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: 2024**

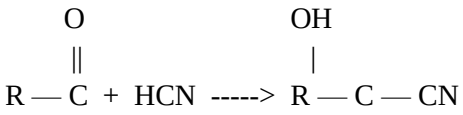
Instructions

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.

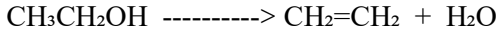
1. (a) Briefly explain the following concepts by giving one example for each:

(i) Nucleophilic addition reaction.
A nucleophilic addition reaction occurs when a nucleophile attacks an electrophilic center, typically in carbonyl compounds, forming a new covalent bond. An example is the addition of hydrogen cyanide (HCN) to an aldehyde or ketone, forming a cyanohydrin.
Reaction:



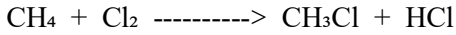
This reaction occurs due to the partial positive charge on the carbonyl carbon, making it susceptible to nucleophilic attack.

(ii) Elimination reaction.
An elimination reaction involves the removal of two atoms or groups from adjacent carbon atoms, forming a double or triple bond. An example is the dehydration of ethanol to ethene in the presence of sulfuric acid:
Reaction:



This occurs via an E1 or E2 mechanism depending on conditions.

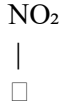
(iii) Substitution reaction.
A substitution reaction involves replacing one atom or functional group with another. An example is the halogenation of alkanes, such as the reaction of methane with chlorine under UV light:
Reaction:



This occurs via a free radical mechanism.

(iv) Mesomeric effect.
The mesomeric effect refers to the delocalization of electrons in a conjugated system due to resonance. It stabilizes compounds like benzene and carboxylates. An example is the resonance in benzene:

(v) Negative inductive effect.
The negative inductive effect (-I) is the withdrawal of electron density through sigma bonds due to electronegativity. An example is the electron-withdrawing effect of the $-NO_2$ group in nitrobenzene:



The $-NO_2$ group pulls electrons away from the benzene ring, making it less reactive toward electrophilic substitution.

(b) A 20 cm^3 volume of gaseous hydrocarbon was mixed with 140 cm^3 of excess oxygen and exploded. After cooling, the mixture occupied 100 cm^3. Absorption of the gas by concentrated potassium hydroxide solution reduced the volume by 60 cm^3 and the unabsorbed gas relighted the glowing splint. Determine the molecular formula of the hydrocarbon.

Step 1: Identify the products of combustion
The reaction of a hydrocarbon with oxygen forms CO_2 and H_2O. The absorbed gas by KOH is CO_2, and the remaining gas is unreacted O_2.

Step 2: Determine CO_2 volume
The reduction by KOH indicates 60 cm^3 of CO_2 was produced.
Step 3: Determine O_2 volume
The remaining 40 cm^3 is unreacted O_2. The total oxygen before the reaction was 140 cm^3. Therefore, the O_2 used in combustion is:

O_2 used = 140 cm^3 - 40 cm^3 = 100 cm^3

Step 4: Determine the hydrocarbon formula
The general combustion equation is:

$$C_xH_\gamma + O_2 \text{ -------> } CO_2 + H_2O$$

From the reaction:
- 20 cm^3 of hydrocarbon produced 60 cm^3 of CO_2, implying x = 3.
- 100 cm^3 of O_2 was used. Since each carbon requires one O_2 and hydrogen requires O_2 in a 1:4 ratio, solving gives y = 8.

Thus, the molecular formula is C_3H_8 (propane).

2. (a) What is the difference between the following?

(i) Subsidiary quantum number and magnetic quantum number.
- The subsidiary quantum number (l) determines the shape of the orbital (s, p, d, f).
- The magnetic quantum number (m) determines the orientation of the orbital in space.

(ii) Orbitals and degenerate orbitals.
- Orbitals are regions where electrons are most likely found (s, p, d, f).
- Degenerate orbitals are orbitals with the same energy level, such as the three p orbitals in a given energy level.

2. (b) By using a line diagram method, indicate the distribution of electrons in the following orbitals of atoms:

(i) 2p of magnesium

$2p_x$ $2p_\gamma$ $2pz$

(ii) 3d of manganese

$3d_x$ $3d_\gamma$ $3dz$ $3d_xy$ $3dyz$

(iii) 2p of carbon

$2p_x$ $2p_\gamma$

(iv) 4s of potassium

4s

(v) 3p of silicon

$3p_x$ $3p_\gamma$ $3pz$

(c) (i) Given the principal quantum number n = 2, tabulate the related quantum numbers and provide the total number of electrons present in this energy level.

Principal (n)	Azimuthal (l)	Magnetic (m)	Orbitals	Electrons
2	0 (s)	0	1	2
2	1 (p)	-1, 0, 1	3	6
Total			4	8

(ii) Comment on the difference of the de Broglie wavelengths between a ball of 0.2 kg moving with a velocity of 3×10^3 m/s and that of an electron moving with the same velocity.

The de Broglie wavelength is given by:

$\lambda = h / (mv)$

For a heavier object (ball), the mass is much larger, so λ is very small (undetectable).
For an electron, mass is very small, so λ is significantly larger (observable as wave behavior).

3. (a) While giving an example in each case, differentiate:

(i) Homogeneous equilibrium from heterogeneous equilibrium.
- Homogeneous equilibrium: All reactants and products in the same phase (e.g., gas).

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- Heterogeneous equilibrium: Reactants and products in different phases.

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(ii) Equilibrium constant from reaction quotient.
- Equilibrium constant (K): Value at equilibrium conditions.
- Reaction quotient (Q): Value at any point; compared with K to determine shift direction.

3. (b) When 0.4 mol of PCl_5 was heated in a 10 dm^3 vessel, it decomposed according to the equation:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

When the equilibrium was established, the amount of Cl_2 in the vessel was found to be 0.25 mol. Calculate:

(i) The number of moles of PCl_5 and PCl_3 present at equilibrium.

Let the initial moles of PCl_5 be 0.4 mol. Let x be the number of moles dissociated. Since Cl_2 at equilibrium is 0.25 mol, we assume:

$x = 0.25$ mol

So, the moles of PCl_5 at equilibrium = $0.4 - x = 0.4 - 0.25 = 0.15$ mol
The moles of PCl_3 at equilibrium = $x = 0.25$ mol

(ii) The equilibrium concentrations for all the three components.

Concentration = moles/volume
$[PCl_5] = 0.15 \text{ mol} / 10 \text{ dm}^3 = 0.015$ M
$[PCl_3] = 0.25 \text{ mol} / 10 \text{ dm}^3 = 0.025$ M
$[Cl_2] = 0.25 \text{ mol} / 10 \text{ dm}^3 = 0.025$ M

(iii) The equilibrium constant (Kc) for the decomposition reaction.

$K_c = [PCl_3][Cl_2] / [PCl_5]$

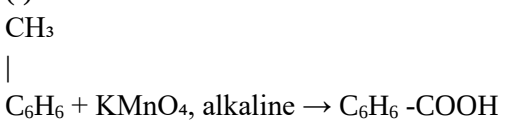
$K_c = (0.025 \times 0.025) / 0.015$

$K_c = 0.000625 / 0.015$

Kc = 0.0417

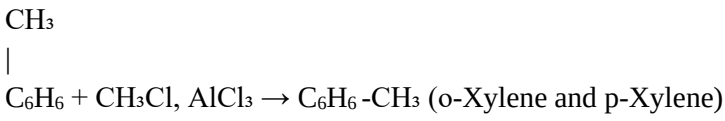
4. (a) Complete the following organic reactions by giving the major product(s) only:

(i)



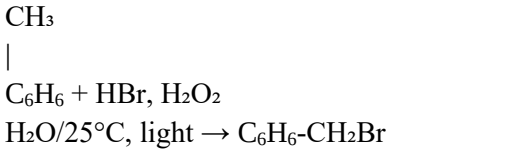
Toluene undergoes oxidation to form benzoic acid.

(ii)



Friedel-Crafts alkylation produces ortho and para xylene.

(iii)



Radical bromination at the benzylic position gives benzyl bromide.

4. (b)

(i) What is the difference between a side chain reaction and an electrophilic substitution reaction?

A side chain reaction involves the modification of the alkyl group attached to an aromatic ring, often through oxidation or radical halogenation. An example is the oxidation of toluene to benzoic acid.

An electrophilic substitution reaction occurs when an electrophile replaces a hydrogen atom in an aromatic ring, such as the nitration of benzene.

(ii) The alkoxy group (-OR) is an ortho-para directing group though oxygen is more electronegative than carbon. Explain briefly.

The lone pair of electrons on oxygen is delocalized into the benzene ring, increasing electron density at the ortho and para positions. This makes these positions more reactive to electrophilic substitution despite oxygen's electronegativity.

4. (c) Draw the structures of the principal organic products obtained on the nitration of each of the following:

(i) p-Methylbenzoic acid
The nitro group ($-NO_2$) substitutes at the para position relative to the -COOH group due to the directing effect of the carboxyl group.

(ii) m-Dinitrobenzene
In the nitration of nitrobenzene, the second nitro group enters the meta position due to the electron-withdrawing nature of the first nitro group.

5. (a)(i) What are the three conditions that must be fulfilled for a solution to exhibit colligative properties? Provide a brief explanation in each condition.

- The solute should be non-volatile: This ensures that only the solvent contributes to vapor pressure reduction.
- The solute should not undergo association or dissociation: Dissociation increases the number of particles (e.g., NaCl in water), while association decreases them (e.g., acetic acid in benzene).
- The solution must be dilute: Colligative properties are proportional to solute concentration but work best in dilute solutions.

(ii) Assume you are given glucose solutions A and B, with concentrations of 1 M and 2 M, respectively. Which of the solutions do you expect to have a higher boiling point than the other? Give a reason to support your answer.

Solution B (2 M) will have a higher boiling point because the elevation in boiling point is directly proportional to solute concentration. Since colligative properties depend on the number of solute particles, the higher concentration raises the boiling point more.

5. (b) The boiling temperature of a solution prepared by dissolving 5.0 g of an organic solid in 100.0 g of benzene is 82.42°C. If the boiling temperature of pure benzene is 80.10°C, determine the molecular weight of the organic solid. (Kb = 2.53°C/m)

Step 1: Calculate boiling point elevation
$\Delta Tb = 82.42 - 80.10 = 2.32°C$

Step 2: Use the boiling point elevation formula
$\Delta Tb = Kb \times m$

$m = \Delta Tb / Kb$
$m = 2.32 / 2.53$
$m = 0.916$ mol/kg

Step 3: Calculate the number of moles of solute

moles = mass / molar mass
Let M be the molar mass:
0.916 = (5.0 / M) / (0.100 kg)
0.916 × 0.100 × M = 5.0
M = 5.0 / 0.0916
M = 54.6 g/mol

The molecular weight of the organic solid is 54.6 g/mol.

5. (c) Addition of 1 mol of NaCl into 1 litre of water causes the boiling point of water to increase, while addition of 1 mol of methyl alcohol into 1 litre of water decreases the boiling point. How can you justify this statement?

NaCl is a non-volatile solute and undergoes dissociation into Na^+ and Cl^- ions. This increases the number of solute particles, causing boiling point elevation due to the colligative effect.

Methyl alcohol is volatile and forms hydrogen bonds with water. This disrupts the intermolecular forces in water, lowering its boiling point.

6. (a) Complete the following table by filling in the missing information:

Compound	Type of bond	Number of lone pair(s)	Type of hybridization	Geometrical shape
PCl_3	Covalent	1	sp^3	Trigonal pyramidal
NH_3	Covalent	1	sp^3	Trigonal pyramidal
CF_4	Covalent	0	sp^3	Tetrahedral

6. (b) Briefly, comment on the following facts:

(i) H_2O and HF have higher boiling points than PH_3 and HS.

Water and hydrogen fluoride have hydrogen bonding, which is a strong intermolecular force, requiring more energy to break. In contrast, PH_3 and HS lack strong hydrogen bonding, leading to lower boiling points.

(ii) CO_2 and SO_2 have the same empirical formulae; however, CO_2 is a non-polar compound while SO_2 is a polar compound.

CO_2 is linear and symmetrical, causing the dipole moments to cancel, making it non-polar. SO_2 has a bent shape due to lone pairs on sulfur, resulting in an uneven charge distribution, making it polar.

(iii) The type of bond in ethyne is stronger than that present in ethane.

Ethyne (C_2H_2) contains a triple bond (one sigma and two pi bonds), while ethane (C_2H_6) has only single sigma bonds. The presence of pi bonds in ethyne makes its bond stronger and shorter compared to ethane.

7. (a) "The carbonate of sodium exists on heating, while that of iron does not." Briefly, justify this statement while supporting your answer with appropriate chemical equations.

Sodium carbonate (Na_2CO_3) is thermally stable due to the strong ionic nature of Na^+ and CO_3^{2-}, so it does not decompose upon heating. However, iron carbonate ($FeCO_3$) decomposes to iron(II) oxide (FeO) and carbon dioxide (CO_2) upon heating:

$FeCO_3(s) \rightarrow FeO(s) + CO_2(g)$

(b) Briefly explain five uses of metal carbonates in daily life activities.

1. Calcium carbonate ($CaCO_3$) is used in the manufacture of cement and glass.
2. Sodium carbonate (Na_2CO_3) is used in detergents and soap making.
3. Magnesium carbonate ($MgCO_3$) is used as an antacid for relieving acidity.
4. Lithium carbonate (Li_2CO_3) is used in the treatment of bipolar disorder.
5. Calcium carbonate is used as a dietary calcium supplement.

(c) As a chemist in one of the fertilizer companies in Tanzania, you are required to prepare sulfates in one of the synthetic stages in a small scale. Briefly, advise four methods that you can use to prepare soluble metal sulfates.

1. Reacting a metal oxide with sulfuric acid:
   $ZnO + H_2SO_4 \text{ ---> } ZnSO_4 + H_2O$

2. Reacting a metal carbonate with sulfuric acid:
   $CaCO_3 + H_2SO_4 \text{ -----> } CaSO_4 + H_2O + CO_2$

3. Direct reaction of a metal with sulfuric acid:
   $Mg + H_2SO_4 \text{ ----> } MgSO_4 + H_2$

4. Precipitation reaction by mixing a soluble sulfate with a soluble metal salt:
   $BaCl_2 + Na_2SO_4 \text{ -----> } BaSO_4(s) + 2NaCl$

8. (a)(i) Differentiate ion exchange from acidic soil reaction.

Ion exchange is the reversible exchange of ions between a solution and a solid material such as soil, which affects soil fertility. Acidic soil reactions involve the release of H^+ ions, which increase soil acidity and reduce plant growth.

(ii) Why is nitrate more leached than ammonium from the soil? Briefly explain.

Nitrate (NO_3^-) is more leached because it is negatively charged and does not bind well to soil particles, making it highly mobile in water. Ammonium (NH_4^+), being positively charged, is attracted to negatively charged soil particles, reducing its mobility.

(iii) Why do sand soils have zero Cation Exchange Capacity (CEC)?

Sand particles have large grain sizes and low surface area, which prevents them from holding cations. Unlike clay, sand lacks negatively charged sites that retain essential plant nutrients.

(b)(i) Explain two roles of the following ions in liming:

- CO_3^{2-}: Neutralizes acidity by reacting with H^+ to form H_2CO_3, which decomposes to CO_2 and H_2O.
- O^{2-}: Reacts with water to form OH^- ions, which neutralize soil acidity.
- OH^-: Directly neutralizes H^+ ions, reducing soil acidity.
- SiO_3^{2-}: Helps in the slow neutralization of acidity and improves soil structure.

(ii) Calculate the amount of calcium carbonate required to lime an acidic soil that requires 100 g of calcium oxide for the same work.

Reaction:
$CaCO_3$ ----> $CaO + CO_2$

Molar mass of $CaCO_3$ = 100 g/mol
Molar mass of CaO = 56 g/mol

From the equation, 100 g of $CaCO_3$ gives 56 g of CaO.

Required amount of $CaCO_3$ = (100 g × 100 g) / 56 g
= 178.6 g

Therefore, 178.6 g of $CaCO_3$ is required.

(c) (i) Despite the importance of using fossil fuels, they have drawbacks to the environment. Briefly, explain two drawbacks of such fuels.

- Fossil fuels release carbon dioxide (CO_2), a greenhouse gas that contributes to global warming.
- Burning fossil fuels produces pollutants like sulfur dioxide (SO_2) and nitrogen oxides (NO_x), which cause acid rain.

(ii) Briefly, explain three measures that can be taken to reduce depletion of mineral resources.

- Recycling materials like metals and plastics to reduce excessive mining.

- Using alternative materials such as synthetic fibers instead of natural fibers.
- Implementing sustainable mining practices, including reforestation and land restoration.

9. (a) Compare the heat capacity of a 2 kg steel frying pan and that of a 2 g steel pin. Are the heat capacities of these objects different? Explain briefly.

Yes, the frying pan has a higher heat capacity because heat capacity depends on mass. The specific heat capacity of steel is the same for both objects, but total heat capacity increases with mass.

(b) A person took an ice cream from a refrigerator and kept it on a table; unfortunately, after 30 minutes, the ice cream changed into juice. Is the process of changing ice cream into juice, an endothermic or exothermic process? Give a reason for your answer.

The process is endothermic because the ice cream absorbs heat from the surroundings, causing it to melt into liquid juice.

(c) (i) Draw and label a complete Born-Haber cycle of magnesium nitride.

1. Sublimation of Magnesium (conversion of solid magnesium to gaseous magnesium):
   $3\ Mg(s) \text{ ------> } 3\ Mg(g)$
   (Enthalpy change: ΔH_{su}_b)

2. Bond Dissociation of Nitrogen (breaking the nitrogen-nitrogen triple bond):
   $1/2\ N_2(g) \text{ ------> } N(g)$
   (Enthalpy change: $1/2\ D_{n2}$)

3. Ionization of Magnesium Atoms (removal of electrons to form Mg^{2+} ions):
   $3\ Mg(g) \text{ ------> } 3\ Mg^{2+}(g) + 6\ e^-$
   (Enthalpy change: $3 \times IE_1 + 3 \times IE_2$)

4. Electron Affinity of Nitrogen (addition of electrons to form N^{3-} ions):
   $N(g) + 3\ e^- \text{ -------> } N^{3-}(g)$
   (Enthalpy change: $EA_1 + EA_2 + EA_3$)

5. Formation of Magnesium Nitride (combination of Mg^{2+} and N^{3-} ions to form the solid compound):
   $3\ Mg^{2+}(g) + 2\ N^{3-}(g) \text{ -----> } Mg_3N_2(s)$
   (Enthalpy change: $\Delta H_{latti}c_e$)

6. Overall Formation from Elements (direct formation of Mg_3N_2 from solid magnesium and nitrogen gas):
   $3\ Mg(s) + 1/2\ N_2(g) \text{ ----> } Mg_3N_2(s)$
   (Enthalpy change: ΔH_f)

(ii) Enthalpy of solution of $BaCl_2 \cdot 2H_2O$ and $BaCl_2$ are 8.8 and -20.6 kJ/mol, respectively. Calculate the enthalpy change (ΔH) of the following reaction:

$BaCl_2(g) + 2H_2O(l) \text{ ---> } BaCl_2 \cdot 2H_2O(s)$

$\Delta H = \Delta H(\text{solution of } BaCl_2 \cdot 2H_2O) - \Delta H(\text{solution of } BaCl_2)$
$= 8.8 - (-20.6)$
$= 8.8 + 20.6$
$= 29.4 \text{ kJ/mol}$

10. (a) Predict what will happen to the average kinetic energy of ideal gas molecules when the conditions change as follows:

(i) The pressure of the gas is increased by reducing the volume at constant temperature.
- The kinetic energy remains constant since temperature does not change.

(ii) The pressure of the gas is increased by increasing the temperature at constant volume.
- The kinetic energy increases as it is directly proportional to temperature.

(iii) The average velocity of the molecules is increased by a factor of two.
- The kinetic energy increases by a factor of four, as KE $\propto$ velocity^2.