THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2021**

Instructions

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

1 (a) (i) Distinguish between an electrolytic cell and a galvanic cell.
An electrolytic cell uses electrical energy to drive a non-spontaneous chemical reaction, while a galvanic cell produces electrical energy from a spontaneous chemical reaction.
(ii) Lead rods are placed in each of the following solutions: $AgNO_3$, $CuSO_4$, $FeSO_4$, $ZnSO_4$. In which solution would you expect a coating of one metal on lead rod? Give a reason.

Lead will get coated by the metal which has a higher reduction potential than Pb^{2+}/Pb ($E^0 = -0.13$ V).
Given E^0 values:
$Ag^+/Ag = +0.81$ V → Ag will be deposited on Pb
$Cu^{2+}/Cu = +0.34$ V → Cu will be deposited on Pb
$Fe^{2+}/Fe = -0.44$ V → No deposition
$Zn^{2+}/Zn = -0.76$ V → No deposition

Hence, deposition is expected in $AgNO_3$ and $CuSO_4$ solutions.

(b) Why the Kohlrausch's law of independent migration of ions applies at infinite dilution of electrolytes? Briefly explain.

At infinite dilution, interionic interactions are negligible. Each ion migrates independently, and the total conductivity is the sum of individual ionic conductivities. This independence justifies Kohlrausch's law.

(c) Show that for the cell reaction:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
with different cell concentrations and at 298 K, the cell potential is given by:
$E = E^0\text{cell} - 0.0295 \log [Zn^{2+}]/[Cu^{2+}]$

This is derived from the Nernst Equation:
$E\text{cell} = E^0\text{cell} - (0.0591/n) \log Q$
For this reaction, $n = 2$
$E\text{cell} = E^0\text{cell} - (0.0591/2) \log ([Zn^{2+}]/[Cu^{2+}])$
$E\text{cell} = E^0\text{cell} - 0.0295 \log ([Zn^{2+}]/[Cu^{2+}])$

(d) A galvanic cell consists of metallic zinc and lead plates immersed in 0.1 M $Zn(NO_3)_2$ and 0.02 M $Pb(NO_3)_2$ solution.

(i) Write the chemical equations for the electrode reactions.

Anode: $Zn(s) \rightarrow Zn^{2+} + 2e^-$
Cathode: $Pb^{2+} + 2e^- \rightarrow Pb(s)$

(ii) Write the cell notation for the reaction.

$Zn(s) \mid Zn^{2+}(0.1\text{ M}) \parallel Pb^{2+}(0.02\text{ M}) \mid Pb(s)$

(iii) Calculate the e.m.f. of the cell.

$E^ocell = E^ocathode – E^oanode = (-0.13) – (–0.76) = 0.63$ V
Use Nernst Equation:
$Ecell = 0.63 – 0.0295 \log([Zn^{2+}]/[Pb^{2+}])$
$= 0.63 – 0.0295 \log(0.1 / 0.02) = 0.63 – 0.0295 \log(5)$
$= 0.63 – 0.0295 \times 0.699 = 0.609$ V

2 (a) Write a mathematical expression for distribution law.

$C_1/C_2 = Kd$
Where C_1 and C_2 are concentrations in two solvents and Kd is the distribution coefficient.

(b) Compound P has a partition coefficient of 4.00 between ethoxyethane and water. Given that 2.0 g of P is obtained in solution, in 50 cm^3 of water, calculate the mass of P that can be extracted:

(i) By 50 cm^3 of ethoxyethane.

Kd = amount in ether / amount in water
$4 = x / (2 – x) \rightarrow 4(2 – x) = x$
$8 – 4x = x \rightarrow 5x = 8 \rightarrow x = 1.6$ g

(ii) Two successive extractions of 25 cm^3 each of ethoxyethane.

Let x = amount left after first extraction
Kd = y/x, where y = amount extracted
$4 = y / (2 – y) \rightarrow y = 1.6$ g after first extraction
Remaining = 0.4 g
Repeat for 0.4 g:
$4 = z / (0.4 – z) \rightarrow 4(0.4 – z) = z \rightarrow z = 0.32$ g

Total extracted = 1.6 + 0.32 = 1.92 g

(c) Comment on the variation of the amount extracted in (b) (i) and (ii)

Two successive extractions yield a higher total mass than one single extraction of equal volume. This is due to better partitioning when extraction is done in smaller portions.

(d) When 500 cm^3 of aqueous solution containing 4 g of solute G per litre was shaken with 100 cm^3 of pentan-1-ol, 1.5 g of the solute G was extracted.

(i) The partition coefficient of G between pentan-1-ol and water.

Partition coefficient = amount in organic / amount in aqueous
G in 100 cm^3 pentan-1-ol = 1.5 g
Remaining in aqueous = 4 – 1.5 = 2.5 g
Kd = 1.5 / 2.5 = 0.6

(ii) Mass of solute G which will remain in aqueous solution after further shaking with 100 cm^3 pentan-1-ol.

Let x = remaining mass in aqueous
Kd = (2.5 – x)/x → 0.6 = (2.5 – x)/x → 0.6x = 2.5 – x
1.6x = 2.5 → x = 1.56 g

3 (a) To a solution containing 0.1 M Cl^- and 0.01 M CrO_4^{2-}, a solution of $AgNO_3$ is added slowly.

(i) Which salt will precipitate first between AgCl and Ag_2CrO_4?

Use Ksp comparison:
Ksp(AgCl) = 2.72×10^{-10}
Ksp(Ag_2CrO_4) = 2.4×10^{-12}
Since Ag_2CrO_4 has lower Ksp, it should precipitate first, but CrO_4^{2-} concentration is 0.01 M while Cl^- is 0.1 M.
AgCl starts precipitating when $[Ag^+]$ = Ksp / $[Cl^-]$ = 2.72×10^{-10} / 0.1 = 2.72×10^{-9} M
Ag_2CrO_4 starts when $[Ag^+]^2$ = Ksp / $[CrO_4^{2-}]$ = 2.4×10^{-12} / 0.01 = 2.4×10^{-10}
$[Ag^+]$ = sqrt(2.4×10^{-10}) = 1.55×10^{-5} M
Since $2.72\times10^{-9} < 1.55\times10^{-5}$, AgCl will precipitate first.

(ii) Find the concentration of the ion that will precipitate first at the time the second ion will start precipitating.

When Ag_2CrO_4 starts precipitating, $[Ag^+]$ = 1.55×10^{-5} M
Cl^- concentration needed for AgCl at this Ag^+ concentration:
$[Cl^-]$ = Ksp / $[Ag^+]$ = 2.72×10^{-10} / 1.55×10^{-5} = 1.75×10^{-5} M

3 (b) Calculate the solubility of Ag_2CrO_4 in water if the value of solubility product Ksp is 1.3×10^{-11} mol^2/L^2

Let solubility of Ag_2CrO_4 be s mol/L.
$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$
$[Ag^+] = 2s$, $[CrO_4^{2-}] = s$
Ksp = $[Ag^+]^2 \times [CrO_4^{2-}] = (2s)^2 \times s = 4s^3$
$1.3 \times 10^{-11} = 4s^3 \rightarrow s^3 = 3.25 \times 10^{-12}$
$s = 1.48 \times 10^{-4}$ mol/L

(i) The solubility of AgCl in g/dm^3

Ksp of AgCl = 2.72×10^{-10}
Let solubility be s mol/L → $s^2 = 2.72 \times 10^{-10}$ → s = 1.65×10^{-5} mol/L
Mass = 1.65×10^{-5} mol × 143.5 g/mol = 2.37×10^{-3} g/L = 0.00237 g/dm^3

(ii) The solubility product of AgCl at the given temperature is already known: Ksp = 2.72×10^{-10} mol^2/L^2

3 (c) A standard solution of AgCl(aq) at 26°C has a conductivity of 1.32×10^{-4} cm^{-1} mol^{-1}. If its molar conductivity at infinite dilution is 120 cm^2 mol^{-1}, calculate:

(i) The degree of dissociation α = molar conductivity at current concentration / molar conductivity at infinite dilution
$\alpha = 1.32 \times 10^{-4} / 120 = 1.1 \times 10^{-6}$

(ii) Dissociation constant (Kd) = $\alpha^2 \times C$
Assuming C = solubility = 1.65×10^{-5} mol/L
Kd = $(1.1 \times 10^{-6})^2 \times 1.65 \times 10^{-5} = 1.99 \times 10^{-17}$ mol/L

4 (a) State the reason(s) for the following facts:

(i) Although Na^+, Mg^{2+} and Al^{3+} ions have the same electronic configuration, they have different radii.
Because they have increasing nuclear charge which pulls the electrons closer. Al^{3+} has the smallest radius, Na^+ the largest.

(ii) At ordinary temperature, phosphorous pentachloride (PCl_5) is a white solid with unexpected high melting point.
PCl_5 exists in ionic form as $[PCl_4]^+$ and $[PCl_6]^-$ in solid state, leading to ionic lattice and high melting point.

(iii) Sodium chloride (NaCl) and anhydrous aluminium chloride ($AlCl_3$) are both chlorides of metals of period III. Molten sodium chloride can be electrolysed while molten unhydrous aluminium chloride cannot.
$AlCl_3$ is covalent and sublimes easily; does not conduct electricity in molten state, unlike ionic NaCl.

(iv) The first ionization energy increases from left to right across a period but the first ionization energy of magnesium is larger than that of aluminium.
Due to electron entering a higher energy p-orbital in aluminium, which is easier to remove than magnesium's s-electron.

(v) Lithium and potassium are metals of group I. In aqueous solution, lithium is a poor conductor of electricity while potassium is a good conductor.
Potassium ion is larger, more hydrated, and moves faster in solution, improving conductivity.

(vi) Boiling point of water (H_2O) is higher than that of hydrogen sulphide (H_2S). All are hydrides of group VI elements.
Due to hydrogen bonding in water which is absent in H_2S, leading to stronger intermolecular forces.

4 (b) (i) Which factors are used to classify elements in the periodic system of elements?
- Atomic number
- Electronic configuration
- Chemical properties
- Physical properties

(ii) Account for the fact that the third period of the periodic system of elements has only eight elements and not eighteen as expected.
The 3d orbitals belong to fourth shell and do not fill in third period. Third period contains only s and p orbitals ($3s^2 3p^6$), giving eight elements.

4 (c) Ammonia NH_3 and phosphene PH_3 are hydrides of the first two elements in group VA. Some physical properties are given in the table:

Compound	Boiling point (°C)	Solubility in water (mol/dm³)
Ammonia, NH_3	-33	31.1
Phosphene, PH_3	-88	8.88×10^{-3}

(i) Suggest one reason for the difference in boiling temperature.
Ammonia forms hydrogen bonds due to N–H bonds, while phosphene does not, hence ammonia has a higher boiling point.

(ii) Why is ammonia more soluble in water than phosphene?
Ammonia forms hydrogen bonds and interacts strongly with water molecules, while phosphene lacks this ability.

4 (d) Why do elements exhibit diagonal relations? Briefly explain by giving two examples.

Diagonal relationship occurs due to similarity in charge density and electronegativity of diagonally adjacent elements in second and third periods.
Examples:
- Lithium and magnesium
- Beryllium and aluminium

5 (a) From the knowledge you have on hydroxyl group, write the chemical reaction equations with their IUPAC names showing what happens when propan-1-ol is treated with:

(i) Excess HBr under reflux
Reaction: $CH_3CH_2CH_2OH + HBr \text{ -----> } CH_3CH_2CH_2Br + H_2O$
Product: 1-bromopropane (n-propyl bromide)

(ii) A small amount of concentrated H_2SO_4

Dehydration occurs forming alkene
$CH_3CH_2CH_2OH$ ----> $CH_3CH=CH_2 + H_2O$
Product: Propene

(iii) Acidified $KMnO_4$
Propan-1-ol undergoes oxidation
$CH_3CH_2CH_2OH + 2[O]$ ----> $CH_3CH_2COOH + H_2O$
Product: Propanoic acid

(iv) Ethanoic acid in the presence of concentrated H_2SO_4
Esterification reaction
$CH_3CH_2CH_2OH + CH_3COOH$ ---> $CH_3COOCH_2CH_2CH_3 + H_2O$
Product: Propyl ethanoate (an ester)

(v) $SOCl_2$
Substitution reaction forming alkyl chloride
$CH_3CH_2CH_2OH + SOCl_2$ ----> $CH_3CH_2CH_2Cl + SO_2 + HCl$
Product: 1-chloropropane

5 (b) Compound A ($C_{10}H_{12}O$) gives off oxygen on treatment with sodium metal and decolorizes Br_2 in CCl_4 to give organic compound B. Compound A on treatment with I_2 in NaOH gives iodoform and a salt C which after acidification gives a white solid D ($C_7H_6O_2$). Using knowledge of organic chemistry, identify structures A, B, C, and D.

Clues:
- $C_{10}H_{12}O$ with Br_2 decolorization = presence of double bond
- Iodoform test = presence of CH_3–CO– group
- Salt C becomes benzoic acid ($C_7H_6O_2$) = D

So:
A = 4-hydroxy-3-phenylbutan-2-one (contains hydroxyl and methyl ketone groups)
B = Unsaturated compound after bromination (removal of double bond)
C = Benzoate salt ($C_7H_5O_2^-Na^+$)
D = Benzoic acid ($C_7H_6O_2$)

6 (a) How can you distinguish the following? Support your answer with chemical equations:

(i) Propanal and propanone
Use Tollens' test:
Propanal (CH_3CH_2CHO) gives silver mirror with Tollens' reagent:
$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+$ ---> $CH_3CH_2COOH + 2Ag + 4NH_3$
Propanone (CH_3COCH_3) gives negative result.

(ii) Ethanol and benzaldehyde
Use Fehling's solution:
Benzaldehyde gives red precipitate of Cu_2O, ethanol does not.

(iii) Pentanal and pentan-2-one
Iodoform test: Pentan-2-one ($CH_3COCH_2CH_2CH_3$) gives yellow precipitate of CHI_3
Pentanal ($CH_3CH_2CH_2CH_2CHO$) gives no precipitate.

(iv) 3-pentanone and 2-pentanone
Only 2-pentanone ($CH_3COCH_2CH_2CH_3$) gives iodoform test
3-pentanone ($CH_3CH_2COCH_2CH_3$) does not.

6 (b) An organic compound A with a characteristic odour is treated with 50% NaOH to give B (C_7H_5O) and C which is a sodium salt of an organic acid. Oxidation of B gives back A. Heating C with soda lime yields an aromatic hydrocarbon D. Deduce the structures A, B, C and D.

Clues:
- A has an odour and oxidizes back from B
- Reaction in alkali suggests a benzaldehyde derivative
- C is sodium benzoate
- D is benzene (decarboxylation)

So:
A = Benzaldehyde (C_6H_5CHO)
B = Benzyl alcohol ($C_6H_5CH_2OH$)
C = Sodium benzoate (C_6H_5COONa)
D = Benzene (C_6H_6)

6 (c) Complete the following equations by giving the missing reagents/products:

(i) $C_6H_5CH{=}CHCHO + [Ag(NH_3)_2]^+$ ----> $C_6H_5CH{=}CHCOOH$ (oxidation to carboxylic acid)

(ii) $C_6H_5OH + CrO_3$ ---> C_6H_5COOH (oxidation of phenol to benzoic acid)

(iii) $CH_3CH{=}CHCH{=}CHCH_3 + O_3/Zn\text{-}H_2O$ ----> $2CH_3CH{=}O$ (Ozonolysis to ethanal)

(iv) $CH_3CH{=}CHCH_2CH(CH_3)_2 + O_3/Zn\text{-}H_2O$ ----> $CH_3COCH_3 + CH_3CH_2COOH$
(Products: propanone and propanoic acid)