1.50 \times 10^{-3} + 4.27 \times 10^{-6} = 1.50 \times 10^{-3}$ M
$[F^-] \approx 6.25 \times 10^{-5} + (2 \times 4.27 \times 10^{-6}) = 7.10 \times 10^{-5}$ M

7. With the aid of balanced chemical equations where necessary, explain how pure copper is obtained from copper pyrites.

Copper is extracted from copper pyrites ($CuFeS_2$) through the following steps:

1. Concentration of ore: The ore is concentrated by froth flotation.
2. Roasting: The concentrated ore is heated in the presence of oxygen to form copper(I) sulfide and iron(II) oxide.

$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$

3. Smelting: The mixture is heated in a blast furnace with silica (SiO_2), forming iron silicate (slag) and molten copper(I) sulfide.

$FeS + SiO_2 \rightarrow FeSiO_3$ (slag)

4. Bessemerization: Air is blown through molten copper(I) sulfide to oxidize it to copper metal.

$Cu_2S + O_2 \rightarrow 2Cu + SO_2$

Pure copper is obtained through electrorefining.

8. (a) List the postulates which led to the derivation of the fundamental gas equation.

1. A gas consists of a large number of identical molecules in random motion.
2. The volume of individual gas molecules is negligible compared to the volume of the gas.
3. Gas molecules undergo elastic collisions with each other and container walls.
4. There are no intermolecular forces except during collisions.
5. The kinetic energy of gas molecules is directly proportional to the absolute temperature.

(b) Find the density of oxygen gas at 25°C and 0.987 atmospheres.

Using the ideal gas equation:

$PV = nRT$

Density (ρ) = (PM) / (RT)

Where:
P = 0.987 atm
M = 32 g/mol (molar mass of O_2)
R = 0.0821 $L \cdot atm \cdot mol^{-1} \cdot K^{-1}$
T = 298 K

$\rho = (0.987 \times 32) / (0.0821 \times 298)$

$\rho \approx 1.29$ g/L

(c) 280 cm^3 of nitrogen diffuse through a membrane in 70 seconds. How long will it take for 400 cm^3 of carbon dioxide to diffuse through the same membrane under the same conditions?

Using Graham's law of diffusion:

Rate of diffusion $\propto 1/\sqrt{\text{Molar mass}}$

Molar mass of N_2 = 28 g/mol
Molar mass of CO_2 = 44 g/mol

$t_2 / t_1 = \sqrt{(M_2 / M_1)}$

$t_2 / 70 = \sqrt{(44 / 28)}$

$t_2 = 70 \times \sqrt{(44/28)}$

$t_2 \approx 98.6$ seconds

9. (a) Write short notes on the following terms.

(i) Diffusion: The process by which molecules move from a region of higher concentration to a region of lower concentration.

(ii) Osmosis: The movement of solvent molecules through a semi-permeable membrane from a dilute solution to a more concentrated solution.

(iii) Osmotic pressure: The pressure required to prevent the flow of solvent molecules through a semi-permeable membrane.

(iv) Effusion: The movement of gas molecules through a small hole without collisions between them.

(b) (i) What is the difference between osmosis and diffusion?

- Diffusion occurs in gases and liquids and involves the movement of solute and solvent molecules, while osmosis involves only solvent molecules moving through a membrane.
- Osmosis requires a semi-permeable membrane, while diffusion does not.

(ii) When 15 g of glucose, $C_6H_{12}O_6$, was dissolved in 50 g of 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.

$\Delta T = Kf \times m$

Where:
$\Delta T = 8.0°C$
m = (15 g / 180 g/mol) / 0.050 kg
m = (0.0833 mol) / (0.050 kg)
m = 1.666 mol/kg

Kf = 8.0 / 1.666

$Kf \approx 4.8°C \cdot kg \cdot mol^{-1}$

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

Using the equation:

$\pi = cRT$

$c = \pi / (RT)$

$\pi = 136300\ N/m^2$
R = 8.314 J/mol·K
T = 293 K

$c = 136300 / (8.314 \times 293)$
$c \approx 55.94\ mol/m^3$

Mass concentration = 19.15 g/dm^3

Molar mass = 19.15 / 55.94

Molar mass ≈ 343 g/mol

10. (a) State Hund's rule of maximum multiplicity.

Hund's rule states that electrons occupy degenerate orbitals singly with parallel spins before pairing occurs to maximize stability.

(b) What is the maximum number of electrons in an atom which has the following quantum numbers?

(i) n = 2, and l = 1.

For n = 2 and l = 1, we have the 2p orbital, which holds a maximum of 6 electrons.

(ii) n = 2, l = 1, $m_l = -1$ and $m_s = -½$.

This specifies a single electron in the 2p orbital. The maximum number of such electrons is 1.

(c) 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 are 0.42, 0.74, and 1.5 MJ/mol. The atomic radii are 1.60 Å, 0.94 Å, and 1.97 Å.

Matching configuration with properties:

X is a noble gas with the smallest atomic radius and the highest ionization energy (1.5 MJ/mol).
X = Argon (Ar), radius = 0.94 Å.

Y is an alkaline earth metal with an intermediate radius and moderate ionization energy (0.74 MJ/mol).
Y = Magnesium (Mg), radius = 1.60 Å.

Z is an alkali metal with the largest radius and lowest ionization energy (0.42 MJ/mol).
Z = Potassium (K), radius = 1.97 Å.

11. (a) Explain briefly what is meant by the terms

(i) Addition polymerisation

Addition polymerisation is a type of polymerisation in which monomers containing double or triple bonds undergo successive addition reactions to form a polymer without the elimination of any by-product. The reaction occurs through free-radical or ionic mechanisms.

Example: The polymerisation of ethene to form polyethene.

$nCH_2=CH_2 \rightarrow (-CH_2-CH_2-)_n$

(ii) Condensation polymerisation

Condensation polymerisation is a type of polymerisation in which monomers containing two different functional groups react together with the elimination of a small molecule, such as water or hydrogen chloride, to form a polymer.

Example: The formation of nylon-6,6 from hexamethylenediamine and adipic acid.

$nH_2N-(CH_2)_6-NH_2 + nHOOC-(CH_2)_4-COOH \rightarrow (-NH-(CH_2)_6-NHCO-(CH_2)_4-CO-)_n + 2nH_2O$

(b) Give three properties of nylon.

1. Nylon is strong and has high tensile strength, making it suitable for use in ropes, fabrics, and mechanical parts.
2. Nylon is resistant to wear, abrasion, and chemicals, giving it durability in various applications.

3. Nylon has a low moisture absorption rate, which makes it suitable for use in waterproof materials and synthetic fibers.

(c) Write a correct structural formula for each of the following compounds.

(i) 2-bromo-2,5-dimethylhexane

CH_3-CH_2-C(Br)(CH_3)-CH_2-CH(CH_3)-CH_3

(ii) 3-ethyl-6-methyloctane

CH_3-CH_2-CH(CH_2CH_3)-CH_2-CH(CH_3)-CH_2-CH_2-CH_3

(iii) 2,4,4-trimethylpent-1-ene

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

(iv) 4-methylhydroxybenzene

C_6H_4(OH)(CH_3) (also known as 4-methylphenol or p-cresol)

(v) 2,2-dichloro-5,6-diethylnonane

CH_3-CH_2-CH(Cl)-CH(Cl)-CH_2-CH(C_2H_5)-CH(C_2H_5)-CH_2-CH_3

12. (a) Give the systematic IUPAC name for each of the following compounds:

(i) 1,1,3-trimethylcyclohexane

(ii) 3-methylpent-1-yne

(iii) 3-chloro-4-methylhex-2-ene

(iv) 3-methylcyclopentene

(v) 2-ethyl-3-methylbutanal

(vi) Propyl ethanoate

(b) Study the following organic reactions carefully and answer the questions which follow.

(i) A + O_3 → Zn / H_2O → B(C_2H_4O) + C(C_2H_4O)

This is an ozonolysis reaction.

(ii) B + $KMnO_4$ → D

This is an oxidation reaction.

(iii) 2B + cold NaOH → $E(C_2H_4O_2)$

This is a haloform reaction.

(iv) D + $SOCl_2$ → F + HCl(g) + SO_2(g)

This is a halogenation reaction.

(v) C_6H_6 → CH_3COCl + $AlCl_3$ → $CH_3COC_6H_6$

This is a Friedel-Crafts acylation reaction.

(vi) $CH_3COC_6H_4CH_3$ + conc. HCl → G

This is a nucleophilic substitution reaction.

(c) Write the systematic IUPAC names and structures of compounds A, B, C, D, E, F, and G given in question 12(b).

A: 2-butene
B: Ethanal
C: Acetone
D: Ethanoic acid
E: Sodium ethanoate
F: Ethanoyl chloride
G: 4-methylbenzophenone

13. (a) With the help of chemical equations show clearly how the following conversions can be achieved (not more than 4 steps).

(i) CH_3CH_2Cl → CH_3COOH

1. Hydrolysis: CH_3CH_2Cl + NaOH → CH_3CH_2OH + NaCl
2. Oxidation: CH_3CH_2OH + [O] → CH_3CHO + H_2O
3. Further oxidation: CH_3CHO + [O] → CH_3COOH

(ii) $CH_3CH_2C≡CH \rightarrow CH_3CH_2CH(CH_3)Cl$

1. Hydrohalogenation: $CH_3CH_2C≡CH + HCl \rightarrow CH_3CH_2C=CHCl$
2. Markovnikov addition: $CH_3CH_2C=CHCl + HCl \rightarrow CH_3CH_2CH(CH_3)Cl$

(iii) Ethylbenzene → Acetophenone

Oxidation: $C_6H_5CH_2CH_3 + [O] \rightarrow C_6H_5COCH_3$

(iv) Toluene → Benzyl alcohol

Oxidation-reduction: $C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl$
$C_6H_5CH_2Cl + NaOH \rightarrow C_6H_5CH_2OH$

(v) Cyclohexanone → Cyclohexene

Reduction: $C_6H_{10}O + Zn/HCl \rightarrow C_6H_{10}$

(vi) $CH_3C(OH)CH_2CH_3 \rightarrow CH_3C≡CCH_2Br$

1. Dehydration: $CH_3C(OH)CH_2CH_3 \rightarrow CH_3C=CHCH_3 + H_2O$
2. Bromination: $CH_3C=CHCH_3 + Br_2 \rightarrow CH_3C=CHCH_2Br$

(b) Two alternative routes to compound A are given below. Which route is likely to be more successful? Explain.

Route I:
$CH_3C≡CCH_3 \rightarrow NaNH_2 + CH_3CH_2Br \rightarrow CH_3C≡CCH_2CH_3$

Route II:
$CH_3C≡CH + NaNH_2 + (CH_3)_3CBr \rightarrow CH_3C≡C(CH_2)_2CH_3$

Route II is more successful because it avoids side reactions and provides better regioselectivity, leading to a higher yield of the desired compound.

14. (a) Explain each of the following observations.

(i) The fishy odor of a solution of dimethylamine in water is lost when an equimolar amount of hydrochloric acid is added.

Dimethylamine $(CH_3)_2NH$ is a weak base. When HCl is added, it forms dimethylammonium chloride $(CH_3)_2NH_2^+Cl^-$, which is non-volatile and odorless.

(ii) The acidity of phenol, cyclohexanol, and cyclohexane follows the trend:

Phenol > Cyclohexanol > Cyclohexane

Phenol is the most acidic because the negative charge on the phenoxide ion is delocalized by resonance. Cyclohexanol is less acidic because it lacks resonance stabilization. Cyclohexane is the least acidic as it does not contain an -OH group.

(iii) When water is carefully added to benzoyl chloride, a white precipitate is formed, but on addition of excess sodium hydroxide, a clear solution is obtained.

Benzoyl chloride reacts with water to form benzoic acid, which is sparingly soluble and precipitates. In excess NaOH, benzoic acid dissolves as sodium benzoate.

$C_6H_5COCl + H_2O \rightarrow C_6H_5COOH + HCl$
$C_6H_5COOH + NaOH \rightarrow C_6H_5COONa + H_2O$

(b) An allyl bromide X contains 35.04% carbon, 6.56% hydrogen, and 58.40% bromine. Treatment of X with a mixture of ethanol and potassium hydroxide yields compound Y. Oxidation of Y gives propanone, carbon dioxide, and water. Y also reacts with hydrobromic acid to give Z, which is isomeric to X.

Using this information, suggest structures for X, Y, and Z.

X: 3-bromopropene ($CH_2=CHCH_2Br$)
Y: Propene ($CH_3CH=CH_2$)
Z: 1-bromopropene ($CH_3CBr=CH_2$)