THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2017**

Instructions

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

1 (a) Distinguish between the following terms:

(i) Average rate and instantaneous rate
The average rate is the change in concentration of reactants or products over a time interval.
The instantaneous rate is the rate of reaction at a specific moment in time, found by taking the slope of the concentration vs. time curve at that point.

(ii) Elementary step and rate-determining step
An elementary step is a single step in a reaction mechanism that describes an actual molecular event.
The rate-determining step is the slowest step in a reaction mechanism that controls the overall reaction rate.

(iii) Molecularity and order of reaction
Molecularity refers to the number of reactant molecules participating in an elementary step.
Order of reaction is the sum of the powers of concentration terms in the rate law and is determined experimentally.

(iv) Activated complex and activation energy
The activated complex is an unstable high-energy intermediate formed during the transition from reactants to products.
Activation energy is the minimum energy required for reactants to transform into products by overcoming the energy barrier.

1 (b) Determine the rate law and rate constant for:
$2N_2O_5(g) \text{ ----> } 4NO_2(g) + O_2(g)$

Initial $[N_2O_5]$ (M)	Initial Rate (M/s)
0.186	9.68×10^{-4}
0.372	19.34×10^{-4}
1.490	77.67×10^{-4}

From experiment 1 and 2: Doubling $[N_2O_5]$ doubles the rate → First-order reaction.
From experiment 2 and 3: Quadrupling $[N_2O_5]$ quadruples the rate → Confirms first order.

Rate law: Rate = $k[N_2O_5]$
Using experiment 1:
$9.68 \times 10^{-4} = k\ (0.186)$
$k = 9.68 \times 10^{-4} / 0.186 = 5.2 \times 10^{-3}\ s^{-1}$

(c) The reaction $CH_4 + 2S_2 \text{ ----> } CS_2 + 2H_2S$
Rate constant at 550°C = $2.2\ L\ mol^{-1}\ s^{-1}$
Rate constant at 625°C = $12.8\ L\ mol^{-1}\ s^{-1}$

Using Arrhenius equation:
$\ln(k_2/k_1) = (E_a/R)\ (1/T_1 - 1/T_2)$
$\ln(12.8/2.2) = (E_a/8.314) \times (1/823 - 1/898)$
$\ln(5.818) = (E_a/8.314) \times (1.215 \times 10^{-4})$
$1.76 = (E_a/8.314) \times 1.215 \times 10^{-4}$
$E_a = (1.76 \times 8.314) / 1.215 \times 10^{-4}$
$E_a = 120.5$ kJ/mol

2 (a) Oxidation numbers:
(i) $Cl_2 = 0$ (elemental state)
(ii) $Cl_2O_7 = Cl^{+7}$ (O is -2, total oxidation sum = 0, so Cl must be +7)
(iii) $Na_2Cr_2O_7 = Cr^{+6}$ (Na is +1, O is -2, so Cr must balance charge)

2 (b) Balance the following redox equations:

(i) $Cr_2O_7^{2-} + Br^- + H^+ \text{---->} Cr^{3+} + Br_2 + H_2O$
Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \text{---->} 2Cr^{3+} + 7H_2O$
Oxidation: $2Br^- \text{---->} Br_2 + 2e^-$
Balanced: $Cr_2O_7^{2-} + 14H^+ + 6Br^- \text{---->} 2Cr^{3+} + 7H_2O + 3Br_2$

(ii) $MnO_4^- + I^- \text{---->} MnO_2 + I_2$ (basic medium)
Reduction: $MnO_4^- + 2H_2O + 3e^- \text{---->} MnO_2 + 4OH^-$
Oxidation: $2I^- \text{---->} I_2 + 2e^-$
Balanced: $MnO_4^- + 2H_2O + 2I^- \text{---->} MnO_2 + I_2 + 4OH^-$

2 (c) $KMnO_4$ and KI reaction:
(i) Balanced equation:
$2MnO_4^- + 10I^- + 16H^+ \text{---->} 2Mn^{2+} + 5I_2 + 8H_2O$
$I_2 + 2S_2O_3^{2-} \text{---->} 2I^- + S_4O_6^{2-}$

(ii) Molarity of $Na_2S_2O_3 \cdot 10H_2O$:
Mass = 31.64 g/L, Molar mass = 248 g/mol
Moles per liter = 31.64 / 248 = 0.1275 M
Using titration:
Moles $I_2 = 5 \times$ moles MnO_4^-
Moles $MnO_4^- = (3.16/158) \times 25/1000 = 5 \times 10^{-4}$
Moles $I_2 = 5 \times 5 \times 10^{-4} = 2.5 \times 10^{-3}$
Molarity of $Na_2S_2O_3 \cdot 10H_2O = 2.5 \times 10^{-3} / 26.7 \times 10^{-3} = 0.094$ M

2 (d) Molar conductivity and ionization constant:
$\Lambda^0(NH_4Cl) = 129.8$ S cm² mol⁻¹
$\Lambda^0(NaOH) = 217.4$ S cm² mol⁻¹
$\Lambda^0(NaCl) = 108.9$ S cm² mol⁻¹

$\Lambda^o(NH_4OH) = \Lambda^o(NH_4Cl) + \Lambda^o(NaOH) - \Lambda^o(NaCl)$
$= 129.8 + 217.4 - 108.9 = 238.3$ S cm² mol⁻¹

Degree of ionization (α) = $\Lambda(NH_4OH) / \Lambda^o(NH_4OH)$
$= 9.33 / 238.3 = 0.0392$

Ionization constant:
$Ka = (\alpha^2 \times C) / (1 - \alpha)$
$Ka = (0.0392^2 \times 0.01) / (1 - 0.0392)$
$Ka = (1.54 \times 10^{-5}) / 0.9608$
$Ka = 1.6 \times 10^{-5}$

3 (a) Define the following:

(i) Common ion effect
The common ion effect is the suppression of ionization of a weak electrolyte by the presence of a strong electrolyte containing a common ion.

(ii) Buffer solutions
Buffer solutions are solutions that resist change in pH when small amounts of acid or base are added. They typically contain a weak acid and its conjugate base or a weak base and its conjugate acid.

(iii) Ionic product of water
The ionic product of water (Kw) is the product of the concentrations of hydrogen ions and hydroxide ions in water at a particular temperature:
$Kw = [H^+][OH^-]$

(iv) Salt hydrolysis
Salt hydrolysis is the reaction of the anion or cation (or both) of a salt with water to produce acidic or basic solution.

3 (b) Briefly explain each of the following observations:

(i) Ammonia (NH_3) is one of the Lowry-Brønsted bases.
NH_3 accepts a proton (H^+) to form NH_4^+, so it acts as a Bronsted base.

(ii) Al^{3+} ion behaves as a Lewis acid when it is in water.
Al^{3+} accepts electron pairs from water molecules to form complexes, hence acts as a Lewis acid.

(iii) Lead(II) chloride is soluble in concentrated HCl solution.
$PbCl_2$ dissolves in concentrated HCl due to formation of complex ion $PbCl_4^{2-}$.

(iv) Aqueous aluminium nitrate solution turns blue litmus paper red.
$Al(NO_3)_3$ hydrolyzes to form H_3O^+ ions, making the solution acidic and turning litmus paper red.

3 (c) For each of the following pairs, write an equation to show how the pair reacts to form a conjugate acid and conjugate base. Identify the acid, base, conjugate acid and conjugate base.

(i) Bicarbonate ion and water
$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$
Acid: HCO_3^-
Base: H_2O
Conjugate acid: H_2CO_3
Conjugate base: OH^-

(ii) Ammonia and water
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
Acid: NH_3
Base: H_2O
Conjugate acid: NH_4^+
Conjugate base: OH^-

(iii) Nitrous ion and hydronium ion
$NO_2^- + H_3O^+ \rightleftharpoons HNO_2 + H_2O$
Acid: H_3O^+
Base: NO_2^-
Conjugate acid: HNO_2
Conjugate base: H_2O

(iv) Ammonium ion and carbonate ion
$NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$
Acid: NH_4^+
Base: CO_3^{2-}
Conjugate acid: HCO_3^-
Conjugate base: NH_3

3 (d) Briefly explain how an acidic buffer solution works to maintain its pH value when a small amount of acid is added to it.

An acidic buffer contains a weak acid and its conjugate base (e.g., CH_3COOH/CH_3COO^-). When acid is added, the conjugate base neutralizes the excess H^+ ions to maintain the pH. When base is added, the weak acid neutralizes OH^- ions to maintain the pH.

4 (a) Silver chloride has a measured solubility of 1.024×10^{-4} mol/dm³ at 18°C. Calculate its Ksp value.
$K_{sp} = [Ag^+][Cl^-] = (1.024 \times 10^{-4})^2 = 1.05 \times 10^{-8}$

4 (b) (i) Briefly describe the term "common ion effect".
The suppression of ionization of a weak acid or base by the presence of a strong electrolyte having an ion common to the weak acid/base is called the common ion effect.

(ii) Calculate the solubility of solid CaF_2 in a 0.05 M NaF solution. Ksp of $CaF_2 = 4.0 \times 10^{-11}$
$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$
Let solubility of CaF_2 be x.
$[Ca^{2+}] = x$
$[F^-] = 2x + 0.05 \approx 0.05$ (since x is small)
$K_{sp} = x \times (0.05)^2 = 4.0 \times 10^{-11}$
$x = 4.0 \times 10^{-11} / 0.0025 = 1.6 \times 10^{-8}$ mol/L

4 (c) Should a precipitate of barium fluoride be obtained when 100 mL of 0.25 M NaF and 100 mL of 0.015 M $Ba(NO_3)_2$ are mixed?

Total volume = 200 mL
$[Ba^{2+}] = (0.015 \times 100/200) = 0.0075$ M
$[F^-] = (0.25 \times 100/200) = 0.125$ M
$Q = [Ba^{2+}][F^-]^2 = 0.0075 \times (0.125)^2 = 0.0075 \times 0.015625 = 1.17 \times 10^{-4}$
Since $Q > K_{sp}$ (1.7×10^{-6}), precipitation will occur.

5 (a)(i) State the periodic law:
The physical and chemical properties of elements are periodic functions of their atomic numbers.

(ii) What is the advantage of arranging elements in the periodic table on the basis of atomic numbers rather than atomic masses?
It ensures that elements with similar properties fall in the same group, correcting anomalies in earlier arrangements based on atomic masses (e.g., Ar and K placement).

(iii) Give three diagonal similarities between Be and Al:
- Both form amphoteric oxides and hydroxides.
- Both form covalent chlorides ($BeCl_2$ and $AlCl_3$).
- Both form complexes, e.g., $[BeF_4]^{2-}$ and $[AlF_6]^{3-}$.

(b) Basic characters of elements in the modern periodic table always increase down the group. Justify this statement by considering the oxides of group V elements:
As we move down group V (N, P, As, Sb, Bi), the oxides become increasingly basic.

N_2O_5 and P_2O_5 are acidic oxides, As_2O_3 is amphoteric, while Sb_2O_3 and Bi_2O_3 are basic. This trend confirms that basicity increases down the group.

(c) Explain the following:

(i) Silicon has a higher melting point than it is expected:
Silicon has a giant covalent structure with strong Si–Si bonds which require high energy to break, resulting in a high melting point.

(ii) Graphite is used as a lubricant as well as a cell electrode but not diamond:
Graphite has layered structure with weak van der Waals forces between layers allowing them to slide (lubricant). It also conducts electricity due to delocalized electrons. Diamond lacks free electrons and is not used for electrical purposes.

(iii) The first ionization energy of boron is lower than that of beryllium although boron is towards the right across period 2 in the periodic table:
Beryllium has a fully filled $2s^2$ subshell which is more stable than boron's $2s^22p^1$ configuration. It requires more energy to remove electron from Be than from B.

(d) A researcher decided to place a newly discovered element at the bottom of group VII. What would be the expected physical and chemical properties of the new element?

(i) The state of the element at room temperature and pressure:
It would be a solid (like astatine).

(ii) Redox properties of the element:
It would act as an oxidizing agent, but weaker than iodine or astatine due to lower electronegativity.

(iii) Atomicity:
Likely to exist as diatomic molecule (X_2).

(iv) Reaction with alkali:
It would form halide salts with alkali metals, e.g., $X_2 + 2NaOH \longrightarrow NaXO + NaX + H_2O$

6 (a) Identify four general principles or steps which are followed during metal extraction:
- Concentration of ore
- Conversion of concentrated ore to oxide
- Reduction of metal oxide
- Purification of crude metal

(b) Extraction of tin from cassiterite:

(i) Thermal reduction of the ore:

$SnO_2 + 2C \text{ ----> } Sn + 2CO$

(ii) Purification of the ore from the impurities:
Sn is purified by liquation or electrolytic refining.

(iii) Its two uses in real life:
Used to make alloys like bronze and as a coating on steel to prevent rusting (tin-plated steel).

(c) Extraction of aluminium from bauxite ($Al_2O_3 \cdot 2H_2O$):
Process steps:
1. Concentration by Bayer's process: Bauxite is treated with NaOH → soluble $NaAlO_2$
2. Filtration removes impurities
3. Precipitation: CO_2 is passed to get $Al(OH)_3$
4. Heating $Al(OH)_3 \rightarrow Al_2O_3$
5. Electrolysis (Hall-Héroult):
Cathode: $Al^{3+} + 3e^- \text{ ----> } Al$
Anode: $C + O^{2-} \text{ ----> } CO_2$

7 (a) With reference to the elements of period III of the periodic table, give the formula of the oxide with the following properties:

(i) The most basic oxide: Na_2O
(ii) The amphoteric oxide: Al_2O_3

(b) Briefly explain the action of water on chlorides of period III elements:
Chlorides of metals (NaCl, $MgCl_2$) dissolve without hydrolysis.
Chlorides of non-metals (e.g., PCl_5, $AlCl_3$, $SiCl_4$) hydrolyze with water forming acidic solutions and releasing HCl.

(c) Give reasons to support the following:

(i) When salts of iron are exposed in air, they turn from blue green colour to brown:
Iron(II) salts oxidize to Iron(III) which forms brown rust ($Fe_2O_3 \cdot xH_2O$).

(ii) Concentrated nitric acid renders aluminium passive:
A protective oxide layer forms on Al surface due to oxidation, preventing further reaction.

(iii) Zinc and tin are used to protect iron from rusting:
Zinc and tin act as sacrificial metals; they oxidize first, protecting iron.

(d) With the help of chemical equations, state the physical changes that will be observed and their inference in each of the following experiments:

(i) Sodium oxalate solution is added into potassium permanganate solution in acidic medium:
$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \text{ ----> } 2Mn^{2+} + 10CO_2 + 8H_2O$
Observation: Purple colour of $KMnO_4$ decolorizes, gas bubbles (CO_2) observed.

(ii) Hydrogen sulphide solution is added into potassium dichromate solution in acidic medium:
$H_2S + K_2Cr_2O_7 + H^+ \text{ ----> } S + Cr^{3+} + H_2O$
Observation: Orange dichromate solution turns green, yellow sulphur precipitate forms.

8 (a) Briefly describe the following:

(i) Ozone layer:
The ozone layer is a region in the stratosphere that contains a high concentration of ozone (O_3) molecules. It absorbs most of the sun's harmful ultraviolet (UV) radiation.

(ii) Greenhouse effect:
It is the trapping of heat in the earth’s atmosphere by greenhouse gases like CO_2, CH_4, H_2O vapor, which allows sunlight in but prevents heat from escaping, thus warming the planet.

(iii) Acid rain:
Acid rain is rainfall made acidic by atmospheric pollution, mainly due to sulfur dioxide (SO_2) and nitrogen oxides (NO_x) reacting with water to form sulfuric and nitric acids.

8 (b) Describe how the ozone layer is formed and destroyed using equations:

Formation:
O_2 + UV light ----> 2O
$O + O_2 \text{ ----> } O_3$

Destruction:
O_3 + UV light ----> O_2 + O
$O + O_3 \text{ ----> } 2O_2$
By CFCs:
$CFCl_3 \text{ ----> } CFCl_2\bullet + Cl\bullet$
$Cl\bullet + O_3 \text{ ----> } ClO\bullet + O_2$
$ClO\bullet + O \text{ ----> } Cl\bullet + O_2$

8 (c) Outline six effects of ozone layer depletion:
- Increased UV radiation on Earth
- Skin cancer and cataracts in humans
- Reduced crop productivity
- Damage to marine ecosystems
- Suppression of immune system
- Material degradation (plastics, rubber)

9 (a) Compare basicity in each pair:

(i) Aniline ($C_6H_5NH_2$) and Cyclohexylamine ($C_6H_{11}NH_2$):
Cyclohexylamine is more basic because in aniline, the lone pair on nitrogen is delocalized into the aromatic ring, reducing availability for protonation.

(ii) CH_3NH_2 and CH_3NHCH_3:
CH_3NHCH_3 is more basic due to electron donating inductive effect from both alkyl groups increasing electron density on nitrogen.

9 (b) Give the products of the following organic reactions:

(i) $CH_3C{\equiv}N + H_2O/H^+$ ----> CH_3COOH (hydrolysis of nitrile)

(ii) $CH_3CH_2CONH_2 + LiAlH_4/H_2O$ ----> $CH_3CH_2CH_2NH_2$ (reduction of amide to amine)

(iii) Nitrobenzene + Conc. HCl/Sn ----> Aniline ($C_6H_5NH_2$) (reduction of nitro group)

(iv) $CH_3CH_2NH_2 + HNO_2$ ----> $CH_3CH_2OH + N_2 + H_2O$ (deamination reaction)

(v) $C_6H_5NH_2 + NaNO_2 + HCl$ ----> $C_6H_5N_2^+Cl^-$ (benzenediazonium salt)

(vi) $CH_3CH_2CONH_2 + Br_2/OH^-$ ----> $CH_3CH_2NH_2 + CO_2$ (Hofmann rearrangement)

9 (c) Briefly describe the laboratory preparation of dimethylamine from methane:
Methane is chlorinated to form chloromethane:
$CH_4 + Cl_2$ ----> $CH_3Cl + HCl$
Then CH_3Cl is reacted with excess NH_3 to get methylamine, dimethylamine and trimethylamine.
$CH_3Cl + NH_3$ ----> CH_3NH_2
$CH_3Cl + CH_3NH_2$ ----> $(CH_3)_2NH$

9 (d) Organic compound A treated with nitrous acid gives B and nitrogen gas. B composition: 60% C, 13.33% H, 26.67% O
Empirical formula calculation:
C = 60/12 = 5, H = 13.33/1 = 13.33, O = 26.67/16 = 1.67 → Simplifies to C_3H_8O
Molar mass from vapor density = 30×2 = 60 g/mol
Compound B = C_3H_8O (propanol)

B oxidized by H_2CrO_4 to compound C → C = C_3H_6O (propanal)
C reacts with hydroxylamine to form oxime
C reacts with Fehling's solution = brick red ppt → C is aldehyde

Compound A = $CH_3CH_2CH_2NH_2$ (propylamine)

Compound B = $CH_3CH_2CH_2OH$ (propanol)
Compound C = CH_3CH_2CHO (propanal)

Equations:
A + HNO_2 ----> B + N_2 + H_2O
B + H_2CrO_4 ----> C + H_2O
C + NH_2OH ----> oxime
C + Fehling's ----> red ppt of Cu_2O
10 (a) Name the following organic compounds:

(i) Benzoic acid
(ii) 3-Methylpentanoic acid
(iii) Malonic acid (IUPAC: Propanedioic acid)
(iv) 4-Hydroxyhexanoic acid

10 (b) What are the effects of the following on the acidity of carboxylic acids?

(i) Chlorine as a withdrawing atom:
Chlorine is an electronegative atom that withdraws electrons from the carboxylic acid group through the inductive effect, stabilizing the conjugate base (carboxylate ion), thus increasing acidity.

(ii) Large sized alkyl group:
Alkyl groups are electron donating by inductive effect, which destabilize the conjugate base by increasing negative charge density. Hence, larger alkyl groups decrease acidity.

10 (c) Show how the following conversions can be carried out:

(i) Benzene to m-nitrobenzoic acid
Benzene ----> Nitrobenzene (nitration using HNO_3/H_2SO_4)
Nitrobenzene ----> m-nitrobenzoic acid (oxidation of side chain using $KMnO_4$ after Friedel-Crafts alkylation followed by oxidation)

(ii) Phenol to benzoyl chloride
Phenol ----> Benzoic acid (oxidation using strong oxidizer like $KMnO_4$)
Benzoic acid ----> Benzoyl chloride (reaction with PCl_5 or $SOCl_2$)

(iii) Propanoyl chloride to Ethyl propanoate
$CH_3CH_2COCl + C_2H_5OH$ ----> $CH_3CH_2COOC_2H_5 + HCl$ (esterification)

(iv) Ethylbenzene to Benzamide
Ethylbenzene ----> Benzoic acid (oxidation using $KMnO_4$)
Benzoic acid ----> Benzoyl chloride (reaction with PCl_5 or $SOCl_2$)
Benzoyl chloride ----> Benzamide (reaction with NH_3)

10 (d) Lactic acid synthesis from ethanol

CH_3CH_2OH --U--> CH_3CHO --V--> $CH_3CH(OH)CN$ --W--> $CH_3CH(OH)COOH$

(i) Reagents and conditions:
U: Acidified potassium dichromate ($K_2Cr_2O_7/H^+$) or PCC – oxidation
V: HCN/KCN and acid catalyst – nucleophilic addition of HCN (cyanohydrin formation)
W: H^+/H_2O (acid hydrolysis) – hydrolysis of nitrile to carboxylic acid
(ii) Names of organic reactions:
Step V – Cyanohydrin formation
Step W – Hydrolysis of nitrile

(iii) IUPAC name of lactic acid:
2-Hydroxypropanoic acid