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: 2000**

Instructions

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

2. Each question carries ten marks.

1. (a) Define the following terms:

(i) Quantum orbital

A quantum orbital is a region in an atom where there is a high probability of finding an electron. Each orbital is defined by a set of quantum numbers and has a specific shape and energy level.

(ii) Quantum numbers

Quantum numbers are a set of four numbers that describe the energy level, shape, orientation, and spin of an electron in an atom. These are the principal quantum number (n), azimuthal quantum number (l), magnetic quantum number (m_l), and spin quantum number (m_s).

(iii) Quantization of energy

Quantization of energy is the concept that electrons in an atom can only occupy discrete energy levels and absorb or emit energy in fixed amounts (quanta) rather than a continuous range.

(iv) Wave-particle duality of matter

Wave-particle duality states that microscopic particles, such as electrons, exhibit both wave-like and particle-like properties. This principle is fundamental to quantum mechanics and is demonstrated by experiments like the double-slit experiment and the de Broglie wavelength equation.

(b) Give the postulates of Bohr's atomic model.

1. Electrons move in fixed orbits (energy levels) around the nucleus without emitting energy.
2. Each orbit corresponds to a specific energy level, and electrons can transition between levels by absorbing or emitting energy.
3. The angular momentum of an electron in an orbit is quantized and follows the equation $mvr = n(h/2\pi)$, where n is an integer.

(c) What are the shortcomings of Bohr's atomic model?

1. It only explains the hydrogen atom and fails for multi-electron atoms.
2. It does not account for electron-electron interactions in multi-electron systems.
3. It does not explain the Zeeman effect (splitting of spectral lines in a magnetic field).
4. It contradicts the uncertainty principle by assuming fixed orbits for electrons.

2. (a) State:

(i) Raoult's law

Raoult's law states that the partial vapor pressure of a component in an ideal solution is directly proportional to its mole fraction in the solution.

$P_a = X_a P°_a$

where P_a is the partial pressure, X_a is the mole fraction, and $P°_a$ is the pure component's vapor pressure.

(ii) Partition law

The partition law states that a solute distributes itself between two immiscible solvents in a fixed ratio of concentrations at equilibrium, provided the temperature remains constant.

(b) The ideality of a solution is approached when it is made more dilute. Explain.

In a dilute solution, solute-solute interactions are minimized, and solvent-solvent interactions dominate, leading to behavior that closely follows Raoult's law, where deviations due to intermolecular forces are negligible.

(c) 10 g of methanol is mixed with 50 g of ethanol. If the vapor pressures of methanol and ethanol at the same temperature are 6265 Pa and 2933 Pa, respectively, calculate:

(i) The partial pressure exerted by each component in the mixture

Molar mass of methanol (CH_3OH) = 32 g/mol
Molar mass of ethanol (C_2H_5OH) = 46 g/mol

Moles of methanol = 10 g / 32 g/mol = 0.3125 mol
Moles of ethanol = 50 g / 46 g/mol = 1.087 mol
Total moles = 0.3125 + 1.087 = 1.3995 mol

Mole fraction of methanol (X_m) = 0.3125 / 1.3995 = 0.2233
Mole fraction of ethanol (X_e) = 1.087 / 1.3995 = 0.7767

Partial pressure of methanol = $X_m \times P°_m$ = 0.2233 × 6265 Pa = 1398 Pa
Partial pressure of ethanol = $X_e \times P°_e$ = 0.7767 × 2933 Pa = 2278 Pa

(ii) The composition of the vapor

Using Dalton's law of partial pressures,

Total pressure = 1398 + 2278 = 3676 Pa

Mole fraction of methanol in vapor = 1398 / 3676 = 0.3803

Mole fraction of ethanol in vapor = 2278 / 3676 = 0.6197

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 molar concentrations of the reactants, each raised to the power of its stoichiometric coefficient.

(b) Distinguish between equilibrium constant and reaction quotient.

The equilibrium constant (K) is the ratio of the concentration of products to reactants at equilibrium. The reaction quotient (Q) is the same ratio but calculated at any point before equilibrium is reached.

(c) SO_2 used in the manufacture of sulfuric acid is obtained from sulphide ores:

$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$

Find the mass of oxygen in the reaction when 75 liters of SO_2 is produced at 100°C and 1.04 atm.

Using the ideal gas equation:

$PV = nRT$

$n = (1.04 \text{ atm} \times 75 \text{ L}) / (0.0821 \times 373)$
$n = 2.54$ moles of SO_2

From the balanced equation,

8 moles of SO_2 require 11 moles of O_2.

O_2 required = $(11/8) \times 2.54 = 3.49$ moles

Mass of $O_2 = 3.49 \times 32$ g/mol $= 111.68$ g

4. (a) Explain why there is a constant pressure of carbon dioxide at a particular temperature over calcium carbonate undergoing thermal decomposition.

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

At equilibrium, the rate of decomposition of $CaCO_3$ is equal to the rate of formation of $CaCO_3$, maintaining a constant CO_2 pressure.

5. The solubility product of lead(II) chloride ($PbCl_2$) has a value of 1.6×10^{-5} mol^3 dm^{-9} at 298 K.

(a) Explain what is meant by the solubility product and calculate the solubility at 298 K.

Solubility product (Ksp) is the equilibrium constant for the dissolution of a sparingly soluble salt.

$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$

Let s be the solubility of $PbCl_2$.

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$1.6 \times 10^{-5} = s(2s)^2$

$1.6 \times 10^{-5} = 4s^3$

$s = (1.6 \times 10^{-5} / 4)^\wedge(1/3)$

$s \approx 1.6 \times 10^{-2}$ M

6. Given the number of electrons in the electron shells of the four atoms below, answer the question that follows.

P = 2,1
Q = 2,8,5
R = 2,8,13,2
S = 2,8,7

(a) For each element, write its electronic configuration and classify it as s, p, or d-block.

P: $1s^2\ 2s^1$ - s-block (alkali metal)
Q: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ - p-block (group 15 element)
R: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{13}\ 4s^2$ - d-block (transition metal)
S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ - p-block (halogen)

(b) Which elements exhibit the following oxidation states?

(i) 1 - P
(ii) 3 - Q
(iii) 7 - S

(c) Consider the process $M(g) \rightarrow M^+(g) + e^-$

(i) State which element has the largest magnitude of energy change involved and whether the process is exothermic or endothermic.

S has the largest ionization energy as it is a halogen. The process is endothermic as energy is required to remove an electron.

7. Cobalt, Copper, Iron, and Manganese are d-block elements.

(a) What is meant by the term "d-block element"?

A d-block element is an element whose valence electrons occupy the d-orbitals of the penultimate shell. These elements are found in groups 3 to 12 of the periodic table and exhibit variable oxidation states and the ability to form colored compounds.

(b) Write the electronic configurations of Cu, Fe^{2+}, and Mn^{2+}.

Cu: [Ar] $3d^{10}$ $4s^1$
Fe^{2+}: [Ar] $3d^6$
Mn^{2+}: [Ar] $3d^5$

(c) Explain in terms of their electronic configurations why Fe^{2+} ions are readily oxidized to Fe^{3+} ions but Mn^{2+} ions are not readily oxidized to Mn^{3+} ions.

Fe^{2+} has the configuration [Ar] $3d^6$, and oxidation to Fe^{3+} results in the more stable half-filled $3d^5$ configuration, which is energetically favorable.

Mn^{2+} has the configuration [Ar] $3d^5$, which is already half-filled and stable. Oxidation to Mn^{3+} disrupts this stable configuration, making it less favorable.

(d) (i) Give the formula of a compound or ion containing manganese in an oxidation state of +7.

MnO_4^- (Permanganate ion)

(ii) How do you account for the existence of the +7 oxidation state for manganese?

Manganese has a large number of valence electrons ($3d^5$ $4s^2$), allowing it to lose all seven electrons to achieve a noble gas configuration. This occurs in highly oxidizing environments.

(e) Cobalt forms a complex compound of formula $[Co(NH_3)_4Cl_2]Cl$.

(i) What is the oxidation state of cobalt in this compound?

Oxidation state of Co = $x + (4 \times 0) + (2 \times -1) + (1 \times -1) = 0$
$x - 2 - 1 = 0$
$x = +3$

(ii) Give the name of the complex ion contained in this compound.

Tetraammine dichlorocobalt(III) ion

(iii) How many moles of silver chloride would be immediately precipitated from one mole of this compound in aqueous solution by the addition of excess silver nitrate?

Only the chloride ion outside the coordination sphere precipitates. One mole of the compound releases one mole of Cl^-, so one mole of AgCl would be precipitated.

8. (a) Write balanced chemical equations for the following reactions:

(i) Action of steam on cobalt

$Co + H_2O \rightarrow CoO + H_2$

(ii) Action of dilute HCl on CoO

$CoO + 2HCl \rightarrow CoCl_2 + H_2O$

(iii) Action of carbon monoxide on cobalt

$CoO + CO \rightarrow Co + CO_2$

(b) 2.5×10^{-3} mole of a compound with the formula $Cr(NH_3)_5Cl_3$ was dissolved in water and immediately titrated with 0.1M silver nitrate solution. 50.0 cm^3 were required for complete precipitation of the free chloride ion present.

(i) Deduce the ionic formula of the compound.

$[Cr(NH_3)_5Cl]Cl_2$

(ii) Draw the structure of the complex ion present and name it.

The complex ion is $[Cr(NH_3)_5Cl]^{2+}$, named pentaamminechlorochromium(III) ion.

9. (a) Outline five ways in which hydrogen

(i) Resembles the alkali metals

1. It has one valence electron like alkali metals.
2. It forms unipositive ions (H^+) like alkali metals.

3. It forms ionic compounds with non-metals, similar to alkali metals.
4. It reacts with oxygen to form oxides like alkali metals.
5. It has a low ionization energy, though not as low as alkali metals.

(ii) Resembles the halogens

1. It forms diatomic molecules like halogens (H_2, Cl_2).
2. It forms hydrides similar to halides (LiH vs LiCl).
3. It has a similar electronegativity to some halogens.
4. It can gain an electron to form the hydride ion (H^-), like halogens forming X^-.
5. It participates in hydrogen bonding, similar to halogens like fluorine.

(b) Give two reasons for the placement of hydrogen in its most suitable group and period on the periodic table.

1. Hydrogen is placed in Group 1 because it has one valence electron, similar to alkali metals.
2. It is also considered in Group 17 (halogens) because it forms covalent compounds and exists as a diatomic gas.

(c) Write short notes on

(i) Hydrogen bonding

Hydrogen bonding is a strong dipole-dipole interaction that occurs when hydrogen is covalently bonded to highly electronegative atoms such as oxygen, nitrogen, or fluorine. It significantly affects boiling points and solubility.

(ii) Ortho and para hydrogen

Ortho hydrogen and para hydrogen refer to the spin states of the two protons in a hydrogen molecule. Ortho hydrogen has parallel spins and is more stable at high temperatures, while para hydrogen has antiparallel spins and is more stable at low temperatures.

10. Explain the following chemical phenomena using equations where possible.

(a) Aluminium oxide is amphoteric.

Al_2O_3 reacts with both acids and bases, demonstrating amphoteric behavior:

$Al_2O_3 + 6HCl$ ----> $2AlCl_3 + 3H_2O$
$Al_2O_3 + 2NaOH + 3H_2O$ ------> $2Na[Al(OH)_4]$

(b) Aqueous solutions of aluminium salts are acidic.

Aluminium forms hexaaqua complexes in water, which undergo hydrolysis, releasing H^+ ions:

$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H^+$

(c) Water has an exceptionally high boiling point compared to the hydrides of its other group members.

Water exhibits extensive hydrogen bonding, which requires more energy to break, resulting in a higher boiling point than H_2S, H_2Se, and H_2Te, which lack strong hydrogen bonding.

(d) Magnesium chloride cannot be prepared by heating the hydrated crystals to eliminate water.

Heating $MgCl_2 \cdot xH_2O$ leads to hydrolysis, forming MgO instead of anhydrous $MgCl_2$:

$MgCl_2 \cdot 6H_2O$ ------> $MgO + HCl + H_2O$

(e) Hydrogen fluoride is a liquid at room temperature while the other hydrogen halides are gases.

HF forms strong hydrogen bonds due to the high electronegativity of fluorine, leading to strong intermolecular forces that keep it in liquid form at room temperature, whereas HCl, HBr, and HI exist as gases.

11. (a) Write structural formulas for each of the following compounds:

(i) 2-methyl-3-hexene
$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$

(ii) Methylcyclopentane
Cyclopentane ring with a $-CH_3$ group attached to one carbon

(iii) 3,5-Dimethylcyclohexane
Cyclohexane ring with two $-CH_3$ groups at positions 3 and 5

(iv) 1-Bromo-3-ethyl-4,6-dimethylcyclohexane
Cyclohexane ring with a -Br at position 1, $-C_2H_5$ at position 3, and $-CH_3$ groups at positions 4 and 6

(v) 2-Methyl-1-pentyne
$CH_3\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_3$

(b) Consider four compounds with nearly the same molecular weights: 1,2-dimethoxyethane, ethyl propyl ether, hexane, and 1-pentanol.

(i) Which would you expect to have the highest boiling point?

1-pentanol would have the highest boiling point due to hydrogen bonding among alcohol molecules.

(ii) Which would be most soluble in water? Explain the reasons for your choices.

1,2-dimethoxyethane would be the most soluble in water because it has two oxygen atoms capable of hydrogen bonding with water molecules.

12. (a) Arrange the following compounds in order of increasing acidity and explain the reasons for your choices.

(i) Phenol
(ii) p-Chlorophenol
(iii) Cyclohexanol
(iv) p-Cresol

Order of increasing acidity: Cyclohexanol < p-Cresol < Phenol < p-Chlorophenol

Explanation: Cyclohexanol is the least acidic because it lacks resonance stabilization. Phenol is more acidic due to the delocalization of the negative charge in its conjugate base. p-Cresol has a methyl group that slightly increases electron density, making it less acidic than phenol. p-Chlorophenol is the most acidic due to the electron-withdrawing effect of the chlorine, which stabilizes the conjugate base.

(b) Indicate how the following mixtures could be separated without the use of distillation.

(i) Benzene and phenol

Extract phenol using an aqueous NaOH solution, forming sodium phenoxide, then acidify to regenerate phenol.

(ii) Phenol and 1-hexanol

Extract phenol using NaOH, leaving 1-hexanol in the organic layer.

(iii) 2-Propanol and 1-heptanol

Use fractional crystallization since 1-heptanol has a significantly higher boiling point and different solubility properties.

13. (a) Give equations that illustrate a good method to synthesize each of the following acids.

(i) Butanoic acid from 1-butanol
$CH_3CH_2CH_2CH_2OH + [O] \rightarrow CH_3CH_2CH_2COOH$

(ii) Butanoic acid from n-propyl alcohol (two ways)

1. $CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2COOH$
   $CH_3CH_2COOH + CH_3I \rightarrow CH_3CH_2CH_2COOH$ (alkylation)

2. $CH_3CH_2CH_2OH \rightarrow CH_3CH{=}CH_2$ (dehydration)
   $CH_3CH{=}CH_2 + KMnO_4 \rightarrow CH_3CH_2CH_2COOH$

(iii) p-Chlorobenzoic acid from p-Chlorotoluene

$C_6H_4ClCH_3 + KMnO_4 \rightarrow C_6H_4ClCOOH$

14. (a) Give equations for two different combinations of reactants that might be used to synthesize methyl sec-butyl ether by the Williamson method. Which combination would be preferred?

1. $CH_3CH(CH_3)CH_2Br + NaOCH_3 \rightarrow CH_3CH(CH_3)CH_2OCH_3 + NaBr$
2. $CH_3CH(CH_3)CH_2OH + CH_3I + NaH \rightarrow CH_3CH(CH_3)CH_2OCH_3 + NaI$

The first combination is preferred because Williamson ether synthesis works best with primary alkyl halides, avoiding elimination side reactions.

(b) Compound A, which has an unbranched carbon chain, reacts with methylmagnesium bromide to give, after hydrolysis, compound B. Chromic acid oxidation of B gives C($C_5H_{10}O$), which gives a crystalline product with 2,4-dinitrophenylhydrazine and a positive iodoform test.

(i) Give the formulas of A, B, and C and equations for all reactions mentioned.

A: Pentanal ($CH_3CH_2CH_2CH_2CHO$)
B: 2-Pentanol ($CH_3CH_2CH_2CHOHCH_3$)
C: Pentan-2-one ($CH_3CH_2CH_2COCH_3$)

Reactions:

$CH_3CH_2CH_2CH_2CHO + CH_3MgBr \rightarrow CH_3CH_2CH_2CH_2CH(OH)CH_3$ (B)
B + [O] $\rightarrow CH_3CH_2CH_2COCH_3$ (C)

(ii) Give the formula of a possible isomer of A that would give the same results as A in the above transformations.

A possible isomer is 3-Pentanone ($CH_3CH_2COCH_2CH_3$).

(c) Give the systematic IUPAC names for each of the following compounds.

(i) Ethoxyethane ($C_2H_5\text{-}O\text{-}C_2H_5$)

(ii) Benzyl alcohol (C_6H_5-CH_2-OH)

(iii) 2-Chloro-3,3-dimethylpent-1-yne ($CH_3C\equiv CCH(CH_3)_2Cl$)

(iv) Methyl propanoate ($CH_3CH_2COOCH_3$)

(v) 2-Butyne (CH_3-$C\equiv C$-CH_3)