THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2001**

Instructions

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

1 (a) Define the following terms giving one example in each case:

(i) Standard heat of atomization
It is the enthalpy change required to produce one mole of gaseous atoms from the element in its standard state.
Example: $H_2(g) \text{ ----> } 2H(g)$

(ii) Standard enthalpy of solution
It is the enthalpy change when one mole of a solute is dissolved in a large amount of solvent so that further dilution does not cause any heat change.
Example: $NaCl(s) \text{ ----> } Na^+(aq) + Cl^-(aq)$

(iii) An exothermic reaction
A chemical reaction that releases heat to the surroundings.
Example: $CH_4 + 2O_2 \text{ ----> } CO_2 + 2H_2O \quad \Delta H < 0$

1 (b) State Hess's Law of constant heat summation
The total enthalpy change in a chemical reaction is the same irrespective of the number of intermediate steps, provided the initial and final conditions are the same.

1 (c)
Given data:
$Li(s) \text{ ----> } Li(g) \quad \Delta H = +155.1$ kJ/mol
$\frac{1}{2}F_2(g) \text{ ----> } F(g) \quad \Delta H = +151.0$ kJ/mol
$Li(g) \text{ ----> } Li^+(g) + e^- \quad \Delta H = +518.3$ kJ/mol
$F(g) + e^- \text{ ----> } F^-(g) \quad \Delta H = -351.1$ kJ/mol
$Li^+(g) + F^-(g) \text{ ----> } LiF(s) \quad \Delta H = -1030.0$ kJ/mol

(i) Calculate the enthalpy of formation of LiF(s):
$\Delta H = \Delta H(\text{atomization Li}) + \Delta H(\text{atomization F}) + \Delta H(\text{ionization energy Li}) + \Delta H(\text{electron affinity F}) + \Delta H(\text{lattice energy})$
$= 155.1 + 151.0 + 518.3 - 351.1 - 1030.0$
$= -556.7$ kJ/mol

(ii) The reaction is exothermic since ΔH is negative.

1 (d) Enthalpies of combustion (kJ/mol):
Hydrogen: –242
Benzene: –3302
Cyclohexene: –3764
Cyclohexane: –3940

(i) Enthalpy of hydrogenation of benzene = ΔH(cyclohexane) – ΔH(benzene) = –3940 – (–3302) = –638 kJ/mol
Enthalpy of hydrogenation of cyclohexene = ΔH(cyclohexane) – ΔH(cyclohexene) = –3940 – (–3764) = –176 kJ/mol

(ii) Comment: Benzene's hydrogenation enthalpy is far lower than expected for three double bonds. This suggests benzene is stabilized by delocalization of electrons (resonance energy), unlike cyclohexene which has a localized double bond.

2 (a) Define the following terms:

(i) Cathode: The electrode where reduction occurs.
(ii) Anode: The electrode where oxidation occurs.
(iii) Standard electrode potential: The potential difference when an electrode is in equilibrium with its ions at 1 mol/dm³ concentration, 1 atm pressure, and 298 K.
(iv) Concentration cell: An electrochemical cell where electrodes are identical but solutions have different concentrations.

2 (b)
(i) A galvanic cell converts chemical energy to electrical energy, while an electrolytic cell converts electrical energy into chemical energy.
(ii) A salt bridge maintains electrical neutrality by allowing ion flow between half-cells and completes the circuit.

2 (c) Standard electrode potentials at 25°C:
$Cl_2 + 2e^- \longrightarrow 2Cl^-$ $E^\circ = +1.36$ V
$Ni^{2+} + 2e^- \longrightarrow Ni$ $E^\circ = -0.23$ V
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$ $E^\circ = -0.50$ V
$Cr^{3+} + 3e^- \longrightarrow Cr$ $E^\circ = -0.73$ V
$Br_2 + 2e^- \longrightarrow 2Br^-$ $E^\circ = +1.09$ V
$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$ $E^\circ = +2.01$ V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ $E^\circ = +1.33$ V

(i) Cell 1: $Ni \mid Ni^{2+} \parallel Br^- \mid Br_2 \mid Pt$
$E^\circ cell = 1.09 - (-0.23) = 1.32$ V

(ii) Cell 2: $Cr^{3+}(1M) + Cl_2 \longrightarrow Cr_2O_7^{2-}(1M) + Cl^-(1M)$
$E^\circ cell = 1.33 - 1.36 = -0.03$ V (non-spontaneous)

2 (d) Galvanic cell diagram:
Cell 1: $Ni(s) \mid Ni^{2+}(1M) \parallel Br^-(1M) \mid Br_2(l) \mid Pt$
Cell 2: $Cl_2(g) \mid Cl^-(1M) \parallel Cr_2O_7^{2-}(1M), Cr^{3+} \mid Pt$

2 (e) For redox reaction:
$S_2O_8^{2-} + Cr^{3+} \text{----}> 2SO_4^{2-} + Cr^{2+}$
(i) E°cell = E°cathode – E°anode = (–0.50) – (2.01) = –2.51 V
(ii) Use Nernst equation:
$E = E° – (0.0592/n) \log Q$

3 (a) Define the following terms:

(i) Allotropy: Existence of an element in more than one form in the same physical state with different structures.
(ii) Enantiotropy: Type of allotropy where one form is stable at low temperature and another at high temperature.

3 (b) Difference:
(i) Allotropy vs Isotropy: Allotropy is about different structural forms of the same element; isotropy refers to uniform properties in all directions.
(ii) Polymorphs and Allotropes: Polymorphs refer to different crystal forms of a compound; allotropes are for elements.

3 (c) Bragg's Equation:
$n\lambda = 2d \sin\theta$
Where:
n = order of reflection
λ = wavelength
d = interplanar spacing
θ = diffraction angle

3 (d) X-ray diffraction problem:
$\lambda = 1.54$ Å, $\theta = 19.5°$
n = 1 ----> $d = \lambda / (2 \sin\theta)$
$d = 1.54 / (2 \times \sin 19.5°)$
$= 1.54 / (2 \times 0.334) = 2.31$ Å = 0.231 nm (distance between planes)
4 (a) Define the following:

(i) Order of reaction
Order of reaction is the sum of the powers of the concentrations of the reactants in the rate equation.
For example, for the rate law: rate = $k[A]^2[B]$, the overall order is 3 (second order with respect to A and first order with respect to B).

(ii) Molecularity
Molecularity is the number of reactant molecules or species taking part in an elementary step of the reaction. It can be unimolecular, bimolecular, or termolecular depending on whether one, two, or three molecules are involved.

4 (b) A gaseous reaction
$2A + B \longrightarrow A_2B$ takes place in two steps:
Step 1: $A + B \longrightarrow AB$
Step 2: $AB + A \longrightarrow A_2B$

It was observed that when the concentration of B was kept constant while that of A doubled, the rate of reaction doubled. When the concentration of A was kept constant while the concentration of B tripled, the rate of reaction was tripled.

(i) Out of the two steps, Step 1 is the rate-determining step since the rate depends on the concentrations of A and B.

(ii) Rate law: Rate = $k[A][B]$

4 (c) For the reaction between G and F the following initial rates were measured at 25°C:

S/N	Initial rate (mol dm^{-3} s^{-1})	G (mol dm^{-3})	F (mol dm^{-3})
1	3.10×10^{-4}	2.0	3.0
2	7.75×10^{-4}	1.0	1.5

Rate = $k[G]^m [F]^n$, given $k = 3.44 \times 10^{-4}$ dm^6 mol^{-2} s^{-1}
From experiment 1: $3.10 \times 10^{-4} = 3.44 \times 10^{-4} \times (2)^m \times (3)^n$
Solve for m and n, then determine overall order = $m + n$

5 (a) What is meant by:

(i) Resonance energy
Resonance energy is the extra stability of a molecule due to delocalization of electrons compared to a hypothetical structure with localized bonds.

(ii) Lattice energy
Lattice energy is the energy released when one mole of an ionic compound is formed from its gaseous ions.

(iii) Disproportionation reaction
A reaction in which the same species is both oxidized and reduced.
Example: $Cl_2 + H_2O \longrightarrow HCl + HOCl$

(iv) Inert pair effect
The reluctance of s-electrons in heavier p-block elements to participate in bonding due to poor shielding and relativistic effects.

5 (b) Complete and balance the following equations:

(i) $Li_3N + 3HCl \longrightarrow 3LiCl + NH_3$
(ii) $Rb_2O + H_2O \longrightarrow 2RbOH$
(iii) $NaH + H_2O \longrightarrow NaOH + H_2$
(iv) $Ca_2C_3 + 4H_2O \longrightarrow 2Ca(OH)_2 + CH_4 + C_2H_2$

5 (c) (i) Arrange the following ions in the order of decreasing size:
$Rb^- > Se^{2-} > Br^- > Sr^{2+}$

(ii) Arrange the following bonds according to polarity:
F–H > O–H > C–H > S–H > H–H

(iii) Magnesium isotopes:

Isotope	Mass (amu)	Abundance (%)
^{24}Mg	23.9850	78.99
^{25}Mg	24.9858	10.00
^{26}Mg	25.9826	11.01

Average atomic mass = $(23.9850 \times 78.99 + 24.9858 \times 10.00 + 25.9826 \times 11.01)/100$
$= 1{,}894.65 + 249.86 + 286.04 = 2430.55 \div 100 = 24.31$ amu

6 (a) Comment with chemical equations:

(i) Iron(II) chloride cannot be prepared by heating iron in chlorine gas as it forms $FeCl_3$:
$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$

(ii) Hydrochloric acid cannot be used in titration involving $KMnO_4$ because Cl^- is oxidized:
$2Cl^- + MnO_4^- + 8H^+ \longrightarrow Cl_2 + Mn^{2+} + 4H_2O$

(iii) $Al(OH)_3$ is amphoteric and dissolves in NaOH:
$Al(OH)_3 + OH^- \longrightarrow [Al(OH)_4]^-$

(iv) Acidified $K_2Cr_2O_7$ with NaCl gives green solution due to Cr^{3+} formation and Cl_2 gas:
$Cr_2O_7^{2-} + 14H^+ + 6Cl^- \longrightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$

6 (b) Electronic configurations:

(i) Cobalt atom (Z=27): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
(ii) Co^{3+} ion: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

6 (c) $[CoF_6]^{3-}$ is paramagnetic because F^- is a weak field ligand, leading to unpaired electrons (high spin complex). $[Co(CN)_6]^{3-}$ is not paramagnetic because CN^- is a strong field ligand, causing pairing of electrons (low spin complex, no unpaired electrons).

7 (a) (i) Define the term "melting point" of a substance:
Melting point is the temperature at which a solid changes into a liquid at atmospheric pressure.

(ii) State the modern periodic law:
The modern periodic law states that the physical and chemical properties of elements are a periodic function of their atomic numbers.

(iii) What are the two factors that helped the classification of elements in the periodic table?
- Atomic number
- Electronic configuration

(b) Table of elements of Period 3 and their melting points:

Element	Na	Mg	Al	Si	P	S	Cl
m.p °C	98	650	660	1423	44	120	-101

Account for the following:

(i) The melting point of magnesium is very high compared to that of sodium:
Magnesium forms stronger metallic bonds due to more delocalized electrons and smaller atomic radius compared to sodium.

(ii) Although aluminium is on the right-hand side across Period 3, its melting point is too close to that of magnesium:
This is because aluminium forms stronger metallic bonds with three delocalized electrons per atom, but the structure causes less dense packing than Mg.

(iii) Silicon has the highest melting point of all elements in Period 3:
Silicon has a giant covalent structure requiring high energy to break strong covalent bonds throughout the lattice.

(iv) The melting point of sulphur is higher than that of phosphorus:
Sulphur exists as S_8 molecules which have stronger van der Waals forces compared to the P_4 molecules of phosphorus.

(v) The melting point of chlorine is very low:
Chlorine exists as Cl_2 molecules held together by weak van der Waals forces, which require little energy to overcome.

8 (a) Using one appropriate example in each case, explain what is meant by the following terms:

(i) Hoffmann's degradation:
Conversion of an amide to an amine with one less carbon atom using Br_2 and NaOH.
Example: $RCONH_2 + Br_2 + 4NaOH$ ----> $RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

(ii) Aldol condensation:
Condensation of two carbonyl compounds (aldehydes or ketones) in presence of base.
Example: $CH_3CHO + CH_3CHO$ ----> $CH_3CH(OH)CH_2CHO$

(iii) Condensation polymer:
Polymer formed by condensation reaction with elimination of small molecules like water.
Example: Nylon-6,6 from adipic acid and hexamethylenediamine

(iv) Ortho and para director:
Electron-donating substituents direct electrophiles to ortho and para positions in aromatic substitution.
Example: –OH directs NO_2 to ortho/para in phenol.

(v) Electrophilic substitution:
Reaction where an electrophile replaces a hydrogen on an aromatic ring.
Example: $C_6H_6 + Br_2/FeBr_3$ ----> $C_6H_5Br + HBr$

(b) Reaction of compound $H_2N–C_6H_4–CHO$ with reagents:

(i) Cold sodium nitrite and HCl (Diazotization):
$C_6H_4–NH_2 + NaNO_2 + HCl$ ----> $C_6H_4–N_2^+Cl^- + H_2O$

(ii) 2,4-Dinitrophenylhydrazine:
Forms yellow/orange precipitate of hydrazone derivative
$C_6H_4–CHO$ + DNPH ----> $C_6H_4–CH=N–NH–$DNP

(iii) Excess sodium hydroxide and iodine (Iodoform test):
Aldehyde with $–CH_3CO$ group gives yellow precipitate of iodoform.

(iv) HCN followed by $LiAlH_4$:
$C_6H_4–CHO + HCN$ ----> $C_6H_4–CH(OH)CN$
$C_6H_4–CH(OH)CN + 4[H]$ ----> $C_6H_4–CH(OH)CH_2NH_2$

(c) IUPAC name of $H_2N–C_6H_4–CHO$:
4-Aminobenzaldehyde

9 (a) A phenolic acid $C_8H_8O_4$ (K) exists in two isomeric forms.
Upon oxidation:
K + [O] ----> Salicylic acid + Oxalic acid
Suggest structures:
Isomer 1: 2-Hydroxybenzoic acid (salicylic acid form)
Isomer 2: Hydroxyethanedioic acid structure

(b) Synthesis methods:

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

(ii) Butanoic acid from n-propyl alcohol (two ways):
1. $CH_3CH_2CH_2OH$ ----> $CH_3CH_2CH_2Br$ ----> Grignard + CO_2 ----> $CH_3CH_2CH_2COOH$
2. $CH_3CH_2CH_2MgBr$ + CO_2 ----> $CH_3CH_2CH_2COOH$

(iii) Para-chlorobenzoic acid from para-chlorotoluene:
$Cl–C_6H_4–CH_3$ + $KMnO_4$ ----> $Cl–C_6H_4–COOH$

(iv) Cyclopentane carboxylic acid from cyclopentane:
C_5H_{10} + COOH source via Friedel–Crafts acylation or oxidation path

(c) Name each of the following compounds:

(i) 4-Nitrobenzoic acid
(ii) Cyclohexanecarboxylic acid
(iii) 2-Ethylbutanoic acid

10. 4.1 g of a bromoalkane was reacted with excess sodium hydroxide solution. The resulting solution was acidified with excess nitric acid and diluted to exactly 250 cm^3. 25 cm^3 of this solution required 33.28 cm^3 of 0.1M silver nitrate solution for complete precipitation of silver bromide.

(a) Calculate the relative formula mass of the bromoalkane.

Moles of $AgNO_3$ used = $(0.1 \times 33.28) \div 1000 = 0.003328$ mol
Since 25 cm^3 of solution was used out of 250 cm^3 total, total moles of Br^- = $0.003328 \times (250 \div 25) = 0.03328$ mol
This means 0.03328 mol of bromoalkane was present in 4.1 g

Relative formula mass (Mr) = mass ÷ moles = $4.1 \div 0.03328 \approx 123.3$

(b) From your answer to (a) deduce the molecular formula of the bromoalkane.

Mr ≈ 123.3 → Br = 80, so remaining = 123.3 – 80 ≈ 43
43 corresponds to C_3H_7 ($3\times12 + 7\times1 = 43$)
Molecular formula = C_3H_7Br

(c) Write the structural formulae of the possible isomers of the bromoalkane.

Possible isomers of C_3H_7Br:

- $CH_3–CH_2–CH_2Br$ (1-bromopropane)
- $CH_3–CH(Br)–CH_3$ (2-bromopropane)

(d) Explain the difference in the reactivity of one of the bromoalkanes you have given in (c) and bromobenzene with sodium hydroxide.

1-bromopropane undergoes nucleophilic substitution readily with OH^- to give alcohol due to the presence of polar C–Br bond and open alkyl chain, allowing attack by OH^-.

Bromobenzene does not undergo such substitution easily because the lone pair on bromine is delocalized into the benzene ring (resonance), making the C–Br bond partially double bond in character, which is stronger and less reactive towards nucleophiles.