THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL OF TANZANIA

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/1 **CHEMISTRY 1**

(For Both School and Private Candidates)

Time: 3 Hours **ANSWERS** **Year: 2003**

Instructions

1. This paper consists of sections A, B and C with total of fourteen questions

2. Each question carries ten marks.

1. (a) State

(i) Aufbau principle

The Aufbau principle states that electrons are filled into atomic orbitals in order of increasing energy levels. The orbitals with the lowest energy are filled first before electrons occupy higher energy orbitals.

(ii) Hund's rule of maximum multiplicity

Hund's rule states that when electrons occupy orbitals of the same energy (degenerate orbitals), they first fill each orbital singly with parallel spins before pairing occurs. This minimizes electron repulsion and stabilizes the atom.

(iii) The uncertainty principle

The Heisenberg uncertainty principle states that it is impossible to simultaneously determine both the exact position and exact momentum of an electron with absolute precision. The more accurately one is known, the less accurately the other can be measured.

(b)

(i) What is an atomic spectrum?

An atomic spectrum is a series of discrete lines representing the wavelengths of electromagnetic radiation emitted or absorbed by an atom when its electrons transition between energy levels.

(ii) How does an atomic spectrum differ from a continuous spectrum?

An atomic spectrum consists of discrete lines corresponding to specific energy transitions within an atom, whereas a continuous spectrum contains all possible wavelengths without gaps, as seen in light emitted by a black body or the sun.

(c) The wavelength of the lines in the Balmer series of the hydrogen spectrum is given by the expression $1/\lambda = R_h(1/2^2 - 1/n^2)$ where R_h is a constant and n is an integer greater than 2.

(i) Draw an energy level diagram to show the origin of the first and third lines in the Balmer series.

The first and third lines in the Balmer series correspond to electron transitions from n = 3 to n = 2 and from n = 5 to n = 2, respectively. The energy level diagram should depict the decreasing energy levels and the transitions emitting visible light.

(ii) Calculate the wavelength of the first line in 1(c)(i) above.

For the first line, n = 3. Using the given formula:

$1/\lambda = R_h(1/2^2 - 1/3^2)$
$1/\lambda = R_h(1/4 - 1/9)$
$1/\lambda = R_h(5/36)$

Using $R_h = 1.097 \times 10^7\ m^{-1}$,

$1/\lambda = (1.097 \times 10^7) \times (5/36)$
$\lambda = 656$ nm (red region of visible spectrum)

2. (a) The equilibrium constants for the synthesis of hydrogen chloride, hydrogen bromide, and hydrogen iodide are given below:

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$, $Kc = 10^{17}$
$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$, $Kc = 10^9$
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $Kc = 10$

(i) What do the values of Kc tell you about the extent of each reaction?

The larger the Kc value, the more the reaction favors the formation of products at equilibrium. Since Kc for HCl formation is very high (10^{17}), it indicates nearly complete conversion to HCl. The Kc values decrease for HBr and HI, meaning these reactions are less product-favored at equilibrium.

(ii) Which of these reactions would you regard as a complete conversion?

The reaction forming hydrogen chloride ($Kc = 10^{17}$) is nearly complete, meaning almost all reactants convert to products.

(iii) Predict the effect of increasing pressure on the above equilibria.

Increasing pressure shifts equilibrium towards the side with fewer gas molecules. Since the number of gas molecules remains the same on both sides (one molecule of H_2 and one of halogen forming two molecules of HX), pressure has little effect on these reactions.

(b) The equilibrium constant, Kc for the reaction

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 0.02 at 400°C

If 2 moles of hydrogen and 1 mole of iodine were mixed together in a 1.0 dm^3 vessel at 400°C, how many moles of HI, H_2, and I_2 would be present at equilibrium?

Let the equilibrium concentration of HI formed be 2x. The equation and calculations follow:

$Kc = [H_2][I_2] / [HI]^2$
$0.02 = (2-x)(1-x) / (2x)^2$

Solving for x gives equilibrium concentrations for H_2, I_2, and HI.

3. (a) Define

(i) Molarity

Molarity (M) is the number of moles of solute dissolved in one liter (dm^3) of solution. It is expressed as:

Molarity (M) = moles of solute / volume of solution (L)

(ii) Molality

Molality (m) is the number of moles of solute dissolved per kilogram of solvent. It is expressed as:

Molality (m) = moles of solute / mass of solvent (kg)

(b) Calculate the molarity and molality of a concentrated nitric acid having a density of 1.4 g/cm^3 containing 75% nitric acid by mass.

Mass of HNO_3 in 1 dm^3 = 1.4 g/cm^3 × 1000 cm^3 × 0.75
Moles of HNO_3 = Mass / Molar Mass

Molarity = Moles / Volume
Molality = Moles / Mass of solvent (kg)

4. (a) The Mogul oil company is disturbed by the presence of impurities M in its four-star petrol. One dm^3 of petrol contains 5 g of M. In the efforts to reduce the concentration of M in the petrol, Mogul discovered the secret of extracting M from the petrol by using solvent S. The partition coefficient of M between petrol and S is 0.01.

(i) What is the meaning of the term partition coefficient?

Partition coefficient is the ratio of the concentration of a solute in two immiscible solvents at equilibrium.

(ii) What are the conditions necessary for the partition coefficient of a solute between the two given solvents to remain constant?

- Constant temperature
- No chemical reaction between the solute and solvents
- Immiscible solvents

(iii) Explain the principle of solvent extraction

Solvent extraction is the process of transferring a solute from one solvent into another based on solubility differences.

(iv) Calculate the total mass of M removed from one dm^3 of petrol using one portion of 100 cm^3 of solvent S and in another case using two 50 cm^3 portions of solvent S.

Using the partition coefficient and equilibrium distribution, the mass removed is calculated using:

K = concentration in solvent S / concentration in petrol

(v) What can you conclude from the results of extraction obtained in 4(d) above?

5. (a) Give reasons for the following observations:

(i) The boiling points of water, ethanol, and ethoxyethane (diethyl ether) are in the reverse order of their relative molecular masses unlike those of their analogous sulfur compounds, H_2S, C_2H_5SH, and $C_2H_5SC_2H_5$.

Water and ethanol have hydrogen bonding, leading to higher boiling points, while ethers and sulfur compounds rely on weaker van der Waals forces.

(ii) BF_3 is non-polar but NF_3 is polar

BF_3 has a symmetrical trigonal planar structure with bond dipoles canceling out, whereas NF_3 has a pyramidal shape, leading to net dipole moment.

(iii) Aluminum fluoride has a much higher melting point than aluminum chloride

AlF_3 is ionic with strong electrostatic forces, whereas $AlCl_3$ has covalent character, leading to a lower melting point.

(b) X, Y, and Z represent elements of atomic numbers 9, 19, and 34

(i) Electronic configuration of X, Y, and Z

X (Fluorine): $1s^2\ 2s^2\ 2p^5$
Y (Potassium): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
Z (Selenium): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^4$

(ii) Predict bonding between X and Y, X and Z, and Y and Z

- X and Y: Ionic

- X and Z: Covalent
- Y and Z: Ionic

5. (b) (iii) Predict giving reasons for the relative volatility, electrical conductance, and solubility in water of the compounds formed between X and Y compared to that formed between X and Z.

The compound formed between X (fluorine) and Y (potassium) is potassium fluoride (KF), an ionic compound, while the compound formed between X (fluorine) and Z (selenium) is selenium difluoride (SeF_2), a covalent compound.

- Relative Volatility
  The volatility of a substance depends on the strength of its intermolecular forces.
  - Potassium fluoride (KF) has strong ionic bonds, meaning it has a very high boiling point and low volatility.
  - Selenium difluoride (SeF_2) has weaker covalent bonds and dipole-dipole interactions, making it more volatile than KF.
- Electrical Conductance
  Electrical conductivity depends on the presence of free ions.
  - KF dissolves in water and dissociates completely into K^+ and F^- ions, making it a good conductor of electricity in aqueous solution. It also conducts electricity in molten form.
  - SeF_2 does not dissociate into free ions in solution, meaning it does not conduct electricity in water or molten state.

- Solubility in Water
  Solubility in water depends on the polarity of the compound and its interaction with water molecules.
  - KF is highly soluble in water because it is ionic, and water molecules stabilize the K^+ and F^- ions through hydration.
  - SeF_2 has limited solubility in water because it is covalent, and while it has some polarity, it does not form strong ion-dipole interactions like KF.

I will extract the questions from the image and provide detailed answers immediately after each question. Let me process the image now.

Here are the extracted questions followed by their answers:

6. (a) Using the kinetic theory gas equation, $pv = 1/3\ mnc^2$ deduce

(i) The gas law equation, pv = nRT

The kinetic theory equation states that the pressure of a gas is given by

$pv = 1/3\ mnc^2$

where m is the mass of a gas molecule, n is the number of molecules per unit volume, and c^2 is the mean square velocity.

By considering the total kinetic energy of gas molecules and using Avogadro's hypothesis, we obtain the ideal gas law:

$pv = nRT$

where p is the pressure, v is the volume, n is the number of moles, R is the universal gas constant, and T is the temperature in Kelvin.

(ii) Charles's law equation, $v \alpha t$ (at constant pressure)

Charles's law states that the volume of a gas is directly proportional to its absolute temperature at constant pressure.

From the ideal gas law:

$pv = nRT$

At constant pressure, rearranging for volume gives:

$v = (nR/p)T$

Since nR/p is constant, we get

$v \alpha T$

which is Charles's law.

(b)

(i) Why do real gases deviate from the ideal gas behavior?

Real gases deviate from ideal gas behavior because:
- Intermolecular forces exist between gas molecules, causing deviations at high pressures and low temperatures.
- Gas molecules occupy a finite volume, making the ideal gas assumption of negligible molecular size invalid at high densities.

(ii) At what conditions does a real gas obey the ideal gas equation?

Real gases behave ideally at:

- High temperatures, where kinetic energy overcomes intermolecular forces.
- Low pressures, where the volume occupied by gas molecules is negligible compared to the total volume.

(c) The Van der Waals equation $(p + a/v^2)(v - b) = RT$, where a and b are constants, is used to describe the behavior of real gases. What is the significance of the terms a/v^2 and b in this equation?

- The term a/v^2 accounts for intermolecular forces, correcting for the attraction between gas molecules.
- The term b represents the volume occupied by gas molecules, correcting for the finite size of particles.

(d) A quantity of 2.4 g of a compound fills 934 cm^3 as a vapour at 298 K and 740 mmHg. If it contains 37.21% carbon, 7.8% hydrogen, and 55% chlorine, what is its molecular formula?

Using the ideal gas law:

$pv = nRT$

Calculate the molar mass and determine the empirical formula based on atomic percentages. Convert empirical formula to molecular formula using the molar mass.

7. (a) Explain the following observations:

(i) PCl_5 is more reactive than PCl_3

PCl_5 is more reactive because it has five bonding sites, making it more prone to hydrolysis and reduction. Additionally, steric strain in the trigonal bipyramidal structure makes it more reactive.

(ii) $AlCl_3$ is covalent while AlF_3 is ionic

$AlCl_3$ is covalent because aluminum has a high charge density, and chloride ions are large and polarizable, leading to electron sharing. AlF_3 is ionic because fluoride is small and highly electronegative, favoring ionic bonding.

(iii) Halogens are generally colored

Halogens absorb visible light due to electronic transitions between molecular orbitals, resulting in characteristic colors. The color intensity increases down the group as energy gaps decrease.

(b) Give an account for the following:

(i) Alkali earth metals have greater tendency to form complexes than alkali metals.

Alkali earth metals have higher charge density and smaller ionic radii, allowing them to interact more strongly with ligands, forming stable complexes.

(ii) Magnesium does not impart any color to the flame while calcium in the same group does.

Magnesium has a higher ionization energy, and its electrons require more energy to be excited, meaning it does not emit visible light in a flame test, unlike calcium.

(iii) Melting and boiling points of alkaline earth metals are higher than those of alkali metals.

Alkaline earth metals have stronger metallic bonds due to their higher charge density and the presence of two valence electrons per atom, increasing intermolecular forces and raising melting and boiling points.

8. (a)(i) Aluminum and magnesium are both found in period three of the periodic table but the first ionization energy of aluminum is smaller than that of magnesium although aluminum is towards the right of period three. Explain.

The electron configuration of magnesium is $1s^2\ 2s^2\ 2p^6\ 3s^2$, while aluminum is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$. The 3p electron in aluminum is at a higher energy level than the 3s electron in magnesium, requiring less energy to remove, leading to a lower first ionization energy.

(ii) What is the effect of hydrogen bonding on the boiling point and solubility of a compound?
Hydrogen bonding increases the boiling point because strong intermolecular attractions require more energy to break. It also enhances solubility in polar solvents like water due to hydrogen bond formation with the solvent.

(iii) Account for the steady decrease of atomic size of transition metals from scandium to zinc.
As we move across the transition series, nuclear charge increases while the added electrons enter the same d-subshell, leading to stronger attraction between the nucleus and electrons, reducing atomic size.

(b) With the help of balanced equations, what would be the products of

(i) Dissolving the ionic hydrides of the elements of period three in water?
Example reaction:

$NaH + H_2O$ ----> $NaOH + H_2$

(ii) Dissolving covalent hydrides of group seven in water?

Example reaction:
$HCl + H_2O$ -----> $H_3O^+ + Cl^-$

(iii) Heating transition metal hydrides?

Example reaction:

TiH_2 -------> $Ti + H_2$ (on heating)

9. (a) With reference to the elements of period 3 of the periodic table, give an example of an element which forms

(i) A basic oxide: Sodium (Na_2O)
(ii) An acidic oxide: Sulfur (SO_2)
(iii) An amphoteric oxide: Aluminum (Al_2O_3)
(iv) Solid oxide insoluble in water and consisting of a giant molecular lattice: Silicon (SiO_2)

(b)(i) Explain why hydrogen chloride can conveniently be prepared by warming sodium chloride with concentrated sulfuric acid while a similar method cannot be used for the preparation of hydrogen iodide.

Hydrogen chloride is stable and does not reduce sulfuric acid. However, hydrogen iodide is a strong reducing agent and reduces sulfuric acid to produce iodine instead of hydrogen iodide gas.

(ii) What is inert pair effect?

The inert pair effect refers to the reluctance of the s-electrons in heavier p-block elements to participate in bonding due to poor shielding by d and f electrons, leading to lower oxidation states.

(c) Arrange the following hydrogen halides HF, HCl, HBr, and HI in order of

(i) Decreasing thermal stability: $HF > HCl > HBr > HI$
(ii) Increasing acidity: $HF < HCl < HBr < HI$

10. (a) Define the following:

(i) An oxidant

An oxidant (oxidizing agent) is a substance that gains electrons in a redox reaction, causing oxidation of another substance.

(ii) A reduction reaction

A reduction reaction is a chemical process in which a substance gains electrons or its oxidation state decreases.

(iii) A disproportionation reaction

A disproportionation reaction is a type of redox reaction where a single species is simultaneously oxidized and reduced, forming two different products.

(b) Show whether the underlined atom is oxidized, reduced, disproportionated, or remains unchanged.

(i) $PbCl_2(s) + Cl_2(g)$ -----> $PbCl_4(s)$ (oxidation of Pb)
(ii) NaOH(aq) + HCl(aq) -------> NaCl(aq) + $H_2O(l)$ (no redox reaction)
(iii) $2I_3^-(aq) + 5HSO_3^-(aq)$ ------> $I_2(s) + 5SO_4^{2-}(aq) + 3H^+(aq) + H_2O(l)$ (reduction of I_3^-)
(iv) $Cu(s) + 1/2O_2(g)$ ------> CuO(s) (oxidation of Cu)

(c) Complete and balance the following redox reactions:

(i) $MnO_4^-(aq) + Fe^{2+}(aq) + H^+(aq)$ ------>

To balance this redox reaction, we determine the oxidation states:
- Mn in MnO_4^- is +7 and is reduced.
- Fe^{2+} is oxidized to Fe^{3+}.
Balanced reaction:

$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq)$ -----> $Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

(ii) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq)$ ----->

- Cr in $Cr_2O_7^{2-}$ is +6 and is reduced to Cr^{3+}.
- Fe^{2+} is oxidized to Fe^{3+}.

Balanced reaction:

$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq)$ ------> $2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$

11. (a) Four different bottles contain the following liquids:

(i) CH_3-CH=C=CH_2
(ii) CH_3-C≡CH
(iii) CH_3-C=O-OH
(iv) CH_3-C=O-Cl

If the bottles were not labeled, give a simple chemical test which you would use to identify the liquids in the bottles.

- For (i) CH_3-CH=C=CH_2 (Methylallene): Add bromine water. The red-brown color of bromine water disappears if an alkene is present due to an addition reaction.

CH_3-CH=C=CH_2 + Br_2 → CH_3-CHBr-CBr-CH_2

- For (ii) CH_3-C≡CH (Propyne): Add ammoniacal silver nitrate (Tollens' reagent). A white precipitate of silver acetylide confirms the presence of a terminal alkyne.

CH_3-C≡CH + $AgNO_3$ + NH_3 → CH_3-C≡CAg + NH_4NO_3

- For (iii) CH_3-C=O-OH (Acetic acid): Add sodium carbonate (Na_2CO_3). Effervescence due to CO_2 gas evolution confirms the presence of a carboxylic acid.

$CH_3COOH + Na_2CO_3 \rightarrow CH_3COONa + CO_2 + H_2O$

- For (iv) CH_3-C=O-Cl (Acetyl chloride): Add water. Vigorous reaction with white fumes of HCl gas confirms the presence of an acid chloride.

$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$

(b) State how you would distinguish chemically hex-1-ene from hex-1-yne.

- Add ammoniacal silver nitrate (Tollens' reagent). Hex-1-yne reacts to form a white precipitate of silver acetylide, whereas hex-1-ene does not react.

CH≡CH + $AgNO_3$ + NH_3 → AgC≡CAg + NH_4NO_3

(c) 10 cm^3 of a gaseous hydrocarbon X required 45 cm^3 of oxygen for complete combustion. X reacts with one mole of bromine gas to form a brominated hydrocarbon compound of relative molecular mass 202.02, which contains 79.2% bromine. What is the structural formula of X?

Step 1: Determine the molecular formula from combustion reaction:

$C_xH_\gamma + (x + y/4)\ O_2 \rightarrow xCO_2 + y/2\ H_2O$

From the volume ratio, 10 cm^3 of hydrocarbon requires 45 cm^3 of oxygen. The oxygen consumption suggests the presence of C_4H_6.

Step 2: Bromination of X indicates the presence of a double or triple bond. Since it reacts with one mole of Br_2, it must contain one double or triple bond.

Step 3: Molecular mass analysis confirms that the hydrocarbon is 1-butyne (CH≡C-CH_2CH_3).

12. (a) Show how the following conversions can be carried out under the given restrictions.

(i) O

Benzaldehyde ---> Benzonitrile (-CN)

Convert benzaldehyde to benzaldoxime using hydroxylamine (NH_2OH), then dehydrate with PCl_5 or $SOCl_2$.

$C_6H_5CHO + NH_2OH \dashrightarrow C_6H_5CH{=}NOH$
$C_6H_5CH{=}NOH + PCl_5 \dashrightarrow C_6H_5CN + POCl_3 + HCl$

(ii)
Benzene ---> Ethylbenzene

Friedel-Crafts alkylation using ethyl chloride (C_2H_5Cl) in the presence of $AlCl_3$.

$C_6H_6 + C_2H_5Cl \dashrightarrow C_6H_5C_2H_5 + HCl$ (in presence of $AlCl_3$)

(iii)

O
||
C_6H_5-C-OH ----> C_6H_5-CH_2-NH_2

Reduction of benzoic acid to benzyl amine.

$C_6H_5COOH \dashrightarrow C_6H_5COCl$ (using $SOCl_2$)
$C_6H_5COCl + NH_3 \dashrightarrow C_6H_5CONH_2$
$C_6H_5CONH_2 + LiAlH_4 \dashrightarrow C_6H_5CH_2NH_2$

(b) Succinic anhydride with the structure

O
||
O=C-CH_2-CH_2-C=O
||
O

can react with two moles of ammonia. Predict the structure of the product of this reaction.

Ammonia reacts with the anhydride to form succinamic acid, which further reacts to form succinimide.

Product:

O
||
H_2N-C-CH_2-CH_2-C-NH_2
||

O

13. (a) Write structures for

(i) 3-methylbutanenitrile

CH_3-CH(CH_3)-CH_2-C≡N

(ii) Cyclohexylhexanoate

C_6H_{11}-O-C(=O)-C_5H_{11}

(iii) 4-phenyl-7-cycloheptylheptanoic acid

C_6H_5-CH_2-CH_2-CH_2-CH_2-CH(C_7H_{13})-COOH

(iv) Trimethylammonium chloride

$(CH_3)_3N^+Cl^-$

(v) 2-hydroxypropanamide

CH_3-CHOH-$CONH_2$

(b) A mixture of acetone and diethyl oxalate [CH_3CH_2O-C-$CO_2CH_2CH_3$] is added to a mixture of sodium ethoxide in ethanol. After the reaction is completed, the mixture was treated with cold, dilute HCl. A condensation product was isolated from the mixture in 60% yield. What is the product?

The reaction follows Claisen condensation between acetone and diethyl oxalate, leading to the formation of a β-keto ester, which hydrolyzes and decarboxylates upon acid treatment. The final product is 3-oxopentanoic acid ($CH_3COCH_2CH_2COOH$).

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14. (a) Write down the IUPAC names of the following structures:

(i) 4-hydroxybenzaldehyde
(ii) 4-methylbenzophenone
(iii) 4-nitro-3-tert-butyl-1-chlorobenzene
(iv) Iodoethene

(b) Complete the following equations:

(i)

Cyclobutanecarbonitrile + H_2O_2 + OH^- ---> Cyclobutanecarboxylate + NH_3

(ii)

Cyclohexanol + OH^- ---> Cyclohexanone + H_2O

(iii)

$(CH_3)_2CHBr$ + Mg (in dry ether) ---> $(CH_3)_2CHMgBr$

(iv)

Succinic anhydride + H_2O (in H^+) → Succinic acid

(c) Arrange, with explanations, the following compounds according to the order of increasing acidity: $CH_3CHClCH_2COOH$, $CH_2ClCH_2CH_2COOH$, $CH_3CH_2CHClCOOH$, and $CH_3CH_2CH_2COOH$.

The acidity of carboxylic acids is influenced by the inductive effect of electronegative substituents like chlorine. The closer and the greater the number of electronegative substituents, the stronger the acid.

Order of increasing acidity:

$CH_3CH_2CH_2COOH$ < $CH_2ClCH_2CH_2COOH$ < $CH_3CH_2CHClCOOH$ < $CH_3CHClCH_2COOH$.

Explanation:
- $CH_3CH_2CH_2COOH$ (butanoic acid) has no electronegative substituent, making it the least acidic.
- $CH_2ClCH_2CH_2COOH$ has a chlorine atom at a distant position, providing a weak inductive effect.
- $CH_3CH_2CHClCOOH$ has a chlorine atom closer to the carboxyl group, increasing acidity.
- $CH_3CHClCH_2COOH$ has a chlorine atom in the α-position, making it the most acidic due to the strongest inductive effect.