THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Year: 2012**

Instructions

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

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1.(a) (i) Describe how Daniel cell is used to supply electricity.

A Daniel cell consists of two half-cells:
- Zinc half-cell: Zinc metal electrode dipped in $ZnSO_4$ solution.
- Copper half-cell: Copper metal electrode dipped in $CuSO_4$ solution.
- A salt bridge connects the two half-cells allowing ion flow.

Working: Zinc undergoes oxidation, releasing electrons which travel through an external circuit to the copper electrode where reduction occurs. The flow of electrons generates electric current.

Labelled diagram:
$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

(ii) Write equations for the reactions taking place at the electrodes and the overall equation at (a)(i).

At anode (oxidation): $Zn(s)$ ----> $Zn^{2+}(aq) + 2e^-$
At cathode (reduction): $Cu^{2+}(aq) + 2e^-$ ----> $Cu(s)$
Overall cell reaction: $Zn(s) + Cu^{2+}(aq)$ ----> $Zn^{2+}(aq) + Cu(s)$

(b) (i) Calculate the e.m.f. of a cell operating under standard conditions given that:
$E^0Cu^{2+}/Cu = +0.34$ V
$E^0Zn^{2+}/Zn = -0.76$ V
$E^0Ag^+/Ag = +0.799$ V

$E^0cell = E^0cathode - E^0anode$
For Zn/Cu cell:
$E^0cell = 0.34 - (-0.76) = 1.10$ V

For Zn/Ag cell:
$E^0cell = 0.799 - (-0.76) = 1.559$ V

(ii) Explain how the e.m.f. of the cell would be affected by increasing either $[Cu^{2+}]$ or $[Zn^{2+}]$.

- Increasing $[Cu^{2+}]$ shifts equilibrium toward product (reduction), increasing e.m.f.
- Increasing $[Zn^{2+}]$ shifts equilibrium toward reactant (oxidation), decreasing e.m.f.

(iii) If the Zn^{2+}/Zn electrode system was replaced by Ag^+/Ag electrode system, what would be the e.m.f. of the cell?

$E^0Ag^+/Ag = +0.799$ V
$E^0Cu^{2+}/Cu = +0.34$ V
$E^0cell = 0.799 - 0.34 = 0.459$ V

4 (a) The dissociation constant Ka for the reaction $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ is 4.8×10^{-11} mol/dm³. Calculate the pH of 0.02 M sodium bicarbonate solution.

$HCO_3^- \rightleftharpoons CO_3^{2-} + H_3O^+$
$Ka = [H_3O^+][CO_3^{2-}] / [HCO_3^-]$
Let $[H_3O^+] = x$, then $[CO_3^{2-}] = x$ and $[HCO_3^-] \approx 0.02$ M

$Ka = x^2 / 0.02$
$4.8 \times 10^{-11} = x^2 / 0.02$
$x^2 = 9.6 \times 10^{-13}$
$x = 9.8 \times 10^{-7}$ M
$pH = -\log[H_3O^+] = -\log(9.8 \times 10^{-7}) \approx 6.01$

(b) A solution is initially 0.1 M Fe^{3+} and 0.1 M Zn^{2+}. From their solubility products, calculate the hydroxyl ion concentration needed to cause precipitation of each hydroxide. Which begins to precipitate first?

For $Fe(OH)_3$: $Ksp = [Fe^{3+}][OH^-]^3$
$1.1 \times 10^{-36} = 0.1 \times [OH^-]^3$
$[OH^-]^3 = 1.1 \times 10^{-35}$
$[OH^-] = (1.1 \times 10^{-35})^\wedge(1/3) \approx 4.8 \times 10^{-12}$ M

For $Zn(OH)_2$: $Ksp = [Zn^{2+}][OH^-]^2$
$1.8 \times 10^{-14} = 0.1 \times [OH^-]^2$
$[OH^-]^2 = 1.8 \times 10^{-13}$
$[OH^-] = \sqrt{}(1.8 \times 10^{-13}) \approx 1.34 \times 10^{-7}$ M

$Fe(OH)_3$ precipitates first because it needs much lower $[OH^-]$.

(c) Given Ksp of silver chromate = 9×10^{-12} mol²/dm⁶, calculate molar solubility in:
(i) Water:
$Ksp = [Ag^+]^2[CrO_4^{2-}]$
Let solubility = s
$[Ag^+] = 2s$, $[CrO_4^{2-}] = s$
$Ksp = (2s)^2 \times s = 4s^3$
$4s^3 = 9 \times 10^{-12}$
$s^3 = 2.25 \times 10^{-12}$
$s = 1.32 \times 10^{-4}$ mol/dm³

(ii) 0.1 M potassium dichromate provides $CrO_4^{2-} = 0.1$ M
$Ksp = (Ag^+)^2 \times 0.1$
$(Ag^+)^2 = 9 \times 10^{-12} \div 0.1 = 9 \times 10^{-11}$
$[Ag^+] = \sqrt{}(9 \times 10^{-11}) = 3 \times 10^{-6}$ mol/dm³
Molar solubility of $Ag_2CrO_4 = 1.5 \times 10^{-6}$ mol/dm³

5 (a) Explain each of the following and give balanced chemical equations where necessary:

(i) Nitrogen dioxide is paramagnetic but dinitrogen tetroxide is not.
NO_2 has an unpaired electron, making it paramagnetic. N_2O_4 is a dimer without unpaired electrons, hence diamagnetic.

(ii) Silicon tetrachloride reacts vigorously with water, but carbon tetrachloride does not.
$SiCl_4$ hydrolyzes: $SiCl_4 + 4H_2O \text{ ----> } Si(OH)_4 + 4HCl$
CCl_4 lacks available d-orbitals and does not hydrolyze easily.

(iii) $HClO_4$ is a stronger acid than HNO_3.
$HClO_4$ has more electronegative oxygen atoms, stabilizing its conjugate base more effectively than NO_3^-.

(iv) Boron hydroxide is more acidic than aluminium hydroxide.
$B(OH)_3$ is a weak Lewis acid. $Al(OH)_3$ acts amphoterically and tends to accept protons.

(v) Aqueous solution of aluminium chloride is acidic while sodium acetate is basic.
Al^{3+} hydrolyzes in water releasing H_3O^+. Acetate ion accepts protons making the solution basic.

(vi) When magnesium is added to ammonium chloride solution, hydrogen gas is evolved.
$Mg + 2NH_4Cl \text{ ----> } MgCl_2 + 2NH_3 + H_2\uparrow$

(vii) Action of concentrated sulphuric acid on calcium phosphate:
$Ca_3(PO_4)_2 + 3H_2SO_4 \text{ ----> } 3CaSO_4 + 2H_3PO_4$

(viii) Reaction of orange potassium dichromate with hydrogen chloride:
$K_2Cr_2O_7 + 14HCl \text{ ----> } 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$

6 (a) Briefly explain the following terms:
(i) Interstitial hydrides: Hydrogen occupies interstitial spaces in metals.
(ii) Clathrates: Cage-like structures where gas molecules are trapped in host lattice.
(iii) Inert pair effect: Tendency of s-electrons to remain non-bonding in heavier p-block elements.
(iv) Rusting of iron: Electrochemical oxidation of iron in moist air forming $Fe_2O_3\cdot xH_2O$.

(b) A complex compound of cobalt forms two ionization isomers.
(i) Formula and names:
$[Co(NH_3)_5Br]SO_4$ – pentaamminebromocobalt(III) sulfate
$[Co(NH_3)_5SO_4]Br$ – pentaamminesulfatocobalt(III) bromide

(ii) Distinguishing the isomers:
Add $BaCl_2$ to test for SO_4^{2-} ion:
White precipitate indicates SO_4^{2-} is outside the coordination sphere in $[Co(NH_3)_5Br]SO_4$.
Add $AgNO_3$ to test for Br^- ion:
White precipitate shows Br^- is outside coordination in $[Co(NH_3)_5SO_4]Br$

7 (a) With the aid of balanced chemical equations, explain the following observations:

(i) In aqueous solution, copper (II) ions are blue but turn green when excess hydrochloric acid is added to it.
Initially, Cu^{2+} in water forms $[Cu(H_2O)_6]^{2+}$ (blue solution).
When excess HCl is added, chloride ions displace water ligands:
$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$
$[CuCl_4]^{2-}$ complex gives green coloration.

(ii) The addition of aqueous alkali to aqueous solution of iron (III) ions gives gelatinous reddish brown precipitate.
$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$ (reddish brown precipitate)

(iii) Anhydrous magnesium chloride ($MgCl_2$) cannot be obtained by heating the hydrated magnesium chloride ($MgCl_2{\cdot}6H_2O$).
On heating $MgCl_2{\cdot}6H_2O$, it hydrolyzes and decomposes:
$MgCl_2{\cdot}6H_2O \rightarrow MgO + HCl + H_2O$
Instead of forming anhydrous $MgCl_2$, MgO is formed.

(iv) The addition of aqueous ammonia solution to the solution of nickel (II) ions gives green precipitate which dissolves to form blue solution when excess ammonia is added.
$Ni^{2+}(aq) + 2NH_3(aq) \rightarrow Ni(OH)_2(s)$ (green precipitate)
With excess NH_3: $Ni^{2+}(aq) + 6NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}$ (blue solution)

(b) Account for the following chemical phenomena:

(i) Some lithium compounds are covalent while compounds of other elements in the same group are electrovalent.
Li^+ has small ionic size and high polarizing power, distorting electron cloud of large anions like I^-, leading to covalent character. Other group members like Na^+ are larger, polarizing less, forming ionic compounds.

(ii) The first ionization energy of magnesium is comparatively higher than that of aluminium even though magnesium is less electronegative than aluminium.
Magnesium has filled $3s^2$ sublevel which is more stable, whereas aluminium has $3s^23p^1$ configuration. It is easier to remove the $3p^1$ electron in Al, so it has lower ionization energy.

(iii) Potassium manganate (VII) is not used as a primary reagent in volumetric analysis as potassium dichromate (VI) does.
$KMnO_4$ is not a primary standard due to instability in air, self-decomposition, and reacts with organic impurities. $K_2Cr_2O_7$ is more stable, can be weighed accurately and used in standard preparations.

(iv) Concentrated nitric acid has no practical reaction with iron.

Iron reacts with concentrated HNO_3 and becomes passive due to formation of protective Fe_2O_3 oxide layer, preventing further attack by the acid.

8. The extraction of aluminum from its primary ore, bauxite, involves two main processes: the Bayer process and the Hall-Héroult process.

1. Bayer Process: Refining Bauxite to Alumina (Al_2O_3)

Bauxite mainly contains aluminum hydroxide minerals such as gibbsite ($Al(OH)_3$), boehmite (γ-$AlO(OH)$), and diaspore (α-$AlO(OH)$). The steps involved are:

Digestion:
Bauxite is treated with hot concentrated sodium hydroxide (NaOH) under pressure. Aluminum hydroxide dissolves forming sodium aluminate:

$Al(OH)_3 + NaOH \text{ ----> } NaAl(OH)_4$

Clarification:
The undissolved impurities (red mud) are filtered off.

Precipitation:
The solution is cooled and seeded with aluminum hydroxide crystals to precipitate $Al(OH)_3$:

$NaAl(OH)_4 \text{ ----> } Al(OH)_3\downarrow + NaOH$

Calcination:
The precipitated $Al(OH)_3$ is heated to form alumina (Al_2O_3):

$2\ Al(OH)_3 \text{ ----> } Al_2O_3 + 3\ H_2O$

2. Hall-Héroult Process: Electrolytic Reduction of Alumina to Aluminum

Dissolution in Cryolite:
Alumina is dissolved in molten cryolite (Na_3AlF_6) to lower the melting point and improve conductivity.

Electrolysis:
Electrolysis is carried out using carbon electrodes.

At the cathode:
$Al^{3+} + 3\ e^- \text{ ----> } Al$ (molten aluminum)

At the anode:
$2\ O^{2-} \text{ ----> } O_2 + 4\ e^-$

$C + O_2$ ----> CO_2

Overall reaction:
$2\ Al_2O_3 + 3\ C$ ----> $4\ Al + 3\ CO_2$

9 (a) Name the following compounds:

(i) 2,4,6-Trimethylheptane
(ii) 1,3-Dibromobenzene
(iii) Benzyl bromide
(iv) Ethylbenzene
(v) Isopropylbenzene (Cumene)

(b) When benzene is first nitrated, and that product is chlorinated, the product is different from when the order of carrying out the two mono-substitution reactions is reversed (i.e. chlorination then nitration). Explain this by using equations.

When benzene is nitrated first:

$C_6H_6 + HNO_3$ ----> $C_6H_5NO_2 + H_2O$ (Nitrobenzene)
$C_6H_5NO_2 + Cl_2$ ----> m-chloronitrobenzene + HCl

When benzene is chlorinated first:

$C_6H_6 + Cl_2$ ----> $C_6H_5Cl + HCl$ (Chlorobenzene)
$C_6H_5Cl + HNO_3$ ----> o- and p-nitrochlorobenzene + H_2O

Thus, the nitro group directs substitution to the meta-position while the chlorine directs substitution to ortho and para positions.

(c) Using benzene or toluene as the only aromatic organic starting material, devise syntheses for the following:

(i) m-bromonitrobenzene:
$C_6H_6 + HNO_3$ ----> $C_6H_5NO_2 + H_2O$
$C_6H_5NO_2 + Br_2$ ----> m-bromonitrobenzene + HBr

(ii) p-nitroethylbenzene:
$C_6H_5CH_3 + Br_2$ (hv) ----> $C_6H_5CH_2Br + HBr$
$C_6H_5CH_2Br + KCN$ ----> $C_6H_5CH_2CN$
$C_6H_5CH_2CN + H_2/Ni$ ----> $C_6H_5CH_2CH_2NH_2$
$C_6H_5CH_2CH_3 + HNO_3$ ----> p-nitroethylbenzene + H_2O

(iii) p-bromobenzoic acid:
$C_6H_5CH_3$ + $KMnO_4$ ----> C_6H_5COOH + H_2O
C_6H_5COOH + Br_2 ----> p-bromobenzoic acid + HBr

(iv) p-toluenesulfonic acid:
$C_6H_5CH_3$ + fuming H_2SO_4 ----> p-toluenesulfonic acid + H_2O

10. (a) Write the structures of compounds A to E in the following synthetic sequence:

$CH_3CH_2CH(CH_3)CH(OH)CH_2COCl$ or PCl_3
SOC l_2/N aCN/H_2/Pt or $LiAlH_4$
→ A → B → C → D → E
(Structure za A mpaka E hutegemea mfuatano wa kemikali kama vile esterification, nucleophilic substitution, reduction n.k. Zinahitaji mchoro wa kimuundo, ambazo unaweza kuchora au kuomba nikuchoree kama picha.)

(b) Name the following structures by using the IUPAC rules:

(i) $CH_3CH(CH_3)CHO$
Name: 2-Methylpropanal

(ii) $CH_3CH(CH_3)CH_2CH_2CHBrCH_3$
Name: 4-Bromo-3-methylhexane

(iii) Cyclopentanone
Name: Cyclopentanone

(iv) $CH_3CH_2CH_2CH(CH_3)COCH(CH_3)_2$
Name: 4-Methyl-2-heptanone

(v) $CH_3CH_2CH=CHCH_3$
Name: Pent-2-ene

(c) Write the structural formulae and IUPAC names of four isomers of the compound with molecular formula $C_5H_{10}O_2$

Isomer 1: $CH_3CH_2CH_2COOCH_3$ = Methyl butanoate
Isomer 2: $CH_3CH_2COOCH_2CH_3$ = Ethyl propanoate
Isomer 3: $CH_3COOCH_2CH_2CH_3$ = Propyl ethanoate
Isomer 4: $CH_3CH_2CH(CH_3)COOH$ = 2-Methylbutanoic acid

11. (a) Distinguish between
(i) Inductive effect and mesomeric effect

- Inductive effect is the electron withdrawing or donating effect transmitted through sigma bonds due to difference in electronegativity.
- Mesomeric effect (resonance effect) involves delocalization of electrons through pi bonds.

(ii) Activating group and deactivating group
- Activating group increases the reactivity of benzene ring towards electrophilic substitution e.g. -OH, -NH_2.
- Deactivating group reduces the reactivity of benzene ring e.g. -NO_2, -COOH.

(b) An aromatic derivative of benzene M is composed of 80% carbon, 6.66% hydrogen and 13.33% oxygen. M has molecular mass of 120 and it does not respond to silver mirror test.

(i) Find empirical and molecular formula of M.
% C = 80/12 = 6.67 mol
% H = 6.66/1 = 6.66 mol
% O = 13.33/16 = 0.83 mol
Simplified ratio C:H:O = 8:8:1 ----> Empirical formula = C_8H_8O
Molecular formula = C_8H_8O (Molar mass = 120)

(ii) Write the molecular structure of M
Possible compound: Phenyl methyl ketone ($C_6H_5COCH_3$)

(c) Write the structures of the products obtained when M
(i) reacts with iodine in presence of alkali ---> Iodoform (CHI_3) test positive
$C_6H_5COCH_3 + 3I_2 + 4NaOH \text{ ----> } C_6H_5COONa + CHI_3 + 3NaI + 3H_2O$

(ii) reacts with hydrogen cyanide followed by lithium aluminium hydride in dry ether
$C_6H_5COCH_3 + HCN \text{ ----> } C_6H_5C(OH)(CN)CH_3$
Then reduction: $C_6H_5CH(OH)CH_2NH_2$

(iii) reacts with chlorine in presence of ferric chloride
Electrophilic substitution at para position:
$C_6H_5COCH_3 + Cl_2/FeCl_3$ ----> para-chloroacetophenone

(iv) dimerises ---> forms benzoin type dimer (dimerization via coupling)

12. (a) Briefly explain the following terms:
(i) Green manure – Plants grown and incorporated into soil to improve fertility.
(ii) Farm yard manure – Decomposed mixture of cattle dung, urine, bedding.
(iii) Compost manure – Organic manure prepared from household and farm waste.
(iv) Organic fertilizers – Derived from plant or animal origin.
(v) Artificial fertilizers – Chemically synthesized fertilizers like NPK, urea.

(b) The exchangeable hydrogen from 5.0 g of oven dry soil was neutralized with 10 cm^3 of 0.1 M NaOH. If the total c.e.c. of the soil was 25 meq/100g of soil, calculate the

(i) percentage of base saturation of the soil sample

Base saturation = (Total bases / CEC) × 100 = (10 meq / 25 meq) × 100 = 40%

(ii) concentration of the H^+ ions in meq in 75 g of the oven dry soil.

(5 g soil ----> 10 meq H^+)

So for 75 g

(10/5) × 75 = 150 meq

(c) Comment on the nature of the soil at (b)(i) above.

Low base saturation (40%) indicates acidic nature of soil.

(d) A soil sample of 20 g was analysed and found to contain 0.0015 g of Ca. What is the concentration of calcium in the soil in milliequivalent per 100 g of soil?

0.0015 g Ca

moles = 0.0015/40 = 3.75×10^{-5} mol

Meq in 20 g = $2 \times 3.75 \times 10^{-5} \times 1000 = 0.075$ meq

So per 100 g = (0.075 meq / 20 g) × 100 = 0.375 meq/100 g