THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2010**

Instructions

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

1(a) Explain the following terms:

(i) Common ion effect

This is the shift in equilibrium that occurs when an ion already present in the solution is added from another source. It suppresses the ionization of a weak acid or weak base due to the presence of a common ion from a strong electrolyte.

(ii) Buffer solution

A buffer solution is a solution that resists changes in pH when small amounts of acid or base are added. It usually contains a weak acid and its conjugate base or a weak base and its conjugate acid.

(iii) Acid dissociation

It refers to the process by which an acid releases hydrogen ions (H^+) in aqueous solution. The degree of dissociation determines the strength of the acid.

(iv) Ionic product of water

It is the product of the molar concentrations of hydrogen ions and hydroxide ions in pure water at a particular temperature. At 25°C, it is $Kw = [H^+][OH^-] = 1.0 \times 10^{-14}$ mol² dm⁻⁶.

(v) Salt hydrolysis

This is the reaction of the ions of a salt with water to produce either acidic or basic solution depending on the nature of the salt formed from a strong/weak acid or base.

1(b) Calculate the molar solubility of silver chromate in water at 25°C.

Given: $Ksp = 2.4 \times 10^{-12}$ mol² dm⁻⁶

Let solubility = s

$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$Ksp = [Ag^+]^2[CrO_4^{2-}] = (2s)^2(s) = 4s^3$

$4s^3 = 2.4 \times 10^{-12}$

$s^3 = 0.6 \times 10^{-12} = 6.0 \times 10^{-13}$

$s = (6.0 \times 10^{-13})^{1/3} = 8.4 \times 10^{-5}$ mol dm⁻³

1(c)(i) Will the solubility of silver chromate in 0.1 M aqueous solution of potassium dichromate be greater or lower than that of water? Explain.

The solubility will be lower. This is because K_2CrO_4 provides CrO_4^{2-} ions, a common ion with silver chromate, which shifts equilibrium backward due to common ion effect, decreasing solubility.

(ii) What are the three limitations of solubility product?

- It is valid only for saturated solutions.
- Assumes complete dissociation of ionic compounds.
- Assumes ideal solution behavior (activity coefficients are unity).

2(a)(i) State two laws which govern the depression of freezing point.
- Raoult's Law
- Van't Hoff Law of colligative properties

(ii) What are the three uses of colligative properties?
- Determining molecular mass
- Studying degree of dissociation
- Understanding nature of solute particles in solution

2(b) Electrolyte A dissociates into B, C, D +..., as shown in the equation:

$A \rightleftharpoons B + C + D + \ldots$

If degree of dissociation is α, then Vant Hoff's factor, $i = 1 + \alpha(n - 1)$, where n is the total number of ions formed from one molecule.

2(c) A solution of calcium nitrate containing 15 g of anhydrous salt in 1000 g of water freezes at –0.435°C. Calculate the degree of dissociation of the salt.

$\Delta Tf = iKf\ m$

Kf for water = 1.86°C mol^{-1}

Molar mass of $Ca(NO_3)_2$ = 164 g/mol

molality = 15 g /164 $gmol^{-1}$ / 1 kg water = 0.0915 mol/kg

$\Delta Tf = 0.435$

$0.435 = i \times 1.86 \times 0.0915$

$i = 0.435 / (1.86 \times 0.0915) = 2.57$

$i = 1 + \alpha(n - 1)$

$2.57 = 1 + 2\alpha$

$\alpha = 0.785$

3(a)(i) Define Kohlrausch's law of independent ionic mobilities.

Kohlrausch's law states that at infinite dilution, each ion makes a definite contribution to the total molar conductivity of an electrolyte, independent of the presence of other ions.

(ii) Give ionic representation of Kohlrausch's law of independent ionic mobilities.

$\Lambda\infty(\text{electrolyte}) = \lambda\infty(\text{cation}) + \lambda\infty(\text{anion})$

For example: $\Lambda\infty(NaCl) = \lambda\infty(Na^+) + \lambda\infty(Cl^-)$

3(b)(i) Give three applications of Kohlrausch's law of independent ionic mobilities.
- Determination of molar conductivity of weak electrolytes
- Calculation of degree of ionization of weak electrolytes
- Calculation of solubility of sparingly soluble salts

(ii) Show how you can obtain molar conductivity at infinite dilution ($\Lambda\infty$) of ethanoic acid from molar conductivities at infinite dilution of hydrochloric acid and potassium chloride.

$\Lambda\infty(CH_3COOH) = \Lambda\infty(HCl) + \Lambda\infty(CH_3COOK) - \Lambda\infty(KCl)$

3(c) The electrolytic conductivity of saturated solution of silver chloride at 18°C after deducting the conductivity of water is 1.22×10^{-4} S m^{-1}.
Molar conductivity of $Ag^+ = 0.54 \times 10^2$ S cm^2 mol^{-1}
Molar conductivity of $Cl^- = 0.652 \times 10^2$ S cm^2 mol^{-1}
$\Lambda = \kappa / c$
$c = \kappa / \Lambda = 1.22 \times 10^{-4}$ S m^{-1} / [$(0.54 + 0.652) \times 10^{-2}$ S m^2 mol^{-1}]
$= 1.22 \times 10^{-4} / (1.192 \times 10^{-2}) = 1.024 \times 10^{-2}$ mol/m^3
$= 1.024 \times 10^{-5}$ mol/kg (Assuming dilute solution in water)

4(a) Describe the following:
(i) Half life of chemical reaction
It is the time taken for the concentration of a reactant to reduce to half of its initial value.

(ii) Molecularity of chemical reaction
It is the number of molecules or atoms colliding in an elementary reaction.

(iii) Rate determining step
It is the slowest step in a reaction mechanism which determines the overall reaction rate.

(iv) Reaction mechanism
It is the step-by-step sequence of elementary reactions by which an overall chemical change occurs.

(v) Order of reaction
It is the sum of the powers to which the concentration terms are raised in the rate law expression.

4(b) The reaction AB ---> A + B is a first-order reaction with $k = 2.02 \times 10^{-5}$ sec^{-1} at 540 K.
Calculate % decomposition after 1 hour.
$t = 3600$ s
% decomposed = $[1 – e^{(-kt)}] \times 100 = [1 – e^{(-2.02 \times 10^{-5} \times 3600)}] \times 100$
$= [1 – e^{(-0.0727)}] \times 100 = [1 – 0.930] \times 100 = 7.0\%$

4(c) Isomerisation of cyclopropane to propene at 433°C

Time(h)	0	2	5	10	20	30
% remaining	100	91	79	63	40	25

(i) Write an equation for the reaction involved
C_3H_6 (cyclopropane) ----> C_3H_6 (propene)

(ii) Show that the reaction is first order with respect to cyclopropane.
Use first order kinetics: $\ln [A_0/A] = kt$
Take $\ln(100/91) = kt$, $\ln(100/79) = kt$, etc
Check whether $\ln [A_0/A]$ is proportional to time — if yes, reaction is first order.

(iii) Calculate rate constant using any data
From t = 0 to 2 h: ln(100/91) = kt
k = ln(100/91)/2 = 0.0943/2 = 0.0472 h^{-1}

5(a)(i) Only lithium reacts with nitrogen to form nitride in group I elements.
Lithium is the smallest and most electropositive element in group I. Its small ionic size allows it to form a stable Li_3N nitride by reacting with nitrogen, which is not possible for other group I elements due to their larger size and lower lattice energy in nitrides.

(ii) Standard electrode potentials become more negative down the group, but the standard electrode potential of lithium is the most negative in the group.
This is due to the high hydration energy of the small lithium ion, which compensates for its high ionization energy, making lithium the strongest reducing agent among alkali metals.

(iii) Group IV elements have in common the +2 and +4 oxidation states.
Carbon, silicon, germanium, tin and lead show +4 oxidation states commonly. As we move down the group, the stability of +2 oxidation state increases due to the inert pair effect. Lead prefers +2 while carbon and silicon are stable in +4.

(iv) B^{3+} does not exist.
Boron prefers covalent bonding due to its small size and high ionization energy. The formation of a stable B^{3+} ion would require removal of three electrons, which is energetically unfavorable. Hence, boron forms covalent bonds, not B^{3+} ions.

(v) Group III elements largely show covalency.
Due to small size and high ionization energy, group III elements (especially boron and aluminium) form covalent bonds rather than ionic bonds.

(vi) Although it is hard to have Al^{3+}, $[Al(H_2O)_6]^{3+}$ is stable. At the same time it is difficult to find $[B(H_2O)_6]^{3+}$.
Al^{3+} has a lower charge density than B^{3+} and hence attracts water molecules to form stable hydration complex. B^{3+} has extremely high charge density, polarizing water molecules strongly, making its hydrated form less stable.

(vii) Nitrogen and phosphorus are non-metals; arsenic and antimony are metalloids (semi-metals); bismuth is a true metal.
As we go down the group, metallic character increases due to larger atomic size and lower ionization energy. Nitrogen and phosphorus have non-metallic properties, arsenic and antimony show both metallic and non-metallic properties (metalloids), while bismuth behaves like a true metal with metallic luster, high conductivity and malleability.

6(a)(i) Diamagnetism
Diamagnetism is a property of substances that are repelled by a magnetic field. It occurs in substances where all electrons are paired and there are no unpaired electrons. Such substances do not have permanent magnetic moments.

(ii) Coordination number

Coordination number is the number of ligand atoms that are directly bonded to the central metal atom or ion in a complex compound.

(iii) Complex ion

A complex ion is a species consisting of a central metal ion bonded to one or more ligands (ions or molecules) through coordinate covalent bonds.

6(b) Write the electronic configuration of the following:

(i) Neutral scandium atom: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$

(ii) Scandium (III) ion: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

(iii) Neutral nickel atom: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

(iv) Nickel (II) ion: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

6(c) Name the following complex compounds:

(i) $[Ag(NH_3)_2]_3[Fe(CN)_6]$ – Tris(diamminesilver) hexacyanoferrate(III)

(ii) $K[Co(H_2O)_2(NO_2)_2]$ – Potassium diaquodinitritocobaltate(III)

6(d) Write the formula of the following complex compounds:

(i) Dichlorotetraaquocobalt(III) chloride – $[Co(H_2O)_4Cl_2]Cl$

(ii) Tetraaquocopper(II) tetrabromoplatinate – $[Cu(H_2O)_4][PtBr_4]$

7(a) What is the relationship between ideal gas equation and Van der Waals equation?

The ideal gas equation is $PV = nRT$ and assumes no intermolecular forces and negligible volume of gas molecules.

The Van der Waals equation is $(P + a(n/V)^2)(V - nb) = nRT$, which corrects for intermolecular forces (a) and finite volume of molecules (b), making it applicable to real gases.

7(b) 3.50 moles of a gas occupies 5.20 litres at 50°C. Calculate the pressure of the gas in atmospheres using

(i) Ideal gas equation:

$PV = nRT$

$P = nRT/V$

$T = 50 + 273 = 323\ K$, $R = 0.0821\ atm \cdot L \cdot mol^{-1} \cdot K^{-1}$

$P = (3.50 \times 0.0821 \times 323) \div 5.20 = 17.83\ atm$

(ii) Using Van der Waals equation requires a and b constants which are not given, so this part cannot be completed numerically.

7(c) In the light of Dalton’s law of partial pressures, establish a relationship which exists in a mixture of two gaseous substances A and B found in a container of volume V at a constant temperature T.

Total pressure $P = PA + PB$

Where $PA = (nA \times R \times T)/V$ and $PB = (nB \times R \times T)/V$

Therefore, $P = (nA + nB)RT/V$

7(d) Oxygen produced in the thermal decomposition of potassium chlorate at 25°C and atmospheric pressure of 752 mmHg is 150 mL. What is the mass in grams of oxygen produced during this reaction?
Reaction: $2KClO_3 \rightarrow 2KCl + 3O_2$
Use ideal gas law:
$P = 752$ mmHg $= 0.989$ atm, $V = 0.150$ L, $R = 0.0821$, $T = 298$ K
$n = PV/RT = (0.989 \times 0.150) \div (0.0821 \times 298) = 0.00605$ mol
Mass $= 0.00605$ mol $\times 32$ g/mol $= 0.1936$ g

8(a) Name the following compounds according to IUPAC system:

(i) $C_6H_5COCH_3$ — 1-Phenylethanone (also called Acetophenone)

(ii) C_6H_5CHO — Benzaldehyde

(iii) $CH_3CH=CHCOOH$ — But-2-enoic acid

(iv) $C_6H_5CH_2C_6H_5$ — 1,2-Diphenylethane

(v) $C_6H_5CH(CH_3)NH_2$ — 1-Phenylethanamine

8(b) Giving an example in each case define the following:
(i) Organic substitution: This is a type of reaction where an atom or a group of atoms in a molecule is replaced by another atom or group.
Example: $CH_4 + Cl_2$ (in sunlight) ---> $CH_3Cl + HCl$

(ii) Addition reaction: A type of reaction in which atoms or groups are added to a molecule without removing any atom.
Example: $CH_2=CH_2 + Br_2$ ----> CH_2BrCH_2Br

(iii) Elimination reaction: A type of reaction in which two atoms or groups are removed from a molecule forming a double or triple bond.
Example: CH_3CH_2OH (with concentrated H_2SO_4 and heat) ---> $CH_2=CH_2 + H_2O$

8(c) Compound B is unsaturated hydrocarbon (C_4H_6), requires 2 moles of H_2 for hydrogenation using nickel catalyst, and gives white precipitate with $Ag(NH_3)_2OH$. It is acidic in nature.
Since it reacts with 2 moles of hydrogen and gives a white precipitate with ammoniacal silver nitrate (a test for terminal alkyne), the compound B is but-2-yne ($CH\equiv C–CH_2–CH_3$).

Identification and reasoning:
- Requires 2 moles of H_2 suggests a triple bond
- Reacts with $Ag(NH_3)_2OH$ indicates terminal alkyne
- Acidic confirms terminal alkyne

- Molecular formula C_4H_6 matches butyne

Compound B is But-1-yne ($CH\equiv CCH_2CH_3$)
Step 1: Hydrogenation $CH_3CH_2CH_2CH_3$ (Butane)
Step 2: Reaction with $Ag(NH_3)_2OH$ formation of white precipitate ($AgC\equiv CCH_2CH_3$)