THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2000**

Instructions

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

1 (a) Define the following terms:

(i) Molarity

Molarity is the number of moles of solute dissolved in one litre (1 dm^3) of solution. It is expressed in mol/dm^3.

(ii) Buffer solution

A buffer solution is a solution that resists change in pH when small amounts of acid or base are added. It usually consists of a weak acid and its conjugate base or a weak base and its conjugate acid.

(iii) Solubility product

Solubility product (Ksp) is the product of the molar concentrations of the ions of a sparingly soluble salt, each raised to the power of its coefficient in the balanced equation.

(iv) Ionic equilibrium

Ionic equilibrium is the dynamic equilibrium established between ions and unionized molecules in a reversible ionic reaction in solution.

(b) The solubility of lead (II) sulphate at 20°C is 0.40 g/dm^3.

(i) What is its solubility product?

$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$

Molar mass of $PbSO_4 = 207 + 32 + (16\times4) = 303$ g/mol

Solubility in $mol/dm^3 = 0.40 \div 303 = 0.00132\ mol/dm^3$

$Ksp = [Pb^{2+}][SO_4^{2-}] = (0.00132)^2 = 1.74 \times 10^{-6}$

(ii) Calculate its solubility in g/dm^3 in 0.01 M sodium sulphate solution.

In presence of common ion ($SO_4^{2-} = 0.01\ mol/dm^3$),

$Ksp = [Pb^{2+}][SO_4^{2-}]$ ---> $[Pb^{2+}] = Ksp \div [SO_4^{2-}]$

$= 1.74 \times 10^{-6} \div 0.01 = 1.74 \times 10^{-4}\ mol/dm^3$

Mass $= 1.74 \times 10^{-4} \times 303 = 0.0527\ g/dm^3$

(c) Calculate the concentration of calcium carbonate precipitate in g/dm^3 if 0.1M calcium chloride was added to 0.1M sodium carbonate solution.

$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$

$Ksp = 1.65 \times 10^{-8}\ mol^2/dm^6$

Let solubility of $CaCO_3 = s\ mol/dm^3$

$Ksp = s^2$

$s = \sqrt{(1.65 \times 10^{-8})} = 1.28 \times 10^{-4}\ mol/dm^3$

Mass $= 1.28 \times 10^{-4} \times 100$ ($CaCO_3$ molar mass) $= 0.0128\ g/dm^3$

2 (a) What is meant by:

(i) Activated complex
An activated complex is a temporary unstable structure formed during the conversion of reactants into products at the transition state of a chemical reaction.

(ii) Molecularity
Molecularity refers to the number of reactant species involved in an elementary step of a reaction.

(iii) Rate law
Rate law is an equation that relates the rate of reaction to the concentration of reactants, often expressed as rate = k[A]^m[B]^n.
(iv) Zero-order reaction
A zero-order reaction is a reaction whose rate is independent of the concentration of reactants.

(b) For each of the following reactions, suggest any two properties which can be followed in measuring the rate of reaction:

(i) $2KMnO_4(aq) + 5H_2C_2O_4(aq) \text{ ----> } K_2SO_4(aq) + 2MnSO_4(aq) + 8H_2O + 10CO_2$
- Volume of CO_2 gas evolved
- Colour change (purple MnO_4^- fading)

(ii) $CuCl_2(aq) + Zn(s) \text{ ----> } Cu(s) + ZnCl_2(aq)$
- Mass of copper deposited
- Disappearance of zinc

(c) Rate of decomposition of hydrogen peroxide by titration with $KMnO_4$:

Volume of $KMnO_4$ used (cm^3): 75, 47, 30, 13, 7.2
Time (minutes): 0, 6, 9, 20, 29

(i) Show that the reaction is first order
A plot of ln(volume of $KMnO_4$ remaining) vs time should be linear for first-order reaction.

(ii) Find the rate constant
Use integrated first-order equation: $\ln[A] = \ln[A_0] – kt$

3 (a) Distinguish between conductance, conductivity, and molar conductivity. Discuss the effect of dilution:

- Conductance: reciprocal of resistance (S)
- Conductivity: conductance of unit length and cross-section (S/cm)
- Molar conductivity: conductivity per mole of electrolyte ($S \cdot cm^2/mol$)

As dilution increases:
- Conductance decreases
- Conductivity decreases
- Molar conductivity increases

(b) Calculate molar conductivity and degree of dissociation:
$\Lambda_m = \kappa / c = 0.0064 / 0.0005 = 12.8$ S·cm²/mol
$\alpha = \Lambda_m / \Lambda_0 = 12.8 / 133.3 = 0.096$

(c) Given standard redox potentials at 25°C:

$Zn^{2+}/Zn = –0.76$ V
$Sn^{2+}/Sn = –0.14$ V
$Fe^{2+}/Fe = –0.44$ V
$H^+/H_2 = 0.00$ V
$Cu^{2+}/Cu = +0.34$ V
$Ag^+/Ag = +0.80$ V
$Cl_2/Cl^- = +1.36$ V
$F_2/F^- = +2.85$ V
Compare zinc and tin as protective materials:
Zinc is more reactive (lower E°), oxidizes first protecting metal from corrosion. Tin is less reactive and ineffective if coating is damaged.

(d) Define Standard Electrode Potential:
It is the potential of a half-cell under standard conditions measured against a standard hydrogen electrode.

(e) Redox series questions:

(i) $Zn(s) + 2Ag^+(aq) \text{ ----> } Zn^{2+}(aq) + 2Ag(s)$
Will occur; E°cell = 0.80 – (–0.76) = +1.56 V

(ii) $Cu(s) + 2H^+(aq) \text{ ----> } H_2(g) + Cu^{2+}(aq)$
Will not occur; E°cell = 0.00 – 0.34 = –0.34 V (non-spontaneous)

(iii) $Cl_2(g) + 2F^-(aq) \text{ ----> } F_2(g) + 2Cl^-(aq)$
Will not occur; E°cell = 2.85 – 1.36 = +1.49 V (Cl_2 can’t displace F_2)

(iv) $H_2 + 2Ag^+ \text{ ----> } 2H^+ + 2Ag$
Will occur; E°cell = 0.80 – 0.00 = +0.80 V

4 (a) Define the following terms giving one example in each case:

(i) Standard enthalpy of combustion

The standard enthalpy of combustion is the enthalpy change when one mole of a substance is completely burned in oxygen under standard conditions (298 K, 1 atm, 1 mol/dm³ solution).
Example: $CH_4(g) + 2O_2(g) \text{----}> CO_2(g) + 2H_2O(l)$ $\Delta H = -890.3$ kJ/mol

(ii) Standard enthalpy of formation
The standard enthalpy of formation is the enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions.
Example: $C(s) + 2H_2(g) \text{----}> CH_4(g)$

(iii) Lattice energy
Lattice energy is the energy released when one mole of an ionic solid is formed from its gaseous ions.
Example: $Na^+(g) + Cl^-(g) \text{----}> NaCl(s)$

(iv) Electron affinity
Electron affinity is the energy change when one mole of gaseous atoms gains one mole of electrons to form negative ions.
Example: $Cl(g) + e^- \text{----}> Cl^-(g)$

(b) State Hess's Law of constant heat summation
Hess's Law states that the total enthalpy change for a chemical reaction is the same regardless of the route by which the reaction occurs, provided the initial and final conditions are the same.

(c) Calculate the enthalpy of formation of $Ca(OH)_2$ from the following data:
$H_2(g) + \frac{1}{2}O_2(g) \text{----}> H_2O(l)$ $\Delta H = -68.3$ kcal
$CaO(s) + H_2O(l) \text{----}> Ca(OH)_2(s)$ $\Delta H = -15.3$ kcal
$Ca(s) + \frac{1}{2}O_2(g) \text{----}> CaO(s)$ $\Delta H = -151.8$ kcal

Overall: $Ca(s) + H_2(g) + O_2(g) \text{----}> Ca(OH)_2(s)$
$\Delta H = -151.8 + (-68.3) + (-15.3) = -235.4$ kcal

(d) Calculate ΔH for the reaction:
$Fe_2O_3(s) + 3CO(g) \text{----}> 3CO_2(g) + 2Fe(s)$
Given:
ΔHf $Fe_2O_3(s) = -196.5$ kcal
ΔHf $CO(g) = -26.41$ kcal
ΔHf $CO_2(g) = -94.05$ kcal
ΔHf $Fe(s) = 0$

$\Delta H = [3 \times (-94.05) + 2 \times 0] - [-196.5 + 3 \times (-26.41)]$
$= (-282.15) - (-196.5 - 79.23) = -282.15 - (-275.73) = -6.42$ kcal

5 (a) What is meant by:

(i) Atomic (covalent) radius
It is the average distance between the nucleus of an atom and the outermost covalent bond-forming electrons.

(ii) Electronegativity
It is the ability of an atom to attract the shared pair of electrons in a chemical bond towards itself.

(iii) Polarisation
It refers to the distortion of the electron cloud of an anion by a cation.

(iv) Polarising power
The ability of a cation to distort the electron cloud of an anion. It increases with charge density (charge/size ratio).

(b) Consider the following ions:
F^-, Na^+, K^+, O^{2-}, Mg^{2+}

(i) Increasing ionic size:
$Mg^{2+} < Na^+ < K^+ < F^- < O^{2-}$

(ii) Increasing polarising power:
$O^{2-} < F^- < K^+ < Na^+ < Mg^{2+}$

(iii) Increasing Polarisability:
$Mg^{2+} < Na^+ < K^+ < F^- < O^{2-}$

(c) Outline the unique features of nitrogen (^{14}N) as compared to other Group V elements:
- Small size and high electronegativity
- Strong tendency to form multiple bonds (e.g., $N\equiv N$)
- No d-orbitals available for bonding
- Forms stable π-bonds (e.g., in N_2, NO_2^-)
- Exists as diatomic gas (N_2) unlike P, As, Sb which exist as polyatomic molecules

These features make nitrogen's chemistry distinct from that of the other members of the group.

6 (a) Name the three most abundant elements in nature.
- Oxygen
- Silicon
- Aluminium

(b) Give the names and formulae of three common ores from which each of the following elements is extracted:

(i) Aluminium:
- Bauxite ($Al_2O_3 \cdot 2H_2O$)
- Cryolite (Na_3AlF_6)
- Corundum (Al_2O_3)

(ii) Manganese:
- Pyrolusite (MnO_2)
- Manganite ($Mn_2O_3 \cdot H_2O$)
- Rhodochrosite ($MnCO_3$)

(c) One of the above two named elements is used in the extraction of the other. Use equations to show how this extraction occurs from a named ore.
Aluminium is used to extract manganese from its oxide:
$3MnO_2 + 4Al \text{ ----> } 3Mn + 2Al_2O_3$

(d) Compare and contrast the chemistry of these two elements in:

(i) Formation and nature of ions:
- Aluminium forms Al^{3+} (small, highly charged, strong polarising power)
- Manganese forms multiple oxidation states: Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{7+}

(ii) Their affinity for oxygen:
- Aluminium forms stable oxide (Al_2O_3), amphoteric in nature
- Manganese forms multiple oxides (MnO, Mn_2O_3, MnO_2, Mn_2O_7), some are basic, some acidic

(iii) Nature of their chlorides:
- $AlCl_3$ is covalent and hydrolyses in water
- $MnCl_2$ is ionic and stable in water

(iv) Nature of their oxides:
- Aluminium oxide (Al_2O_3) is amphoteric
- Manganese oxides range from basic (MnO) to acidic (Mn_2O_7)

7 (a) Complex compounds can sometimes exhibit isomerism. The compound $[Co(NH_3)_5Br]SO_4$ is isomeric with $[Co(NH_3)_5SO_4]Br$.

(i) Give the IUPAC name for each isomer:
- $[Co(NH_3)_5Br]SO_4$: Pentaamminebromidocobalt(III) sulfate
- $[Co(NH_3)_5SO_4]Br$: Pentaamminesulfatocobalt(III) bromide

(ii) What ions will each isomer yield in solution?
- $[Co(NH_3)_5Br]SO_4$: $[Co(NH_3)_5Br]^{2+}$ and SO_4^{2-}

- $[Co(NH_3)_5SO_4]Br$: $[Co(NH_3)_5SO_4]^+$ and Br^-

(iii) What is the oxidation state and the coordination number of cobalt in each complex?
- Oxidation state: +3
- Coordination number: 6 (5 NH_3 + 1 ligand)

(iv) How can you distinguish the two isomers?
- By precipitation test with $AgNO_3$: $[Co(NH_3)_5SO_4]Br$ gives white AgBr precipitate; the other does not.

(b) Explain in terms of electronic configuration why iron (atomic number 26):

(i) Conducts electricity
- Iron has delocalized electrons in its 4s orbital that move freely, allowing conduction.

(ii) State which oxidation state is most stable and why.
- +3 is most stable due to half-filled $3d^5$ configuration (greater stability due to symmetrical distribution of electrons).

(c) Write the formula for each of the following complexes:

(i) Tetrammine copper(II) sulfate monohydrate: $[Cu(NH_3)_4]SO_4 \cdot H_2O$
(ii) Potassium heptoxodichromate(VI): $K_3Cr_2O_7$
(iii) Trichlorotriammine platinum(IV) chloride: $[Pt(NH_3)_3Cl_3]Cl$

(d) Explain how atomic size, ionization energy, and electron affinity vary along the period in the periodic table.
- Atomic size decreases across the period due to increasing nuclear charge.
- Ionization energy increases due to stronger attraction between nucleus and electrons.
- Electron affinity becomes more negative due to increasing nuclear attraction for added electrons.

8 (a) Show how ethanol reacts with:

(i) Hydroxylamine:
$CH_3CH_2OH + NH_2OH$ ----> (No significant reaction unless ethanol is oxidized to acetaldehyde, which then forms oxime)

(ii) Phenylhydrazine:
Ethanol reacts only if oxidized first to aldehyde; the aldehyde then forms hydrazone with phenylhydrazine.
$CH_3CH_2OH \rightarrow CH_3CHO + [O]$
$CH_3CHO + C_6H_5NHNH_2$ ----> $CH_3CH{=}N{-}NH{-}C_6H_5$

(iii) Excess mixture of sodium hydroxide and iodine (Iodoform test):
$CH_3CH_2OH \rightarrow CH_3CHO \rightarrow CHI_3$ (yellow ppt) + $HCOONa$

Ethanol gives a positive iodoform test.

(iv) A mixture of amalgamated zinc and concentrated hydrochloric acid (reduction conditions):
Not a typical reaction for ethanol; no effect unless ethanol acts as substrate for reduction (rare).

(v) Sodium hydrogensulphite:
No reaction occurs directly with ethanol; bisulphite addition typically occurs with aldehydes or ketones.

(b) Identify the more acidic compound and give reasons:

(i) $CH_2ClCOOH$ vs $CH_2BrCOOH$
$CH_2BrCOOH$ is more acidic because Br is more electronegative than Cl and exerts a stronger -I effect, stabilizing the carboxylate ion.

(ii) CH_2FCH_2COOH vs $CH_3CHBrCOOH$
$CH_3CHBrCOOH$ is more acidic due to the closer proximity of Br to the –COOH group than F in CH_2FCH_2COOH, hence stronger inductive effect.

(iii) $CH_3–C_6H_4–COOH$ vs $HOOC–C_6H_4–NO_2$
$HOOC–C_6H_4–NO_2$ is more acidic due to the presence of an electron-withdrawing NO_2 group, which stabilizes the carboxylate ion.

(c) Consider the following organic compounds and answer:
Q and S contain alkyl halides (alkyl chlorides), which ionize to release Cl^-. When $AgNO_3$ is added, Cl^- forms white precipitate of AgCl.
R and T contain aryl chlorides (C–Cl attached to benzene), which are covalently bonded and do not ionize easily in solution, hence no Cl^- ions are free to react with $AgNO_3$.

(d) Explain why alkylation of nitrobenzene is slower than methylbenzene:
Nitrobenzene contains an electron-withdrawing group (NO_2) that deactivates the benzene ring, making it less reactive toward electrophilic substitution (alkylation). In contrast, methylbenzene has an electron-donating methyl group that activates the ring, facilitating substitution.

9 (a) Complete the following equations:
(i) $R–COOH + NaHCO_3$ ----> $R–COONa + CO_2 + H_2O$
(ii) $R–COOH + PCl_3$ ----> $R–COCl + HCl + H_3PO_3$
(iii) $R–COOH + LiAlH_4$ ----> $R–CH_2OH$
(iv) $R–COOH + NaOH$ ----> $R–COONa + H_2O$
(v) $C_6H_5CH_3 + Cl_2$ ----> $C_6H_4CH_2Cl + HCl$

(b) Give the IUPAC names of the following compounds:

(i) $H_2NCH_2CH_2NH_2$ ---> Ethane-1,2-diamine

(ii) $(CH_3CO)_2O$ ----> Acetic anhydride or ethanoic anhydride
(iii) $CH_2=CHCN$ ---> Prop-2-enenitrile or acrylonitrile
(iv) $NH_2CH(CH_3)COOH$ ---> 2-Aminopropanoic acid (Alanine)
(v) $C_6H_5N(CH_3)_2$ ---> N,N-dimethylaniline

10. (a) The names below are incorrect according to the IUPAC system. Draw the structural formula for each compound named and give its correct IUPAC name.

(i) 2,2-Dimethyl-3-pentene
Structure: $CH_2=C(CH_3)-CH_2-CH(CH_3)_2$
Correct IUPAC name: 3,3-Dimethyl-1-pentene

(ii) 2-Methyl-4-heptene
Structure: $CH_3-CH_2-CH=CH-CH(CH_3)-CH_2-CH_3$
Correct IUPAC name: 4-Methyl-2-heptene

(iii) 2,2,3-Methylbutane
Structure: $CH_3-C(CH_3)_2-CH(CH_3)-CH_3$
Correct IUPAC name: 2,2,3-Trimethylbutane

(iv) 3-Ethyl-4-methylpentane
Structure: $CH_3-CH(CH_2CH_3)-CH(CH_3)-CH_2-CH_3$
Correct IUPAC name: 3-Ethyl-2-methylpentane

(b) Give the expected product(s) from the reaction of 2-butene with each of the following reagents:

(i) $H^+/H_2O \rightarrow$ Butan-2-ol (Markovnikov addition)
(ii) H_2 / catalyst → Butane (hydrogenation)
(iii) $Cl_2 \rightarrow$ 2,3-Dichlorobutane (halogen addition)
(iv) HOCl → 3-Chlorobutan-2-ol (halohydrin formation)
(v) O_2 / flame → $CO_2 + H_2O$ (complete combustion)

(c) Reaction sequence:

P: C_4H_6 = Butyne
P + H_2O/H^+ --->Q: Butan-2-one (C_4H_8O)
Q + $SOCl_2$ ---> R: 2-Chlorobutane (C_4H_9Cl)
R + Mg/ether ---> S: Butyl magnesium chloride (C_4H_9MgCl)
S + CH_3OH ---> T: Pentan-2-ol ($C_5H_{12}O$)
T + [O] $KMnO_4$ ---> U: Pentanoic acid ($C_5H_{10}O_2$)
U + $SOCl_2$ ---> V: Pentanoyl chloride (C_5H_9ClO)
V + C_6H_6 / $AlCl_3$ ---> W: Benzene derivative ($C_{10}H_{12}O$) = Phenylpentanone or phenylpentanoate depending on conditions

Structural formulae:

$P = CH\equiv C{-}CH_2{-}CH_3$

$Q = CH_3{-}CO{-}CH_2{-}CH_3$

$R = CH_3{-}CHCl{-}CH_2{-}CH_3$

$S = CH_3{-}CH(MgCl){-}CH_2{-}CH_3$

$T = CH_3{-}CH(OH){-}CH_2{-}CH_2{-}CH_3$

$U = CH_3{-}CH_2{-}CH_2{-}CH_2{-}COOH$

$V = CH_3{-}CH_2{-}CH_2{-}CH_2{-}COCl$

$W = C_6H_5{-}CO{-}CH_2{-}CH_2{-}CH_2{-}CH_3$