THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2015**

Instructions

1. This paper consists of a total of six questions
2. Answer five questions.

1 (a) According to Brønsted-Lowry theory, HSO_4^- ion behaves as an acid in the reaction:

$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$

(i) Explanation:
HSO_4^- donates a proton (H^+) to H_2O forming SO_4^{2-} and H_3O^+, hence acts as a Brønsted acid.

(ii) Conjugate base:
SO_4^{2-} is the conjugate base of HSO_4^-

(iii) As a base:
$HSO_4^- + H_3O^+ \rightleftharpoons H_2SO_4 + H_2O$
Here, HSO_4^- accepts a proton and behaves as a Brønsted base.

1 (b) Calculate the pH at neutralization point:

Reaction: $NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$
Use Henderson-Hasselbalch equation:
$pH = pKa + \log([salt]/[base])$
$Ka(NH_4^+) = 5.7 \times 10^{-10} \rightarrow pKa = 9.24$
Since at equivalence point $[salt] = [base] \rightarrow \log 1 = 0$
$pH = 9.24$

1 (c) Buffer with CH_3COOH 1 M and pH = 4.742

(i) Concentration of CH_3COONa:
Using Henderson-Hasselbalch:
$pH = pKa + \log([salt]/[acid])$
$4.742 = 4.744 + \log([salt]/1.00) \rightarrow \log([salt]) = -0.002$
$[salt] = 10^{-0.002} \approx 0.995$ M

(ii) After adding 0.01 mol HCl to 1 dm^3:
New acid = 1 + 0.01 = 1.01 M
New salt = 0.995 - 0.01 = 0.985 M
$pH = 4.744 + \log(0.985/1.01) = 4.744 + \log(0.975) = 4.744 - 0.011 = 4.733$

(iii) After adding 0.01 mol NaOH:
New acid = 1 - 0.01 = 0.99 M
New salt = 0.995 + 0.01 = 1.005 M
$pH = 4.744 + \log(1.005/0.99) = 4.744 + \log(1.015) = 4.744 + 0.006 = 4.750$

(iv) pH when 0.01 mol NaOH is added to 1.0 dm^3 water:
$[OH^-] = 0.01\ M \rightarrow pOH = 2 \rightarrow pH = 14 - 2 = 12$

2 (a) (i) $AgNO_3 + HCl \rightarrow AgCl(s) + HNO_3$
White AgCl precipitate dissolves in excess NH_3:
$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^-$

(ii) $ZnS + HCl \rightarrow H_2S$ (gas) released in acidic medium
H_2S prevents precipitation of ZnS in acidic medium

(iii) $CO_2 + Ca(OH)_2 \rightarrow CaCO_3$ (ppt) + H_2O
Further CO_2 dissolves ppt:
$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$ (soluble)

2 (b) (i) $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$ (s)
$BaSO_4$ Ksp = 1.1×10^{-10}
$[Ba^{2+}] = [SO_4^{2-}] = 2 \times 10^{-5}$
$Q = (2 \times 10^{-5})^2 = 4 \times 10^{-10} \rightarrow Q > Ksp \rightarrow$ ppt forms

(ii) Mass of $Ca(OH)_2$ precipitated:
$Ksp(Ca(OH)_2) = 4.42 \times 10^{-4}$
$[OH^-] = 0.02 \rightarrow [Ca^{2+}] = Ksp / [OH^-]^2 = 4.42 \times 10^{-4} / (0.02)^2 = 1.105$ M
Moles $Ca(OH)_2 = 1.105 \times 0.04 = 0.0442$ mol
Mass = $0.0442 \times 74 = 3.27$ g

2 (c) (i) Ksp = 1.6×10^{-5} means:
At 298 K, solubility equilibrium of $PbCl_2$ gives product of ion concentrations $[Pb^{2+}][Cl^-]^2 = 1.6 \times 10^{-5}$

(ii) Let s be solubility
$Ksp = s \times (2s)^2 = 4s^3$
$4s^3 = 1.6 \times 10^{-5} \rightarrow s^3 = 4 \times 10^{-6} \rightarrow s = 1.6 \times 10^{-2}$ mol/L

(iii) In presence of 0.1 M $Pb(NO_3)_2$:
$[Pb^{2+}] = 0.1 \rightarrow Ksp = 0.1 \times [Cl^-]^2 \rightarrow [Cl^-]^2 = 1.6 \times 10^{-4}$
$[Cl^-] = \sqrt{1.6} \times 10^{-4} = 1.26 \times 10^{-2}$ mol/L

3 (a) Four factors affecting reaction rate:
- Temperature
- Concentration
- Surface area
- Catalyst

3 (b) $k = 3.46 \times 10^{-3}\ s^{-1}$ at 298 K, Ea = 50.2 kJ/mol
Use Arrhenius equation:
$\ln(k_2/k_1) = Ea/R(1/T_1 - 1/T_2)$

$\ln(k_2/3.46\times10^{-3}) = 50200/8.314\ (1/298 - 1/350)$
$\ln(k_2/3.46\times10^{-3}) = 4.35$
$k_2 = 3.46\times10^{-3} \times e^{4.35} \approx 3.46\times10^{-3} \times 77.3 \approx 0.267\ s^{-1}$

3 (c) Reaction: $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$
(i) Formation of NO_2F → rate = $k[NO_2][F_2]$
(ii) Disappearance of F_2 → same rate = $k[NO_2][F_2]$
(iii) Disappearance of NO_2 → rate = $k[NO_2][F_2]$

3 (d) Hydrolysis of ethyl acetate with NaOH:

Time(min): 0 5 10 15 25
Volume(cm^3): 16.00 10.24 6.13 4.32

For second order reaction, plot 1/volume vs time will be linear
Confirm second order by checking if 1/V varies linearly with time.

4 (a) Definitions:

(i) Electric double layer:
Two layers of opposite charges formed at electrode-electrolyte interface

(ii) Electrode potential:
Potential difference between electrode and solution

(iii) Standard electrode potential:
Electrode potential under standard conditions (1 M, 25°C)

4 (b) (i) Zn^{2+}/Zn $E^o = -0.76$ V, Cu^{2+}/Cu $E^o = +0.337$ V
$E_{cell} = E^o(Cu) - E^o(Zn) = 0.337 - (-0.76) = 1.097$ V

(ii) If $[Zn^{2+}]$ increases or $[Cu^{2+}]$ decreases → Ecell decreases

(iii) Zn replaced by Ag ($E^o = +0.80$ V)
$E_{cell} = 0.80 - 0.337 = 0.463$ V

4 (c) (i) Faraday's laws:
1st law: mass $\propto$ quantity of electricity
2nd law: mass $\propto$ equivalent weight of ion

(ii) Importance of 2nd law:
- Helps in quantitative electrolysis
- Determines equivalent weights

(iii) Copper deposited = 2 g
1 Faraday deposits 31.8 g Ag, 127 g I_2
Electric charge = (2 × 96500 × 2) / 63.5 = 6070 C
Mass of Ag = (6070 × 108) / (96500 × 1) = 6.8 g
Mass of I_2 = (6070 × 254) / (96500 × 2) = 7.98 g

5 (a) Explain the following phenomena with the aid of chemical equation(s) where possible:

(i) Common reductants are useless in the manufacture of aluminium from its ore.
Aluminium is a highly electropositive metal. It has a very strong affinity for oxygen, and common chemical reductants like carbon cannot reduce aluminium oxide. Thus, electrolysis is required instead of chemical reduction.

(ii) Aluminium chloride is a good Lewis acid.
$AlCl_3$ is electron-deficient and can accept a lone pair of electrons, hence acts as a Lewis acid in reactions such as Friedel-Crafts alkylation.

(iii) Molecular mass of $AlCl_3$ in vapour state is twice the expected value.
At room temperature, $AlCl_3$ exists as a dimer (Al_2Cl_6) due to electron deficiency of Al, hence molar mass in vapour phase is doubled.

(iv) Aluminium oxide shows basic properties by reacting with HCl.
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
This shows that aluminium oxide can behave as a base.

(b) Describe the process of aluminium extraction starting with bauxite under the following stages:
(i) Purification of the ore from impurities:
- Bauxite ($Al_2O_3 \cdot 2H_2O$) is treated with NaOH (Bayer process)

$Al_2O_3 \cdot 2H_2O + 2NaOH \rightarrow 2NaAlO_2 + 3H_2O$
Impurities are filtered off.

(ii) Electrolysis of aluminium:
- Electrolysis of molten cryolite-Al_2O_3 mixture

Cathode: $Al^{3+} + 3e^- \rightarrow Al$
Anode: $C + O^{2-} \rightarrow CO_2$

(c) Evaluate any four uses of aluminium which reflect its physical and chemical properties:
- Making utensils and aircrafts (lightweight)
- Electrical wires (good conductor)
- Foils for packaging (malleable)
- Window frames and bodies (resistant to corrosion)

6 (a) (i) Write the electronic configurations of the following species:
Mn^{2+} = [Ar] $3d^5$
V^{3+} = [Ar] $3d^2$
Fe^{3+} = [Ar] $3d^5$
(ii) Give reason(s) why in manganese the oxidation state of +2 is more stable than oxidation state of +3.
Mn^{2+} has half-filled $3d^5$ configuration which is highly stable.

(b) Briefly explain each of the following phenomena:

(i) The radii of Fe, Co and Ni show a much smaller variation in size than those of Mg and Al.
Transition elements show poor shielding by d-electrons and similar effective nuclear charge.

(ii) Cadmium has two electrons in the outermost shell as does magnesium but they are not classified in the same group.
Cd is a d-block element (with filled d-subshell), Mg is an s-block element.

(iii) Iron element exhibits magnetic properties while zinc element does not.
Fe has unpaired d-electrons (paramagnetic), Zn has filled d-orbitals (diamagnetic).

(c) (i) Account for the different coordination numbers between $[FeCl_4]^{2-}$ and $[FeF_6]^{3-}$.
Cl^- is a larger ligand and causes steric hindrance → coordination number 4; F^- is small → coordination number 6.

(ii) What are the origins of magnetism in transition elements?
Presence of unpaired d-electrons leads to magnetic moments.

(iii) Use the 3d electron configuration in cobalt (III) ions to explain why $[CoF_6]^{3-}$ is paramagnetic while $[Co(CN)_6]^{3-}$ is diamagnetic.
In $[CoF_6]^{3-}$ (weak field ligand), electrons remain unpaired in high spin complex.
In $[Co(CN)_6]^{3-}$ (strong field ligand), electrons pair in low spin complex.

(iv) Briefly explain why $[Fe(CN)_6]^{4-}$ is said to be an inner orbital complex while $[CoF_6]^{3-}$ is said to be an outer orbital complex.
$[Fe(CN)_6]^{4-}$ involves d^2sp^3 hybridization using inner d-orbitals.
$[CoF_6]^{3-}$ involves sp^3d^2 hybridization using outer d-orbitals.

7 (a) What is the basic difference between Mendeleev's periodic law and the Modern periodic law?
Mendeleev: Properties depend on atomic mass.
Modern: Properties depend on atomic number.

(b) A neutral atom of a certain element has 17 electrons.

(i) Write its ground state electronic configuration:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

(ii) Classify the element into s, p, d or f block.
p-block

(iii) Determine whether it is diamagnetic or paramagnetic.
Paramagnetic (has unpaired electron)

(iv) What is the principal oxidation number of the element?
-1 (common oxidation state for halogens)

(c) Study the following hypothetical elements placed in various groups and periods and then answer the questions:

(i) Element most likely to have highest electron affinity: I (Group VII)
(ii) Element likely to have highest electronegativity: I (Group VII)
(iii) Element likely to have least first ionization energy: A (Group I)
(iv) Pair of elements likely to form strongest electrovalent bond: A (Group I) and I (Group VII)
(v) Two elements likely to have strongest reducing properties: A and J (Group I)
(vi) Two elements which form neither negative nor positive ions: G and O (Group VIII)

(d) (i) Define the term deliquescence and explain what makes a hydrated salt to deliquesce.
Deliquescence is the process by which a substance absorbs moisture from the air and dissolves in it. A salt deliquesces when it is highly hygroscopic.

(ii) Explain the discontinuities in the solubility curve of $CaCl_2$ in water:
At points B and D, structural changes in hydration shells or formation of hydrates cause changes in solubility trend with temperature.

(e) Briefly explain at least three hazards associated with the useful applications of sulphur and lead or their compounds.
- Lead compounds cause neurotoxicity and kidney damage.
- Sulphur dioxide causes respiratory problems.
- Lead accumulation in the environment contaminates food chain.

8 (a) For each of the following compounds, give the structures and the names of two functional isomers:

(i) C_3H_6O
- Propanal (CH_3CH_2CHO) – aldehyde
- Acetone (CH_3COCH_3) – ketone

(ii) $C_2H_4O_2$
- Acetic acid (CH_3COOH) – carboxylic acid

- Methyl formate ($HCOOCH_3$) – ester

(iii) C_2H_6O
- Ethanol (CH_3CH_2OH) – alcohol
- Dimethyl ether (CH_3OCH_3) – ether

(b) Name all the functional groups present in the following compound:
$HOCH_2–(C_6H_4)–CO–CH_2CH_3$
Functional groups:
- Hydroxyl group (–OH)
- Carbonyl group (ketone)
- Aromatic ring (benzene ring)

(c) Predict the product(s) formed when the compound in (b) reacts with:

(i) Warm mixture of iodine and NaOH
- Iodoform test → yellow precipitate of CHI_3

Product: CHI_3 and sodium salt of acid

(ii) Sulphur dichloride oxide ($SOCl_2$)
- –OH replaced with –Cl

Product: Chlorinated aromatic ketone (Ar–Cl) and evolution of SO_2 + HCl

(iii) Acidified $K_2Cr_2O_7$ at 60°C–80°C
- Oxidation of $–CH_2OH$ to –COOH

Product: Aromatic compound with both –COOH and $–CO–CH_2CH_3$ groups

(iv) H_2 and Ni at 140°C
- Hydrogenation of carbonyl group (ketone to alcohol)

Product: Secondary alcohol formed from reduction of ketone group

9 (a) Define the following terms:

(i) Polymer:
A large molecule formed by repeated linking of monomer units.

(ii) Additional polymerization:
Polymer formed without loss of small molecules by opening unsaturated bonds.

(iii) Condensation polymerization:
Polymer formed by the elimination of small molecules like water or HCl during linkage of monomers.

(b) (i) Four common natural polymers:

- Cellulose
- Starch
- Protein
- Natural rubber

(ii) Thermosetting vs Thermoplastic polymer:
Thermoplastic: softens on heating, can be remoulded (e.g. PVC)
Thermosetting: becomes hard permanently on heating, cannot be reshaped (e.g. Bakelite)

(c) Example of polymerization of vinyl chloride (C_2H_3Cl):

(i) Initiation step:
$R\bullet + CH_2{=}CHCl \rightarrow R{-}CH_2{-}CHCl\bullet$

(ii) Propagation step:
$R{-}CH_2{-}CHCl\bullet + n(CH_2{=}CHCl) \rightarrow {-}[CH_2{-}CHCl]{-}n$

(iii) Termination step:
Radical + Radical → Polymer chain

(d) Complete structures of monomers used in condensation polymers:

(i) Protein
Monomers: Amino acids – $NH_2{-}CHR{-}COOH$

(ii) Dacron
Monomers:
$HO{-}CH_2CH_2{-}OH$ (ethylene glycol)
$HOOC{-}C_6H_4{-}COOH$ (terephthalic acid)

(iii) Nylon
Monomers:
$HOOC{-}(CH_2)_4{-}COOH$ (adipic acid)
$H_2N{-}(CH_2)_6{-}NH_2$ (hexamethylene diamine)

10. Conservation of water against pollution is of paramount importance. Discuss:

(i) Categories of water pollution:
- Organic pollution
- Chemical pollution
- Biological pollution
- Thermal pollution

(ii) Causes of water pollution:
- Industrial discharge
- Sewage waste
- Agricultural runoff (fertilizers and pesticides)
- Oil spills

(iii) Effects of water pollution:
- Death of aquatic life
- Spread of diseases
- Eutrophication
- Toxic accumulation in food chains

(iv) Control measures:
- Wastewater treatment
- Industrial regulation
- Public awareness campaigns
- Enforcing pollution control laws