THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2024**

Instructions

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

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1 (a) (i) How does the dilution with water affects the pH of a buffer solution? Briefly, explain.

When a buffer solution is diluted with water, the concentration of both the weak acid and its conjugate base decreases. However, since the ratio of [acid] to [base] remains constant, the pH does not change significantly. Nonetheless, a very slight change might occur due to changes in the ionic strength and activity coefficients, but practically, the pH remains nearly constant upon dilution.

1 (a) (ii) Briefly, explain the role of hydrocyanic acid (HCN) in the mixture of sodium cyanide (NaCN) and hydrocyanic acid when sodium hydroxide is added.

Hydrocyanic acid (HCN) acts as a weak acid in the buffer mixture of HCN and NaCN. When sodium hydroxide (a strong base) is added to the solution, the OH^- ions react with HCN to form CN^- and water. This suppresses the rise in pH, making the solution resist pH change. Hence, HCN neutralizes the added base, maintaining the buffer action.

1 (b) Calculate the mass of hydrochloric acid required to be added in a mixture of equal volumes of 0.5 M CH_3COONa and 0.5 M CH_3COOH to make 250 cm^3 of a solution with a pH of 4. (Ka of CH_3COOH is 1.77×10^{-5}).

Given:
$Ka = 1.77 \times 10^{-5}$
$pH = 4 \rightarrow [H^+] = 10^{-4}$
Using the expression:
$[H^+] = Ka \times ([acid]/[salt])$
$10^{-4} = 1.77 \times 10^{-5} \times ([CH_3COOH]/[CH_3COONa])$
$[CH_3COOH]/[CH_3COONa] = 10^{-4} / 1.77 \times 10^{-5} = 5.65$

Let the concentration of CH_3COOH be x, and CH_3COONa be y
$x/y = 5.65 \rightarrow$ since $y = 0.5$ M, $x = 5.65 \times 0.5 = 2.825$ M

The new moles of $CH_3COOH = 2.825 \times 0.25 = 0.70625$ mol
Initially, CH_3COOH moles $= 0.5 \times 0.25 = 0.125$ mol
Moles of HCl required $= 0.70625 - 0.125 = 0.58125$ mol
Mass of HCl $= 0.58125 \times 36.5 = 21.23$ g

1 (c) (i) Briefly, comment on the solubility of CuS(s) and AgCl(s) when added in acidic solution.

CuS is sparingly soluble in water but becomes more soluble in acidic solutions because H^+ ions react with S^{2-} ions to form H_2S, thereby reducing the S^{2-} concentration and shifting equilibrium to dissolve more CuS. AgCl, on the other hand, is not significantly affected by acidity since Cl^- does not react appreciably with H^+ ions, so its solubility does not increase in acid.

1 (c) (ii) At 25 °C the solubility product of Ag_2CrO_4 is 1.9×10^{-12} mol² dm⁻⁶. What would be the concentration of silver ions in g/dm³?

$Ksp = [Ag^+]^2 \times [CrO_4^{2-}] = 1.9 \times 10^{-12}$
Let $[Ag^+] = 2x$ and $[CrO_4^{2-}] = x \rightarrow (2x)^2 \times x = 4x^3 = 1.9 \times 10^{-12}$
$x^3 = 4.75 \times 10^{-13} \rightarrow x = 7.73 \times 10^{-5}$ mol/L
$[Ag^+] = 2x = 1.546 \times 10^{-4}$ mol/L
Mass = $1.546 \times 10^{-4} \times 107.9 = 0.0167$ g/dm³

2 (a) (i) Components of a binary mixture of liquid A and B were separated by distillation. After a certain amount of time, the separation of the components stopped and the composition of the vapour phase became the same as that of the liquid phase. Why this happened? Explain briefly.

This situation describes the formation of an azeotrope. At this specific composition, the vapour and liquid phases have the same composition and boil at a constant temperature, making further separation by simple distillation impossible.

2 (a) (ii) When alcohols and water are mixed together, the resulting solution deviates positively from the ideal behaviour. Justify this statement.

Positive deviation occurs because the intermolecular interactions between alcohol and water are weaker than those between similar molecules (water-water or alcohol-alcohol). As a result, the mixture has higher vapour pressure and lower boiling point than expected in ideal solutions.
2 (b) (i) The vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg, respectively. Determine:
(i) The vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at 290 K.

Molar mass of $CHCl_3 = 12 + 1 + 35.5\times3 = 119.5$ g/mol
Moles of $CHCl_3 = 25.5 / 119.5 = 0.2135$ mol

Molar mass of $CH_2Cl_2 = 12 + 2\times1 + 35.5\times2 = 84$ g/mol
Moles of $CH_2Cl_2 = 40 / 84 = 0.476$ mol

Total moles = 0.2135 + 0.476 = 0.6895 mol

Mole fraction of $CHCl_3 = 0.2135 / 0.6895 = 0.3096$
Mole fraction of $CH_2Cl_2 = 0.476 / 0.6895 = 0.6904$

Total vapour pressure = $(X\_CHCl_3 \times P^0\_CHCl_3) + (X\_CH_2Cl_2 \times P^0\_CH_2Cl_2)$
= (0.3096 × 200) + (0.6904 × 415) = 61.92 + 286.016 = 347.94 mm Hg

2 (b) (ii) The mole fraction of each component in the vapour phase.

Partial pressure of $CHCl_3$ = 0.3096 × 200 = 61.92 mm Hg
Partial pressure of CH_2Cl_2 = 0.6904 × 415 = 286.02 mm Hg

Total pressure = 347.94 mm Hg

Mole fraction of $CHCl_3$ in vapour = 61.92 / 347.94 = 0.178
Mole fraction of CH_2Cl_2 in vapour = 286.02 / 347.94 = 0.822

2 (c) (i) Briefly, comment on the statement that, "The boiling point of an immiscible solution is less than the boiling point of either of its pure components."

This is because each component in an immiscible mixture exerts its own vapour pressure independently. The total vapour pressure becomes the sum of both components' vapour pressures, reaching atmospheric pressure at a lower temperature than either component's boiling point. Hence, the mixture boils at a lower temperature.

2 (c) (ii) An aromatic compound Z was steam distilled at 98.6 °C and 1 atm pressure. The distillate was found to contain 25.5 g of water and 7.4 g of the aromatic compound Z. Given that the saturated vapour pressure of water at 98.6 °C is 720 mmHg, determine the molecular mass of the aromatic compound Z.

Total pressure = 760 mmHg
Pressure of Z = 760 – 720 = 40 mmHg

Moles of water = 25.5 / 18 = 1.417 mol
Ratio of partial pressures = n_water / n_Z = p_water / p_Z
1.417 / n_Z = 720 / 40 = 18
n_Z = 1.417 / 18 = 0.0787 mol

Molar mass of Z = 7.4 / 0.0787 = 94 g/mol

3 (a) An alcohol H has the structure $CH_3CH_2CH_2CH(OH)CH_3$.

(i) What is the name of the compound H according to IUPAC rules?

The longest carbon chain has 5 carbon atoms and the OH group is on carbon 2. Therefore, the compound is named 2-pentanol.

(ii) What type of the reaction would be involved if compound H reacted with concentrated H_2SO_4 at 170 °C?

This is an elimination reaction (dehydration) where alcohol loses water to form an alkene.

(iii) Write the chemical equation for the reaction between compound H and I_2 in alkaline medium of NaOH.

$CH_3CH_2CH_2CH(OH)CH_3 + 4[O] \rightarrow CH_3CH_2CH_2COOH + H_2O$
(This is for oxidation, but since I_2 in alkaline medium causes iodoform reaction only for alcohols with $CH_3CH(OH)$- group, no iodoform forms here because this alcohol is secondary and does not have the $CH_3CH(OH)$- structure.)

Therefore, no yellow precipitate of iodoform forms.

3 (b) A Chemist visited a chemical store to collect some hydroxyl compounds and found that all the chemicals had lost their actual labels though the store register book showed that phenol, n-propanol, benzyl alcohol and ethanol were in the stock. Due to this, the bottles were re-labelled as I, II, III and IV and placed into two groups as follow:
(i) A (I and II)
(ii) B (III and IV)

How can you differentiate the chemicals in each group? Explain briefly while supporting your answer with appropriate chemical equations in each case.

Group A has phenol and benzyl alcohol – both can react with $FeCl_3$ solution. Phenol gives a purple/violet complex. Benzyl alcohol does not.
Group B has ethanol and n-propanol – both are primary alcohols and undergo oxidation to aldehydes then acids. The differentiation can be done via Lucas test. Ethanol reacts slowly, but n-propanol reacts faster with Lucas reagent ($HCl + ZnCl_2$).

3 (c) An organic compound L contains 60% carbon, 13.33% hydrogen and 26.67% oxygen. A 1.12 dm^3 volume of the gaseous organic compound L at s.t.p has a mass of 3 g. When reacted with iodine under dry ether, compound L gave a yellow compound and when reacted with PCl_5 it gave a colourless gas which on treatment with ammonia, gave white dense fumes.

(i) Determine the molecular formula of compound L.

Assume 100 g of compound L:
Carbon = 60 g ----> 60/12 = 5 mol
Hydrogen = 13.33 g ------> 13.33/1 = 13.33 mol
Oxygen = 26.67 g ----> 26.67/16 = 1.667 mol

Simplest ratio = C:H:O = 5 : 13.33 : 1.667
Dividing by smallest = 5/1.667 : 13.33/1.667 : 1 = 3 : 8 : 1
Empirical formula = C_3H_8O

Empirical molar mass = (12×3) + (1×8) + 16 = 60 g/mol

Now determine molecular mass from gas data:
1 mole of gas at s.t.p occupies 22.4 dm^3

Mass of 22.4 dm^3 of compound L = (3 × 22.4)/1.12 = 60 g
Molecular mass = 60 -----> So molecular formula = C_3H_8O

(ii) Give the structure of compound L.

C_3H_8O can be either propanol or methoxyethane.
However, since it gives yellow precipitate with iodine in dry ether, it must have a $CH_3CH(OH)$- group. This confirms L is 2-propanol (isopropyl alcohol).
Also, its reaction with PCl_5 gives HCl gas (confirmed by white dense fumes with NH_3), which again confirms presence of OH group.

So the structure is $CH_3–CH(OH)–CH_3$

3 (d) (i) Classify polymers based on their structures. Give one example for each type.

Polymers are classified based on structure into:
- Linear polymers: Long straight chains, e.g., Polyethylene
- Branched chain polymers: Chains with side branches, e.g., Low-density polyethylene (LDPE)
- Cross-linked polymers: Chains interconnected by covalent bonds, e.g., Bakelite

(ii) Briefly, describe how branching and cross-linking affect the physical properties of polymers.

Branching decreases the density and crystallinity of polymers, making them soft and flexible. Cross-linking increases the rigidity, hardness, and thermal resistance of the polymer due to strong bonds between chains which limit movement.

(iii) Why rubber is an elastomer? Briefly, explain.
Rubber is an elastomer because its polymer chains are loosely held by weak intermolecular forces, allowing them to stretch and return to original shape upon release of force. The elasticity arises due to coiling and recoiling of chains.

(iv) Addition polymerization is highly used in industrial production of plastics. How can you increase the rate of production of plastics if monomers, temperature and pressure are to be altered?
The rate of addition polymerization can be increased by:
- Using more reactive monomers (e.g., with electron-withdrawing groups)
- Increasing temperature to enhance kinetic energy and collisions
- Increasing pressure to bring monomers closer, especially for gaseous monomers
- Using suitable catalysts or initiators to initiate and speed up the reaction.

4 (a) Write the structural formula of the following organic compounds:

(i) 4-Methylpentan-2-one
This compound has a five-carbon chain with a ketone group (C=O) on the second carbon and a methyl group on the fourth carbon.

Structure: $CH_3–CO–CH_2–CH(CH_3)–CH_3$

(ii) Pent-3-en-2-one
This compound has a five-carbon chain with a ketone group on the second carbon and a double bond between the third and fourth carbons.
Structure: $CH_3–CO–CH=CH–CH_3$

4 (b) Briefly account for each of the following observations:

(i) Although propanal and acetone have the same molar mass, the boiling point of acetone is higher than that of propanal.
Acetone ($CH_3–CO–CH_3$) is a ketone, and propanal ($CH_3–CH_2–CHO$) is an aldehyde. Both have the same molar mass of 58 g/mol. However, acetone has stronger London dispersion forces due to its more symmetrical structure with two alkyl groups on the carbonyl carbon, making its intermolecular attractions stronger and raising its boiling point. Acetone boils at around 56°C while propanal boils at around 49°C.

(ii) Ethanol is more reactive than propanone towards nucleophilic addition reactions.
Ethanol ($CH_3–CH_2–OH$) is a primary alcohol, and propanone ($CH_3–CO–CH_3$) is a ketone. Normally, carbonyl compounds like propanone are more reactive in nucleophilic addition than alcohols, but in some contexts, ethanol undergoes a variety of reactions (oxidation, substitution) that may be interpreted as more reactive overall. However, strictly for nucleophilic addition to a carbonyl group, propanone is more reactive.

(iii) Ethanol gives a positive silver mirror test while butan-2-one does not.
Ethanol ($CH_3–CH_2–OH$) can be oxidized to acetaldehyde ($CH_3–CHO$), which is an aldehyde and gives a positive Tollens' test (silver mirror test). Butan-2-one ($CH_3–CO–CH_2–CH_3$) is a ketone and does not give a positive result in Tollens' test since ketones generally do not oxidize further under these conditions.

4 (c) Compounds H and I have the same molecular formula, $C_5H_{10}O$. When compound H and I were treated with PCl_5, they gave an acidic gas. Compound H gives a positive iodoform test while compound I does not.

(i) What are the possible structures of H and I?
Since both compounds produce acidic gas (HCl) with PCl_5, both contain an –OH group, so they are alcohols. Compound H gives a positive iodoform test, meaning it contains a $CH_3–CH(OH)–$ group. Therefore, H could be pentan-2-ol ($CH_3–CH(OH)–CH_2–CH_2–CH_3$).
Compound I does not give iodoform test, so it could be pentan-1-ol ($CH_3–CH_2–CH_2–CH_2–CH_2–OH$) or pentan-3-ol ($CH_3–CH_2–CH(OH)–CH_2–CH_3$).

(ii) If compound H reacts with iodoform, what will be the chemical equation for the reaction?
$CH_3–CH(OH)–CH_2–CH_2–CH_3 + [O] \text{ ----> } CH_3–CO–CH_2–CH_2–CH_3$ (oxidation to pentan-2-one)
Then,
$CH_3–CO–CH_2–CH_2–CH_3 + 3I_2 + 4NaOH \text{ ----> } CHI_3 + CH_3–CH_2–CH_2–COONa + 3NaI + 3H_2O$

4 (d) Briefly explain the following observations:

(i) Methanoic acid has a larger value of Ka than ethanoic acid.
Methanoic acid (HCOOH) is stronger than ethanoic acid (CH_3COOH) because it does not have an electron-donating alkyl group like the CH_3 in ethanoic acid. The methyl group in CH_3COOH reduces the stability of the carboxylate ion (CH_3COO^-) through inductive effect, thus reducing acidity.

(ii) 4-Hydroxybenzoic acid is less acidic than 4-nitrobenzoic acid.
In 4-hydroxybenzoic acid, the hydroxyl group (-OH) is electron-donating through resonance, destabilizing the carboxylate ion. In contrast, 4-nitrobenzoic acid has a nitro group ($-NO_2$) that is electron-withdrawing, stabilizing the carboxylate ion and making the compound more acidic.
5 (a) You are given a reaction which exhibits a second order with respect to a reactant. Find out how its rate of reaction could be affected if the concentration of the reactant is:

(i) Doubled
For a second-order reaction, rate = $k[A]^2$
If concentration [A] is doubled, the new rate becomes:
Rate = $k(2[A])^2 = 4k[A]^2$
So, the rate becomes four times greater.

(ii) Reduced to half
If concentration [A] is halved, the new rate becomes:
Rate = $k(0.5[A])^2 = 0.25k[A]^2$
So, the rate becomes one-fourth of the original rate.

5 (b) 0.25 g of a radioactive element remained after 5 years of decomposition. If its initial weight was 10 g, calculate:

(i) The rate constant for the decay of the radioactive element
Radioactive decay follows first-order kinetics:
$\ln(N_0/N) = \lambda t$
$\ln(10/0.25) = \lambda \times 5$
$\ln(40) = \lambda \times 5$
$\lambda = \ln(40) / 5 = 3.6889 / 5 = 0.7378 \text{ year}^{-1}$

(ii) The amount left after one year
$\ln(10/N) = 0.7378 \times 1 = 0.7378$
$10/N = e^{0.7378} = 2.091$
$N = 10 / 2.091 = 4.78$ g

(iii) The time required for half of the element to decay (half-life)
$t_{1/2} = 0.693 / \lambda = 0.693 / 0.7378 = 0.94$ years

(iv) The average life of the element

Average life = 1 / λ = 1 / 0.7378 = 1.36 years

5 (c) It is observed that the rate of a chemical reaction doubles with every 10°C rise in temperature. Assume temperature range 298 K to 308 K, compute the value of activation energy for the reaction.

Use the Arrhenius equation:
$k_2/k_1 = e^{[(Ea/R) \times (1/T_1 - 1/T_2)]}$
Given: $k_2/k_1 = 2$, $T_1 = 298$ K, $T_2 = 308$ K, $R = 8.314$ J mol^{-1} K^{-1}
$\ln(2) = Ea/8.314 \times (1/298 - 1/308)$
$0.693 = Ea/8.314 \times (308 - 298)/(298\times308)$
$0.693 = Ea \times 10 / (8.314 \times 91784)$
$Ea = (0.693 \times 8.314 \times 91784) / 10 = 52800$ J mol^{-1} = 52.8 kJ mol^{-1}

5 (d) The decomposition of N_2O_5 at 318 K according to the following equation obeys first order reaction:
$N_2O_5(g) \text{ -----> } 2NO_2(g) + 1/2\ O_2(g)$
If the initial concentration of N_2O_5 was 1.24×10^{-2} mol dm^{-3}, calculate the concentration of N_2O_5 after 60 minutes, given that the rate constant of the reaction at 318 K is 0.0304 min^{-1}.

Use first-order equation:
$\ln([N_2O_5]_0 / [N_2O_5]) = kt$
$\ln(1.24 \times 10^{-2} / [N_2O_5]) = 0.0304 \times 60 = 1.824$
$1.24 \times 10^{-2} / [N_2O_5] = e^{1.824} = 6.2$
$[N_2O_5] = 1.24 \times 10^{-2} / 6.2 = 2.0 \times 10^{-3}$ mol dm^{-3}

6 (a) (i) Differentiate between electron affinity and electronegativity.

Electron affinity is the energy released or absorbed when an atom gains an electron to form a negative ion. Electronegativity is the tendency of an atom to attract electrons in a chemical bond. Electron affinity is a measurable quantity in kJ/mol, while electronegativity is a relative scale (Pauling scale).

(ii) The first ionization enthalpy of magnesium is higher than that of sodium. On the other hand, the second ionization energy of sodium is higher than that of magnesium. Explain briefly.

Magnesium has two electrons in the outer shell ($3s^2$), and sodium has one ($3s^1$). It takes more energy to remove one of magnesium's electrons due to stronger nuclear attraction. After losing one electron, sodium becomes Na^+, which has a stable noble gas configuration (Ne), so removing the second electron from inner shell requires a lot of energy. For magnesium, the second electron is still from 3s, so it is easier to remove compared to sodium's second electron.

6 (b) Describe how the position of an element in the periodic table is located.

An element's position is determined by its atomic number.
Period: Number of electron shells.

Group: Number of valence electrons.
Block: Type of orbital being filled (s, p, d, f). For example, sodium (atomic number 11) has one valence electron in the third shell, so it is in Group 1, Period 3, s-block.

6 (c) (i) All the s-block elements form ionic compounds except lithium and beryllium. Briefly justify this statement.

Lithium and beryllium form covalent compounds due to their small size and high charge density, which polarize the anion and result in covalent character. Other s-block elements have lower charge density and form typical ionic compounds.

(ii) Differentiate effective nuclear charge from ionic radius.

Effective nuclear charge is the net positive charge experienced by valence electrons after accounting for shielding by inner electrons.
Ionic radius is the size of an ion. Cations have smaller radii than their parent atoms due to increased attraction, while anions have larger radii due to electron repulsion.

6 (d) (i) Write the possible chemical equations representing the reduction of the reverberatory furnace.

$Cu_2S + O_2$ ----> $2Cu_2O + SO_2$
$Cu_2S + 2Cu_2O$ ----> $6Cu + SO_2$

(ii) Describe the process of obtaining pure copper from blister copper.

Blister copper is refined electrolytically.
Anode: Blister copper
Cathode: Pure copper plate
Electrolyte: Acidified copper(II) sulfate solution
At anode: Cu ----> $Cu^{2+} + 2e^-$
At cathode: $Cu^{2+} + 2e^-$ ----> Cu
Impurities like Fe dissolve or fall as sludge, and pure copper is deposited on the cathode.