THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2002**

Instructions

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

Prepared by: Maria Marco for TETEA

1 (a) What is meant by the following terms?

(i) Negative catalyst
A negative catalyst is a substance that decreases the rate of a chemical reaction without itself undergoing any permanent chemical change.

(ii) Common ion effect
The common ion effect is the suppression of the degree of dissociation of a weak electrolyte by the presence of a strong electrolyte having a common ion.

1 (b) Explain the following statements:

(i) Hydrogen chloride does not obey Henry's law.
HCl reacts with water to form ions rather than dissolving as an intact gas, hence it does not obey Henry's law which applies to non-reactive dissolution.

(ii) It is incorrect to refer to concentrated hydrochloric acid as strong hydrochloric acid.
Strength refers to the degree of ionization; concentrated refers to the amount of solute per unit volume. A dilute solution of HCl is still a strong acid.

(iii) On dissolving in water hydrogen chloride (HCl) ionizes and dissociates but potassium chloride dissociates only.
HCl is a covalent molecule which ionizes in water to form H^+ and Cl^-. Potassium chloride is ionic and simply dissociates into K^+ and Cl^- ions.

1 (c) Which of the following acids is the strongest and which is the weakest?
Nitrous acid (HNO_2) $Ka = 5.1 \times 10^{-4}$
Sulphurous acid (H_2SO_3) $Ka = 1.7 \times 10^{-2}$
Phosphoric acid (H_3PO_4) $Ka = 7.1 \times 10^{-3}$
Strongest acid: Sulphurous acid
Weakest acid: Nitrous acid (lowest Ka)

1 (d) Sodium thiosulphate reacts with iodine according to the equation:
$2Na_2S_2O_3 + I_2$ ----> $2NaI + Na_2S_4O_6$
Iodine is reduced from 0 to –1 in NaI
Thiosulphate is oxidized, hence this is a redox reaction

Mass of iodine required to react with 30 cm^3 of 0.1 M thiosulphate:
Moles of $Na_2S_2O_3 = 0.1 \times 30 \div 1000 = 0.003$ mol
From equation: 2 mol $Na_2S_2O_3$ reacts with 1 mol $I_2 \rightarrow 0.003$ mol $Na_2S_2O_3$ reacts with 0.0015 mol I_2
Mass of $I_2 = 0.0015 \times 254 = 0.381$ g

2 (a) Define the following terms:

(i) Standard bond dissociation enthalpy
Energy required to break one mole of a particular bond in gaseous molecules under standard conditions.

(ii) Standard enthalpy of atomization
Energy required to form one mole of gaseous atoms from the element in its standard state.

(iii) Standard state of a substance
The pure form of a substance under 1 atm pressure and specified temperature (usually 298 K).

(iv) Standard lattice energy
Energy released when one mole of an ionic solid is formed from its constituent gaseous ions.

2 (b) Use the following bond enthalpies to calculate the enthalpy change of the reaction:
$C=O = 743\ kJ\ mol^{-1}$
$C-H = 412\ kJ\ mol^{-1}$
$C–C = 360\ kJ\ mol^{-1}$
$C\equiv N = 884\ kJ\ mol^{-1}$
$H–O = 463\ kJ\ mol^{-1}$

Reaction: $CH_3COCH_3 + HCN$ ----> $CH_3CH(OH)CN$

Bonds broken:
$C=O$, $C-H$, $H-C\equiv N$ → Total = 743 + 412 + 884 = 2039 kJ

Bonds formed:
$C–OH$, $C–C$, $C–H$, $C–H$, $C\equiv N$ → Total = 463 + 360 + 2×412 + 884 = 2531 kJ

ΔH = Bonds broken – Bonds formed = 2039 – 2531 = –492 $kJ\ mol^{-1}$

2 (c) For reaction: $CO(g) + NO_2(g)$ ----> $CO_2(g) + NO(g)$
Ea forward = 82.1 kJ/mol
Ea reverse = 32.0 kJ/mol

(i) Heat of reaction = Ea forward – Ea reverse = 82.1 – 32.0 = 50.1 $kJ\ mol^{-1}$

(ii) Energy profile: Upward curve reaching 82.1 kJ from reactants, then down to products at –50.1 kJ compared to reactants level. Reverse path rises from product by 32 kJ.

3 (a) Consider: $Mg + Co^{2+}$ ----> $Mg^{2+} + Co$
(i) Reducing agent: Mg (donates electrons)
(ii) Oxidizing agent: Co^{2+} (accepts electrons)

3 (b) Given:
$Cu^{2+} + 2e^{-}$ ----> Cu(s) E° = 0.34 V
$Ag^{+} + e^{-}$ ----> Ag(s) E° = 0.80 V

(i) Feasible reaction: Ag^{+} reduced by Cu
E°cell = 0.80 – 0.34 = +0.46 V

(ii) Half reactions:
Oxidation: Cu ----> $Cu^{2+} + 2e^{-}$
Reduction: $2Ag^{+} + 2e^{-}$ ----> 2Ag

(iii) Redox equation: Cu + $2Ag^{+}$ ----> Cu^{2+} + 2Ag

(iv) Cell diagram: Cu(s) | Cu^{2+} || Ag^{+} | Ag(s)

(v) E°cell = 0.46 V

4 (a) Explain the meaning of the following terms:

(i) Rate-determining step:
The slowest step in a reaction mechanism which controls the overall rate.

(ii) Intermediate product:
Species formed and used up during a reaction mechanism, not seen in the net reaction.

(iii) Elementary reaction:
A single-step reaction where reactants directly form products.

(iv) Reaction rate:
Change in concentration of reactant or product per unit time.

4 (b) CO + NO + O_2 ----> CO_2 + NO_2
Steps:
Step 1: CO + HO ----> CO_2 + H
Step 2: NO + H ----> HNO
Step 3: HNO + O_2 ----> NO_2 + HO
Intermediates: HO, H, HNO
HO acts as a catalyst because it appears in the beginning and is regenerated at end.

4 (c) Results:

Run	A (mol/dm³)	B (mol/dm³)	Rate (mol/dm³/s)

a	0.50	1.0	2.0
b	0.50	2.0	8.0
c	0.50	3.0	18.0
d	1.0	3.0	36.0
e	2.0	3.0	72.0

(i) Order with respect to B: Compare a, b, c
B doubles ---> rate ×4 ---> order 2 in B
(ii) Order with respect to A: Compare c, d, e
A doubles ---> rate doubles ---> order 1 in A
(iii) Overall order = 1 + 2 = 3
Rate constant $k = \text{Rate} \div [A] \times [B]^2$
From run a: $k = 2.0 \div (0.5 \times 1^2) = 4$
Units: $\text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$

5 (a) Explain why:

(i) Aqueous $FeCl_3$ liberates CO_2 from Na_2CO_3
$Fe^{3+} + CO_3^{2-} + H_2O \text{ ----> } Fe(OH)_3 + CO_2$

(ii) SO_2 has low boiling point but sulphates are ionic solids with strong lattice energy.

(iii) K^+ is smaller than Cl^- due to higher effective nuclear charge despite same electrons.

(iv) H_2SO_4 oxidizes H_2S to S, hence cannot be used to dry it.

(v) Iodine dissolves in KI due to formation of I_3^- ions: $I_2 + I^- \text{ ----> } I_3^-$

5 (b) Diagonal relationship:
Similarity of elements diagonally in periodic table.
Examples:
- Li and Mg (similar salts)
- Be and Al (amphoteric oxides)
- B and Si (covalent chlorides)

6 (a) It is often said that the element at the top of each group is not typical of the rest of the group in the periodic table. By choosing four suitable examples of elements and reactions, illustrate briefly this comment.

- Lithium forms normal oxide (Li_2O) while other alkali metals form peroxides or superoxides.
- Beryllium forms covalent compounds while other Group 2 elements form ionic compounds.
- Boron is a metalloid while the rest of Group 13 are metals.
- Carbon forms multiple bonds and shows catenation unlike other Group 14 elements.

6 (b) Below is a representation of two periods of the periodic table:
GROUP | 1 | 2 | 3 | 4 | 5 | 6 | 7
Li Be B C N O F
Na Mg Al Si P S Cl

(i) The most reactive non-metal → F
(ii) The most reactive metal → Na
(iii) The one with the smallest atom → F
(iv) The one which forms the largest anion → F
(v) In the same group as element of atomic number 31 (Gallium) → Al

6 (c) What is meant by the term "metallic bonding"?
Metallic bonding is the force of attraction between positively charged metal ions and the sea of delocalized electrons that move freely throughout the metal lattice.

7 (a) Summarize the trends of the nitrogen and beryllium groups with respect to:

(i) First ionization potential
Increases across the period, decreases down the group. First elements have higher ionization energy due to smaller size.

(ii) Polar character of hydrides
Decreases down the group. NH_3 and BeH_2 are more polar than BiH_3 or BaH_2.

(iii) Acid-base character of oxides
More acidic across period, more basic down group. For nitrogen group: N_2O_5 acidic, Bi_2O_3 basic. For beryllium group: BeO amphoteric, BaO strongly basic.

Comment: The first element in each group behaves anomalously due to small size, high electronegativity, and absence of d-orbitals.

7 (b) Compare and comment on properties of the following pairs of compounds:

(i) CO_2 and SiO_2
CO_2 is a gas with discrete molecules due to double bonds. SiO_2 is a solid with giant covalent structure.

(ii) CCl_4 and $SiCl_4$
CCl_4 is stable in water; $SiCl_4$ hydrolyzes rapidly in water to form HCl and SiO_2 due to vacant d-orbitals in Si.

7 (c) Explain what happens and show all chemical reactions that take place when:

(i) Hydrogen sulphide is passed into aqueous solution of acidified potassium permanganate

$2KMnO_4 + 5H_2S + 3H_2SO_4$ ----> $2MnSO_4 + K_2SO_4 + 5S + 8H_2O$

(ii) Hydrogen peroxide added to solution of ferrous sulphate with potassium ferricyanide
$2Fe^{2+} + H_2O_2 + 2H^+$ ----> $2Fe^{3+} + 2H_2O$
Color change observed due to formation of blue complex with ferricyanide.

(iii) Potassium iodide solution added to Cu^{2+} sulphate solution followed by sodium thiosulphate
$2Cu^{2+} + 4I^-$ ----> $2CuI + I_2$
$I_2 + 2S_2O_3^{2-}$ ----> $2I^- + S_4O_6^{2-}$

(iv) Sulphur dioxide in water passed through acidified potassium permanganate
$5SO_2 + 2KMnO_4 + 2H_2O$ ----> $K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

8 (a) What do you understand by:

(i) Isomerism
Existence of compounds with same molecular formula but different structural or spatial arrangements.

(ii) Functional groups
Group of atoms responsible for characteristic chemical reactions of molecules.

(iii) Homologous series
Series of compounds with same functional group and general formula, differing by CH_2.

(iv) Catenation
Ability of atoms (mainly carbon) to form long chains or rings with itself.

8 (b) Quantitative analysis of W:
$C = 49.3\%$, $H = 9.6\%$, $N = 19.2\%$, $O = 21.96\%$
Empirical formula:
$C = 49.3 \div 12 = 4.11$
$H = 9.6 \div 1 = 9.6$
$N = 19.2 \div 14 = 1.37$
$O = 21.96 \div 16 = 1.37$
Ratio ≈ C_3H_7NO (empirical formula)
Molecular mass from depression in freezing point:
$\Delta T = Kf \times m$
$0.486 = 1.86 \times (0.1825 \div M) \times 100$
$M \approx 70 \rightarrow$ molecular formula = $C_4H_{10}N_2O$

8 (c) Reaction of W with caustic potash gives Z → Suggests presence of amide or urea structure
Structural formula of W could be $CH_3CONHCH_2NH_2$
$Z = CH_3COOK$

9 (a) Conversions:
(i) CH_3CH_2OH ----> CH_3CH_2COOH (oxidation)
(ii) CH_3CH_2COOH ----> CH_3CH_3 (decarboxylation)
(iii) CH_3CH_2COOH ----> $CH_3CHBrCH_2Br$ (Hell-Volhard-Zelinsky)
(iv) CH_3COOH ----> CH_3CH_3 (reduction with $LiAlH_4$)

9 (b) Arrange in order of decreasing basic strength:
Triethylamine > Diethylamine > Ethylamine > Ammonia > Aniline

9 (c) Order of increasing acidic strength:
$CH_3COOH < CH_2ClCOOH < CHCl_2COOH < CCl_3COOH$

9 (d) Functional group reactions:
(i) Acidified $KMnO_4$ ----> Oxidation of $–CH_3$ to $–COOH$
(ii) H_2/Ni ----> Reduction of C=O to $–CH_2OH$
(iii) PCl_5 ----> Conversion of –COOH to –COCl
(iv) I_2 + NaOH ----> Iodoform test (yellow ppt)
(v) 2,4-DNP ----> Orange ppt for C=O

10 (a) Compound: $NH_2–C(OH)–CH(OH)–C(OH)$
Reactions:
(i) Oxidation with $K_2Cr_2O_7$ -----> converts OH to C=O and amide to acid
(ii) With ethanol → esterification
(iii) PCl_5 → conversion to acyl chlorides
(iv) $LiAlH_4$ → reduction of carbonyls to alcohols

10 (b) Isomers P and Q (C_8H_8)
P is ethylbenzene ---> oxidation ----> benzoic acid
Q is m-xylene ---> oxidation ---> benzene tricarboxylic acid ---> electrophilic nitration gives two nitro derivatives at meta positions.