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: 2015**

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 following:

(i) Pauli's exclusion principle: No two electrons in an atom can have the same set of four quantum numbers (n, l, m_l, m_s).

(ii) Aufbau building principle: Electrons occupy the lowest energy orbitals first before filling higher energy orbitals.

(iii) Hund's rule of maximum multiplicity: Electrons occupy degenerate orbitals singly before pairing to minimize repulsion.

(iv) Half-filled and full-filled orbital rule: Orbitals that are exactly half-filled or completely filled have extra stability due to symmetrical charge distribution and exchange energy.

(b) Write down the electronic configuration of each of the following species using orbital diagrams:

(i) Cl → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
(ii) K → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
(iii) Ca^{2+} → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
(iv) F → $1s^2\ 2s^2\ 2p^5$

(c) Element Z occurs naturally as a mixture of ^{69}Z and ^{71}Z.

(i) The numbers 69 and 71 represent the mass numbers of the two isotopes, meaning they have the same number of protons but different numbers of neutrons. This phenomenon is called isotopy.

(ii) If ^{69}Z and ^{71}Z have a relative atomic mass of 69.8, find the percentages of ^{69}Z and ^{71}Z in a sample of Z.

Let x be the percentage of ^{69}Z, then (100 - x) is the percentage of ^{71}Z.

$69x + 71(100 - x) = 69.8 \times 100$
$69x + 7100 - 71x = 6980$
$-2x + 7100 = 6980$
$2x = 120$
$x = 60\%$

So, ^{69}Z is 60% and ^{71}Z is 40%.

2. (a) State the distribution law.

When a solute is distributed between two immiscible solvents, its concentration ratio remains constant at equilibrium at a given temperature.

(b) The concentration of a solute X in water was found to be 8.5 g/dm^3 at room temperature. 100 cm^3 of this solution was shaken with 50 cm^3 of methyl benzene until equilibrium was obtained. The organic layer was separated and found to contain 0.8 g of X.

(i) Calculate the distribution coefficient of X between methyl benzene and water.

$K = C_{org} / C_{aq}$
$= (0.8 / 50) / (8.5 - 0.8 / 100)$
$= (0.016) / (7.7 / 100)$
$= (0.016 \times 100) / 7.7$
$= 0.207$

(ii) What further mass of X would be removed from the aqueous layer if it was shaken with a further 50 cm^3 of methyl benzene?

Let m be the additional mass extracted.

$K = (0.8 + m) / 50 \div (8.5 - 0.8 - m) / 100$
$0.207 = (0.8 + m) / (8.5 - 0.8 - m) \times 2$

Solving for m gives:
$m = 0.66$ g

(iii) Calculate the mass of X extracted if 100 cm^3 of methyl benzene was used at once instead of using 50 cm^3 twice. Which is the more efficient extraction process?

Using one portion of 100 cm^3,
$m = 1.28$ g

Using two portions of 50 cm^3, total mass extracted = 0.8 + 0.66 = 1.46 g

Two extractions are more efficient.

3. (a) Describe two assumptions of kinetic theory of gases that are not obeyed by real gases.

- Gas molecules have negligible volume: In real gases, molecules occupy significant space.
- No intermolecular forces: Real gases have weak intermolecular attractions, affecting pressure.

(b) (i) Differentiate between diffusion and effusion for gases.

- Diffusion: Movement of gas molecules from high to low concentration without a barrier.
- Effusion: Movement of gas molecules through a small hole without collisions.

(ii) Uranium and fluorine form UF_6. It is proposed that the $^{235}UF_6$ and $^{238}UF_6$ isotopes be separated by gaseous diffusion. Which gas would diffuse more rapidly, and by how much?

Using Graham's law,
Rate $\propto 1/\sqrt{M}$

Molar masses:
$^{235}UF_6 = 349$ g/mol
$^{238}UF_6 = 352$ g/mol

Relative rate = $\sqrt{(352/349)}$
= 1.0043

$^{235}UF_6$ diffuses 0.43% faster than $^{238}UF_6$.

(c) A general equation for the breakdown of glucose in a human body:

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

If 856 g of $C_6H_{12}O_6$ is consumed, find the mass of CO_2 produced.

Moles of glucose = 856 / 180 = 4.76 mol
Moles of CO_2 = 4.76 × 6 = 28.56 mol
Mass of CO_2 = 28.56 × 44 = 1256.64 g

4. (a) Write the equilibrium constant expressions (K_c) for the following reactions:

(i) $K_c = [NH_3]^2 / ([N_2][H_2]^3)$
(ii) $K_c = [ZnO]^2[S]^2 / ([ZnS]^2[O_2]^3)$
(iii) $K_c = [HBr]^2 / ([Br_2][H_2])$
(iv) $K_c = [NH_3]^2 / ([N_2]^{1/3}[H_2]^{2/3})$

(b) The equilibrium constant (K_c) for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 4.63×10^{-3} at 25°C. Calculate K_p.

$K_p = K_c(RT)^{(\Delta n)}$
$= (4.63 \times 10^{-3})(0.0821 \times 298)^1$
= 0.113

(c) Given equilibrium constants for hydrosulphuric acid at 25°C:

$H_2S \rightleftharpoons H^+ + HS^-$, $K_1 = 9.5 \times 10^{-8}$
$HS^- \rightleftharpoons H^+ + S^{2-}$, $K_2 = 1.0 \times 10^{-19}$

K for $H_2S \rightleftharpoons 2H^+ + S^{2-}$
$K = K_1 \times K_2$
$= (9.5 \times 10^{-8}) \times (1.0 \times 10^{-19})$
$= 9.5 \times 10^{-27}$

5. (a) 60 cm^3 of a gas was collected at 60°C and 1.05×10^5 Nm^{-2}. Calculate its volume at STP.

Using PV/T = constant:

$V_2 = V_1 \times (P_1/P_2) \times (T_2/T_1)$
$= 60 \times (1.05 \times 10^5 / 1.01 \times 10^5) \times (273 / 333)$
$= 51.86$ cm^3

(b) When 0.5 dm^3 of O_2 and 1.0 dm^3 of CO_2 were mixed at 27°C, total pressure was 1.2 atm. Calculate:

(i) Partial pressure of each gas:

$P\_O_2 = (0.5/1.5) \times 1.2 = 0.4$ atm
$P\_CO_2 = (1.0/1.5) \times 1.2 = 0.8$ atm

(ii) Mass of each gas:

$M\_O_2 = 0.4 \times 32 / 0.0821 \times 300 = 0.521$ g
$M\_CO_2 = 0.8 \times 44 / 0.0821 \times 300 = 1.46$ g

6. (a) Four differences between a positive and negative non-ideal solution.

- Positive deviation increases vapour pressure; negative deviation decreases it.
- Positive deviation has weaker forces; negative deviation has stronger forces.
- Positive deviation has endothermic mixing; negative deviation has exothermic mixing.
- Positive deviation increases volume; negative deviation decreases volume.

(b) Equal moles (0.5 moles) of benzene and toluene mixed.

X_benzene = P_benzene / (P_benzene + P_toluene)
= 95.1 / (95.1 + 28.4)
= 0.770

X_toluene = 1 - 0.770 = 0.230

7. (a) 0.01 M aqueous solution of 92.5% NaCl is dissociated at 18°C. Calculate the osmotic pressure (π) of this solution at the given temperature.

Given:
$C = 0.01$ M
$i = 1 + \alpha(n - 1) = 1 + 0.925(2 - 1) = 1.925$
$T = 18°C = 291$ K
$R = 0.0821$ L atm mol^{-1} K^{-1}

Osmotic pressure:

$\pi = iCRT$
$= (1.925 \times 0.01 \times 0.0821 \times 291)$
$= 0.046$ atm

(b) When 5.8 g of acetic acid (CH_3CO_2H) was dissolved in 90 g of benzene (C_6H_6), the freezing point depression was found to be 3.8°C. Calculate the degree of association of acetic acid in benzene, given that acetic acid dimerizes in benzene and $K_f = 5.1°C$ mol^{-1} kg^{-1}.

Molality:
$m = (5.8 / 60) / (90 / 1000)$
$= 1.078$ mol/kg

Theoretical $\Delta T_f = i \times K_f \times m$

$3.8 = i \times 5.1 \times 1.078$
$i = 3.8 / (5.1 \times 1.078)$
$i = 0.69$

For dimerization, $i = 1 - \alpha/2$, solving for α:

$0.69 = 1 - \alpha/2$
$\alpha = 0.62$ (62% dimerization)

8. (a) State Hess's law of constant heat summation.

The total enthalpy change for a reaction is the same, regardless of the number of steps taken, provided the initial and final conditions are the same.

(b) (i) Difference between standard bond dissociation energy and standard heat of formation.

Bond dissociation energy: Energy required to break one mole of a bond in a gaseous molecule.

Heat of formation: Energy change when one mole of a compound forms from its elements in standard conditions.

(ii) Calculate enthalpy change for $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

E(N-H) = 388 kJ/mol
E(N≡N) = 944 kJ/mol
E(H-H) = 436 kJ/mol

ΔH = Bonds broken - Bonds formed
= [(2 × 3 × 388)] - [(944 + 3 × 436)]
= (2338) - (2252)
= +86 kJ

9. (a) Giving examples, briefly explain the following:

(i) Hydrogen bonding: A strong dipole-dipole attraction between hydrogen and electronegative elements like N, O, or F. Example: Water (H_2O).

(ii) Coordinate bond: A bond in which both shared electrons come from one atom. Example: NH_4^+.

(iii) Van der Waals forces: Weak intermolecular forces due to temporary dipoles. Example: noble gases.

(b) Predict which substance has a higher melting point and explain:

(i) CH_3CH_3 vs. CH_3OH: CH_3OH (hydrogen bonding).
(ii) CO_2 vs. H_2: CO_2 (larger molecular weight).
(iii) HCl vs. H_2O: H_2O (stronger hydrogen bonds).
(iv) Al vs. Mg: Al (more delocalized electrons).
(v) Si vs. Na: Si (strong covalent bonds).

(c) Describe the hybridization of beryllium in beryllium chloride ($BeCl_2$).

$BeCl_2$ has sp hybridization, forming two linear sigma bonds.

10. (a) Distinguish between the following:

(i) Atomic number vs. mass number:
Atomic number is the number of protons in an atom. Mass number is the sum of protons and neutrons.

(ii) A photon vs. a quanta:

A photon is a discrete packet of electromagnetic radiation. Quanta is the general term for discrete energy packets.

(b) A photon was absorbed by a hydrogen atom, and the electron was promoted to the fifth orbit. When the excited atom returned to its ground state, visible radiation was emitted.

(i) Explain electron transitions.

The electron moves to a lower energy level by releasing energy in the form of photons, leading to spectral emission.

(ii) Calculate the wavelength of a photon emitted during a transition from $n_1 = 5$ to $n_2 = 2$ in hydrogen atom given $\Delta E = 2.18 \times 10^{-18}$ J.

Using the equation:

$E = 2.18 \times 10^{-18} \times (1/2^2 - 1/5^2)$
$= 2.18 \times 10^{-18} \times (0.25 - 0.04)$
$= 2.18 \times 10^{-18} \times 0.21$
$= 4.58 \times 10^{-19}$ J

Using $E = hc/\lambda$,
$\lambda = (6.626 \times 10^{-34} \times 3.0 \times 10^8) / 4.58 \times 10^{-19}$
$\lambda = 4.34 \times 10^{-7}$ m or 434 nm

11. (a) Briefly explain each of the following as applied in organic reactions:

(i) Positive inductive effect: The electron-donating effect of alkyl groups (+I effect), which stabilizes carbocations. Example: CH_3 in $CH_3\text{-}CH_2^+$.

(ii) Negative inductive effect: The electron-withdrawing effect of electronegative atoms (-I effect), which destabilizes carbocations. Example: NO_2 in nitrobenzene.

(iii) Mesomeric effect: The delocalization of electrons through π-bonding, which affects reactivity. Example: OH in phenol increases electron density on benzene.

(iv) Steric factors: The physical hindrance caused by bulky groups affecting reaction rates. Example: Tertiary carbocations resist SN2 reactions due to steric hindrance.

(b) Explain the following observations:

(i) Addition reactions in benzene need high energy.
Benzene is stabilized by delocalized π-electrons, so breaking this stability requires high energy.

(ii) Nucleophilic substitution reactions in benzene are not possible.
Benzene's electron-rich nature repels nucleophiles, and the ring lacks a good leaving group.

(iii) Methyl group when attached to benzene ring directs another incoming group to ortho or para position.
The +I and +M effects of the methyl group increase electron density at ortho and para positions.

(iv) Nitro group when attached to benzene ring directs another incoming group to meta position.
The -I and -M effects of the nitro group withdraw electrons, reducing electron density at ortho and para positions, making meta more favorable.

12. Give the mechanism for the following:

(a) Sulphonation of benzene.

Step 1: Protonation of H_2SO_4 forms SO_3H^+.
Step 2: Electrophilic attack of SO_3H^+ on benzene forms arenium ion.
Step 3: Loss of H^+ regenerates aromaticity, forming benzene sulfonic acid.

(b) Chlorination of benzene.

Step 1: Cl_2 reacts with $FeCl_3$ to form Cl^+.
Step 2: Cl^+ attacks benzene, forming a carbocation intermediate.
Step 3: Loss of H^+ restores aromaticity, forming chlorobenzene.

13. (a) Write the mechanism of the following substitution reaction, indicating clearly the nucleophile, substrate, and the leaving group:

$(CH_3)_2C\text{-}Br + NaOH \text{------>} (CH_3)_2C\text{-}OH + NaBr$

Step 1: Br leaves, forming a carbocation (SN1 mechanism).
Step 2: OH^- nucleophile attacks the carbocation, forming tert-butanol.

(b) Carry out the following conversions:

(i) Propane to 1-chloropropane.

$CH_3CH_2CH_3 + Cl_2 \text{------>} CH_3CH_2CH_2Cl + HCl$ (free radical substitution).

(ii) Propane to propene.

$CH_3CH_2CH_3 \text{------>} CH_3CH{=}CH_2 + H_2$ (dehydrogenation using heat and catalyst).

(c) Complete the following reactions and name the organic product formed:

(i) $CH\equiv CH + Cl_2$ ------> $CHCl=CHCl$ (1,2-dichloroethene).

(ii) $CH\equiv CCH_3 + H_2SO_4$, $HgSO_4$ ------> CH_3COCH_3 (acetone).

(iii) $CH\equiv CNa + CH_3I$ ------> $CH_3C\equiv CCH_3$ (but-2-yne).

(iv) $CH_2=CH_2 + KMnO_4$ ------> $HOCH_2CH_2OH$ (ethylene glycol).

14. (a) Write the open structures of five isomers of the compound C_5H_7Cl and their corresponding IUPAC names.

1. 1-chloropent-1-yne
2. 3-chloropent-1-yne
3. 4-chloropent-2-yne
4. 2-chloropenta-1,3-diene
5. 3-chloropenta-1,4-diene

(b) Arrange the following compounds in the order of increasing acidity and give reasons:

$O_2N\text{-}C\equiv CH > Cl\text{-}C\equiv CH > CH_3\text{-}C\equiv CH$

Nitro ($-NO_2$) is highly electron-withdrawing, stabilizing the conjugate base, making it most acidic. Chlorine (-Cl) is moderately electron-withdrawing, and methyl ($-CH_3$) is electron-donating, making it least acidic.

(c) Suggest suitable tests to distinguish the following compounds:

(i) Propyne and propene: Bromine water test. Propyne decolorizes instantly, propene reacts slowly.

(ii) 2-methylpent-2-ene and 3-methylpent-2-ene: Ozonolysis followed by Tollen's test. 2-methylpent-2-ene gives formaldehyde, which reduces Tollen's reagent.

(iii) But-2-yne and butane: Baeyer's test with $KMnO_4$. But-2-yne gives a color change, butane does not react.