**THE UNITED REPUBLIC OF TANZANIA**

**NATIONAL EXAMINATIONS COUNCIL**

# ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

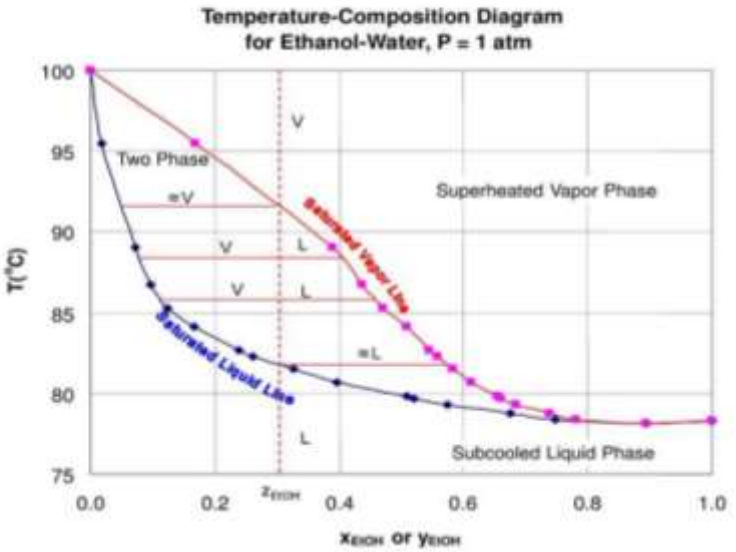
**132/2** **CHEMISTRY 2**

**Time: 3 Hours** **ANSWERS** **Mwaka: 2020**

## Instructions

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

1 (a) (i) Ethanol and water form an azeotropic mixture which boils at 78.01°C and contains 95.6% ethanol at standard pressure. If the boiling points of pure water and ethanol are 100°C and 78.4°C, respectively. Draw and label a temperature versus mole fraction phase-diagram of ethanol and water solution.



The phase diagram of ethanol-water mixture will have temperature on the y-axis and mole fraction of ethanol on the x-axis. The curve starts at 100°C when mole fraction of ethanol is 0 (pure water) and ends at 78.4°C when mole fraction is 1 (pure ethanol). The boiling point curve dips to a minimum point at 78.1°C where an azeotrope forms at 95.6% ethanol. This point indicates that the liquid and vapor phase have the same composition. Two curves appear: the lower one is the boiling point curve (liquid line) and the upper one is the vapor composition curve (vapor line). The azeotrope is the intersection point of both lines.

1 (a) (ii) What happens when a dilute ethanol solution of less than 50% is boiled and condensed several times?

When a dilute ethanol solution (less than 50% ethanol) is boiled and condensed repeatedly (fractional distillation), the ethanol concentration in the vapor phase increases after each distillation. However, upon repeated distillation, the ethanol content will increase only up to the azeotropic composition (95.6%) and cannot go beyond it by simple distillation because both vapor and liquid phases have identical composition at azeotrope.

1 (a) (iii) How would you increase the percentage of ethanol after obtaining a 95.6% ethanol-water mixture?

To increase the percentage of ethanol beyond 95.6%, azeotropic distillation must be used. This involves adding a third component such as benzene or cyclohexane to break the azeotrope, or using drying agents like calcium oxide or molecular sieves to remove water by chemical means or adsorption, respectively.

1 (b) When 500 $cm^3$ of an aqueous solution containing 4 g of a solute G per litre was shaken with 100 $cm^3$ of pentan-1-ol, 1.5 g of the solute was extracted. Assuming the molecular state of the solute remained the same in both solvents, calculate:

(i) Partition coefficient of the solute G between pentan-1-ol and water.

Partition coefficient, K = concentration in pentan-1-ol / concentration in water

Concentration in pentan-1-ol = 1.5 g / 100 $cm^3$ = 0.015 g/$cm^3$
Remaining solute in water = 4 g - 1.5 g = 2.5 g per litre = 0.0025 g/$cm^3$
K = 0.015 / 0.0025 = 6

1 (b) (ii) Mass of the solute G which remained in the aqueous solution after a further shaking with 100 $cm^3$ of pentan-1-ol.

Let remaining mass after second shaking = x
Partition coefficient remains 6 = (mass in pentan-1-ol / volume) / (mass in water / volume)
Let x be remaining mass in water after second shaking
Then amount extracted in second step = 2.5 - x
Concentration in pentan-1-ol = (2.5 - x)/100
Concentration in water = x/500
$K = [(2.5 - x)/100] / (x/500) = 6$
$[(2.5 - x)/100] \times (500/x) = 6$
$(2.5 - x)(5)/x = 6$
$(12.5 - 5x)/x = 6 \rightarrow 12.5 - 5x = 6x \rightarrow 12.5 = 11x \rightarrow x = 1.14$ g

1 (c) Write two practical applications of the partition law.
Partition law is applied in:
Extraction of drugs or organic compounds from aqueous solution using solvents in pharmaceutical and chemical industries.
Separation of components in chromatography techniques such as paper chromatography and liquid-liquid extraction.

2 (a) (i) What are the effects of a catalyst on the activation energy of a reaction?
A catalyst lowers the activation energy of a reaction by providing an alternative reaction pathway. This increases the rate of reaction without being consumed in the process. It enables more reactant particles to possess the required energy to undergo successful collisions, thus increasing the frequency of effective collisions.

2 (a) (ii) Describe how temperature, concentration, light, pressure and surface area can affect the rate of a chemical reaction.
Temperature: Increasing temperature raises the kinetic energy of particles, leading to more frequent and energetic collisions. This increases the rate of reaction.
Concentration: Higher concentration of reactants increases the number of particles per unit volume, resulting in more frequent collisions and hence a faster reaction.
Light: For photochemical reactions, light provides the energy needed to initiate the reaction, hence increasing light intensity can increase the reaction rate.
Pressure: Increasing pressure in reactions involving gases compresses the gas particles closer together, leading to more frequent collisions and an increased reaction rate.
Surface area: A larger surface area of a solid reactant allows more particles to be exposed to reaction, resulting in a faster rate due to more collision sites.

2 (b) The decomposition of a hydrogen peroxide at 25°C was studied by titrating portions of the reaction mixture with a standard potassium permanganate solution at different time intervals. The results obtained were tabulated as follows:

| | | | | | |
|---|---|---|---|---|---|
| Volume of $KMnO_4$ ($cm^3$): | 75 | 47 | 30 | 13 | 7.20 |
| Time (min): | 0 | 5 | 9 | 20 | 25 |

(i) Show that the reaction is a first order.

To verify first-order kinetics, the rate of decrease in concentration (or volume of $KMnO_4$ titrated) should follow an exponential decay pattern, and the half-life should remain constant.

Initial volume = 75 $cm^3$

Half of 75 = 37.5 $cm^3$ (find time to reach this volume)

From data, at 5 min = 47 $cm^3$, at 9 min = 30 $cm^3$. Hence, volume falls from 75 to 37.5 between 5 and 9 minutes, approximated at about 6.5 minutes.

Now, half of 37.5 = 18.75. Between 9 min (30 $cm^3$) and 20 min (13 $cm^3$), volume drops again approximately by half in about 10 minutes. So approximate half-life is almost constant, indicating first-order kinetics.

(ii) Without using a graph, calculate the rate constant at the given temperature.

First-order rate equation:

$k = (1/t) \ln(V_0/Vt)$

Let's take initial volume $V_0 = 75\ cm^3$

At $t = 5$ min, $Vt = 47\ cm^3$

$k = (1/5) \times \ln(75/47)$

$k = 0.2 \times \ln(1.5957)$

$k = 0.2 \times 0.4676$

$k = 0.0935\ min^{-1}$

2 (c) The reaction, $NH_4NO_2(aq) \rightarrow N_2(g) + H_2O(l)$ is a first order with $k = 2.2 \times 10^{-5}\ sec^{-1}$.

(i) Find the percentage of $NH_4NO_2$ that would be decomposed on heating at 310°C for 90 minutes.

First convert time: 90 min = 5400 sec

For first-order: $\ln([A]_0/[A]) = kt$

$\ln(1/(1 - x)) = kt$, where x is fraction decomposed

$kt = 2.2 \times 10^{-5} \times 5400 = 0.1188$

$1/(1 - x) = e^{(0.1188)} = 1.126$

$1 - x = 1/1.126 = 0.8885$

$x = 0.1115 = 11.15\%$ decomposed

(ii) If the rate of reaction triples when the temperature is raised from 20°C to 50°C, calculate the activation energy of the reaction in kJ/mol.

Use Arrhenius equation:

$k_2/k_1 = e^{(Ea/R(1/T_1 - 1/T_2))}$

$\ln(3) = Ea/R(1/293 - 1/323)$
$1/293 - 1/323 = (323 - 293)/(293\times323) = 30/94639 \approx 0.000317$
$\ln(3) = Ea \times 0.000317 / 8.314$
$1.0986 = Ea \times 0.000317 / 8.314$
$Ea = (1.0986 \times 8.314) / 0.000317 = 28827$ J/mol = 28.83 kJ/mol

3 (a) Calculate the pH of a solution obtained when:
(i) 1.0 cm³ of 0.10 M NaOH is added to 100 cm³ of 0.001 M HCl.
Moles of NaOH = $0.10 \times 1.0/1000 = 0.0001$ mol
Moles of HCl = $0.001 \times 100/1000 = 0.0001$ mol
Since both have equal moles, neutralization occurs and solution becomes neutral.
pH = 7
(ii) 1.0 cm³ of 1.0 M HCl is added to 1000 cm³ of a solution mixture prepared by dissolving 0.04 moles of $CH_3COOH$. Use $Ka(CH_3COOH) = 1.84 \times 10^{-5}$.
Moles of HCl added = $1.0 \times 1.0 /1000 = 0.001$ mol
$CH_3COOH$ reacts with HCl, forming $CH_3COOH_2^+$ ions. But $CH_3COOH$ is a weak acid and HCl is a strong acid. The pH will depend on the common ion effect.
Total moles of $CH_3COOH$ = 0.04 mol
Since HCl is strong, it suppresses ionization of $CH_3COOH$.
$[H^+] \approx \sqrt{(Ka \times C)}$
C = 0.04 / 1 L = 0.04 M
$[H^+] = \sqrt{(1.84 \times 10^{-5} \times 0.04)} = \sqrt{(7.36 \times 10^{-7})} \approx 8.58 \times 10^{-4}$
$pH = -\log(8.58 \times 10^{-4}) = 3.07$

3 (b) How does Bronsted-Lowry concept account for the relative strength of acid-base conjugate pairs?
According to Bronsted-Lowry concept, acids donate protons and bases accept protons. The strength of an acid is inversely related to the strength of its conjugate base. A strong acid has a weak conjugate base because once it donates a proton, its conjugate base has little tendency to reaccept a proton. Conversely, a weak acid has a relatively stronger conjugate base. This helps predict acid-base behavior in equilibrium systems.

3 (c) Indicate the acid-base conjugate pairs in each of the following equilibria:
(i) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
Acid: $NH_4^+$ ---> Conjugate base: $NH_3$
Base: $H_2O$ ---> Conjugate acid: $H_3O^+$
(ii) $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$
Acid: $H_2SO_4$ ---> Conjugate base: $HSO_4^-$
Base: $H_2O$ ----> Conjugate acid: $H_3O^+$

(iii) $AH + H_2O \rightleftharpoons A^- + H_3O^+$
Acid: AH -----> Conjugate base: $A^-$
Base: $H_2O$ ----> Conjugate acid: $H_3O^+$

4 (a) Describe four characteristics of s-block elements.
They have low ionization energies.
They are highly reactive metals.
They form mostly ionic compounds.
They have low electronegativities and oxidation state is mostly +1 (Group 1) or +2 (Group 2).

4 (b) (i) What do you understand by the word electronegativity?
Electronegativity is the tendency of an atom to attract a shared pair of electrons towards itself in a chemical bond.

(ii) Explain three factors that affect the size of electronegativity.
Atomic size: Larger atoms have lower electronegativity because the nucleus is farther from the bonding electrons.
Nuclear charge: Higher nuclear charge increases attraction of electrons, thus increasing electronegativity.
Shielding effect: Greater electron shielding reduces the effective nuclear charge felt by bonding electrons, decreasing electronegativity.

4 (c) Briefly, explain how hydrides of period 2 react with water, acids and bases. Support your answers with reaction equations.
Hydrides of period 2 include LiH, $BeH_2$, $BH_3$, $CH_4$, $NH_3$, $H_2O$, HF.
With water:
$LiH + H_2O \text{ -----> } LiOH + H_2$
$BeH_2$ hydrolyzes forming $Be(OH)_2$ and $H_2$
$BeH_2 + 2H_2O \text{ ---> } Be(OH)_2 + 2H_2$
With acids:
$NH_3$ acts as a base and reacts with acids to form ammonium salts.
$NH_3 + HCl \text{ ----> } NH_4Cl$

With bases:
$H_2O$ reacts with strong bases forming hydroxide ions.
$H_2O + Na \text{ ---> } NaOH + H_2$
HF acts as a weak acid in reaction with strong bases.
$HF + NaOH \text{ ---> } NaF + H_2O$

5 (a) With the aid of chemical equations, show how dimethylamine reacts with the following compounds:
(i) $CH_3COCl$ (Acetyl chloride)
$(CH_3)_2NH + CH_3COCl \text{ ----> } CH_3CON(CH_3)_2 + HCl$
Dimethylamine reacts with acetyl chloride to form N,N-dimethylacetamide and hydrogen chloride.

(ii) $CH_3COOCH_3$ (Methyl acetate)
$(CH_3)_2NH + CH_3COOCH_3 \text{ ---> } CH_3CON(CH_3)_2 + CH_3OH$
Dimethylamine reacts with methyl acetate in a nucleophilic acyl substitution reaction to form N,N-dimethylacetamide and methanol.

5 (b) Give the structural formula of the following compounds:

(i) Tripropylamine

$CH_3CH_2CH_2–N(CH_2CH_2CH_3)_2$

(ii) Dipentylamine

$CH_3(CH_2)_4–NH–(CH_2)_5CH_3$

(iii) 2,4-Dimethyl-3-hexanamine

$CH_3–CH(CH_3)–CH(NH_2)–CH_2–CH(CH_3)–CH_3$

5 (c)(i) Show how you can carry out the conversion starting from propanoylchloride to dipropylamine.

Step 1: React propanoyl chloride with ammonia:

$CH_3CH_2COCl + 2NH_3$ ----> $CH_3CH_2CONH_2 + NH_4Cl$

Step 2: Reduce the amide to propylamine using $LiAlH_4$:

$CH_3CH_2CONH_2 + 4[H]$ ----> $CH_3CH_2CH_2NH_2 + H_2O$

Step 3: React two equivalents of propylamine under suitable conditions to form dipropylamine:

$2CH_3CH_2CH_2NH_2$ -----> $(CH_3CH_2CH_2)_2NH + NH_3$

(ii) Write the equation to show the reaction between benzaldehyde ($C_6H_5CHO$) and warm phenylamine.

$C_6H_5CHO + C_6H_5NH_2$ -----> $C_6H_5CH=N–C_6H_5 + H_2O$

This reaction forms a Schiff base (imine).

(iii) Write the general formula and functional group of secondary amine and tertiary amine.

Secondary amine: General formula $R_2NH$, functional group –NH–

Tertiary amine: General formula $R_3N$, functional group –N<

(iv) Write the equation for the equilibrium that exists when diethylamine dissolves in water.

$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$

5 (d) Give the structural formula for compounds B through E, which undergo the following sequence of reactions:

B ----> C: B is $CH_3CH_2CH_2Cl$ (propyl chloride)

C ----> D: C is $CH_3CH_2CH_2CN$ (propyl cyanide)

D ----> E: D is $CH_3CH_2CH_2CH_2NH_2$ (butylamine)

E reacts with HCl: forms butylammonium chloride salt

Sequence of structures:

B = $CH_3CH_2CH_2Cl$

C = $CH_3CH_2CH_2CN$

D = $CH_3CH_2CH_2CH_2NH_2$

E = $CH_3CH_2CH_2CH_2NH_3^+Cl^-$

6 (a) Briefly, explain the following and give one example for each:

(i) Thermoplastic polymers

Thermoplastic polymers are linear or branched polymers that soften on heating and harden on cooling without undergoing any chemical change. This property allows them to be reshaped and reused.
Example: Polyethylene

(ii) Thermosetting polymers
Thermosetting polymers are polymers that undergo a permanent chemical change when heated and molded. Once hardened, they cannot be remelted or reshaped.
Example: Bakelite

(iii) Natural polymers
Natural polymers are polymers that occur naturally and are found in plants and animals. They are made of monomers linked by natural processes.
Example: Cellulose

6 (b) Write the monomers used in synthesis of the following polymers:
(i) Polyvinylchloride (PVC)
Monomer: Vinyl chloride ($CH_2=CHCl$)

(ii) Teflon
Monomer: Tetrafluoroethylene ($CF_2=CF_2$)

(iii) Bakelite
Monomers: Phenol and Formaldehyde

6 (c) (i) Why cationic polymerization is more favored than anionic polymerization when vinylic monomers contain an electron donating group?
Cationic polymerization is more favored because electron donating groups on the vinylic monomer stabilize the positively charged carbocation intermediate, facilitating propagation of the chain. In contrast, such groups destabilize the anionic intermediate in anionic polymerization.

(ii) Why styrene undergo anionic polymerization easily? Briefly explain.
Styrene contains a phenyl group which withdraws electrons through resonance and inductive effects. This stabilizes the negative charge on the anionic intermediate formed during propagation, making styrene suitable for anionic polymerization.

(iii) Differentiate addition from condensation polymers basing on the mode of polymerization. Give one example for each type.
Addition polymers are formed by the addition reaction of monomers with double or triple bonds without the elimination of any by-product.
Example: Polyethylene (from ethene)
Condensation polymers are formed by the condensation reaction of monomers containing two or more functional groups, with the elimination of small molecules like water or HCl.
Example: Nylon-6,6 (from hexamethylene diamine and adipic acid)

6 (d) With reasons, write down the use of each of the following polymers:

(i) Butyl-rubber

Used in making tire tubes and seals due to its excellent air impermeability and resistance to oxidation and chemicals.

(ii) Polyacrylonitriles

Used in the manufacture of synthetic fibers like Orlon due to their strength, durability, and resistance to chemicals.

(iii) Polyhaloalkene

Used in non-stick cookware coatings (e.g., Teflon) and chemical resistant containers due to their high thermal stability and inertness to most chemicals.

.