THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2011**

Instructions

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

1. (a) Using the Brønsted–Lowry theory, define
(i) an acid – A substance that donates a proton (H^+) to another species.
(ii) a base – A substance that accepts a proton (H^+) from another species.

(b) Predict and explain whether the following salts will be acidic, basic or neutral:
(i) $CuSO_4$ – Acidic. Cu^{2+} is a transition metal ion that hydrolyzes water to produce H^+.
(ii) NaCN – Basic. CN^- is the conjugate base of a weak acid (HCN), so it accepts H^+.
(iii) NH_4Cl – Acidic. NH_4^+ is a conjugate acid of a weak base (NH_3), so it donates H^+.
(iv) $NaNO_3$ – Neutral. Both Na^+ and NO_3^- come from strong base and strong acid.

(c) Calculate the equilibrium constant of the reaction between cobalt and nickel from standard redox potentials at 25°C.
$Ni^{2+}(aq) + 2e^- \text{---->} Ni(s) \quad E° = -0.250\ V$
$Co^{2+}(aq) + 2e^- \text{---->} Co(s) \quad E° = -0.277\ V$
E°cell = E°(cathode) - E°(anode) = -0.250 - (-0.277) = 0.027 V
ΔG° = -nFE°cell = -2 × 96500 × 0.027 = -5202 J = -5.202 kJ
ΔG° = -RTlnK
lnK = -ΔG° / RT = 5202 / (8.314 × 298) = 2.096
$K = e^{2.096} \approx 8.13$

2. (a) What is a half-life of a reaction?
It is the time required for the concentration of a reactant to reduce to half of its initial value.

(b) Consider the reaction $H_2(g) + I_2(g) \text{---->} 2HI(g)$
$K_1 = 1.4 \times 10^{-3}$ at 317°C, $K_2 = 6.4 \times 10^{-2}$ at 427°C
Using Arrhenius equation:
$\ln(K_2/K_1) = Ea/R \times (1/T_1 - 1/T_2)$
$\ln(6.4 \times 10^{-2} / 1.4 \times 10^{-3}) = Ea / 8.314 \times (1/590 - 1/700)$
ln(45.71) = Ea / 8.314 × (0.0016949 - 0.0014286)
3.823 = Ea / 8.314 × 0.0002663
Ea = 3.823 × 8.314 / 0.0002663 ≈ 119400 J/mol = 119.4 kJ/mol

(c) Order of reaction determination using table:
Rate = k[Z]^m[Y]^n

From exp 1 and 2 (Z constant, Y changes)
0.00798 / 0.00200 = (0.200 / 0.100)^n
3.99 = 2^n
n = 2

From exp 1 and 3 (Y constant, Z changes)
0.01805 / 0.00200 = (0.200 / 0.100)^m
9.025 = 2^m

$m \approx 3.17 \approx 3$
So:
Order with respect to Y = 2
Order with respect to Z = 3
Overall order = 5

(d) (i) Rate = $k[Z]^3[Y]^2$
Use experiment 1:
$0.00200 = k(0.100)^3(0.100)^2$
$k = 0.00200 / (1.0 \times 10^{-7}) = 2.0 \times 10^4\ mol^{-4}dm^{12}min^{-1}$

(ii) Units of k = $mol^{-4}dm^{12}min^{-1}$

3. (a) pH of 0.01 M NaF
Kb for F^- = Kw / Ka of HF = $1 \times 10^{-14} / 6.4 \times 10^{-4} \approx 1.56 \times 10^{-11}$
$[OH^-] = \sqrt{(Kb \times C)} = \sqrt{(1.56 \times 10^{-11} \times 0.01)} = 1.25 \times 10^{-6}$
pOH = $-\log(1.25 \times 10^{-6}) \approx 5.9$
pH = 14 - 5.9 = 8.1

pH of 0.10 M NH_3
Kb = 1.77×10^{-5}
$[OH^-] = \sqrt{(1.77 \times 10^{-5} \times 0.10)} = \sqrt{1.77 \times 10^{-6}} \approx 1.33 \times 10^{-3}$
pOH = 2.88
pH = 11.12

(b) Solubility of CaF_2 in 0.025 M NaF
$Ksp = [Ca^{2+}][F^-]^2$
$4.0 \times 10^{-11} = x \times (0.025)^2 = x \times 6.25 \times 10^{-4}$
$x = 4.0 \times 10^{-11} / 6.25 \times 10^{-4} = 6.4 \times 10^{-8}$ mol/L

4. (a) Define:
(i) Hess' law – Total enthalpy change of a reaction is the same regardless of the pathway.
(ii) Standard enthalpy of formation – Heat change when one mole of compound forms from its elements under standard conditions.
(iii) Standard enthalpy of neutralization – Heat evolved when one mole of H^+ reacts with one mole of OH^- under standard conditions.

(b) (i)
$\Delta H_1°$ – Atomization of Mg
$\Delta H_2°$ – Ionization of Mg
$\Delta H_3°$ – Atomization of Cl_2
$\Delta H_4°$ – Electron affinity of Cl
$\Delta H_5°$ – Lattice energy of $MgCl_2$

$\Delta H_6°$ – Enthalpy of formation

(ii) $\Delta Hf = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$
= (+242) + (+1448) + (+736) + (-146) + (-1948) = -658 kJ/mol

(c) Comparison of MgCl and $MgCl_3$
MgCl: ΔHf = -110 kJ/mol
$MgCl_3$: ΔHf = +4000 kJ/mol
$MgCl_2$ is energetically most stable as it has most negative enthalpy of formation. MgCl and $MgCl_3$ are less stable due to incomplete/over-ionization or electron repulsion.
Thanks. Let's continue with the solutions.

5. (a) Study the following cathode processes:
(i) $Ag^+(aq) + e^-$ ----> Ag(s)
(ii) $Cu^{2+}(aq) + 2e^-$ ----> Cu(s)
Interpretation:
Metals are deposited at the cathode by gaining electrons (reduction). The number of electrons required depends on the oxidation state of the metal ion. Ag^+ requires 1 electron, Cu^{2+} requires 2 electrons. This also shows that Cu^{2+} is more electropositive than Ag^+.

(b) Whereas metals are deposited at the cathode electrode, nonmetals are liberated at the anode electrode. Explain this electrolytic phenomenon.
At the cathode, cations migrate and gain electrons (reduction) to become neutral metal atoms. At the anode, anions lose electrons (oxidation) to form neutral non-metal molecules such as Cl_2, O_2, or Br_2.

(c) Explain why H^+ ions cannot exist in solution.
Free H^+ ions are extremely small and highly reactive. In aqueous solution, they are immediately hydrated to form hydronium ions (H_3O^+), or even further hydrated as $H_5O_2^+$, $H_9O_4^+$ etc. Hence, H^+ does not exist alone but always as hydrated complexes.

(d) A metal of relative atomic mass 27 is deposited by electrolytic decomposition of its solution. If 0.176 g of the metal is deposited when a current of 0.15 amperes flows for 3½ hours, what is the charge on the cation of this metal?
Step 1: Calculate moles of metal = 0.176 / 27 = 0.00652 mol
Step 2: Charge passed = current × time = 0.15 A × 3.5 h × 3600 s = 1890 C
Faraday = 96500 C/mol
Moles of electrons = 1890 / 96500 = 0.0196 mol
Charge per atom = mol of electrons / mol of metal = 0.0196 / 0.00652 = 3
Therefore, the metal ion has a charge of 3^+
the metal is likely Aluminium (Al^{3+})

6. (a) Describe the four main features of a coordination compound.
- Central metal ion or atom

- Ligands surrounding the central metal
- Coordination number – number of ligand atoms bonded to metal
- Geometry of the complex

(b) (i) Differentiate between coordination number and coordination geometry.
Coordination number is the total number of ligand atoms directly bonded to the central metal. Coordination geometry is the spatial arrangement of the ligands around the central atom (e.g., octahedral, tetrahedral).

(ii) Use sketch diagrams to differentiate the orientation of the 3d atomic orbitals in space.
3d orbitals have distinct shapes:
- dxy, dxz, dyz – between axes in a clover shape
- $dx^2–y^2$ – along x and y axes
- dz^2 – along z axis (dumbbell with torus)

(c) Draw the geometrical structures of the following complexes:
(i) $Ni(CN)_4^{3-}$ – Square planar
(ii) $CuCl_2$ – Linear (or possibly bent depending on ligand field)

(d) Show that
(i) hexaaquatitanium (III) ion is a paramagnetic complex – Ti^{3+} has $3d^1$ configuration, hence has one unpaired electron
paramagnetic.
(ii) hexaminecobalt (III) ion is diamagnetic – Co^{3+} is $3d^6$, in low spin octahedral field, all electrons are paired
diamagnetic.

7. (a) Define the following terms:
(i) Buffer solution – A solution that resists changes in pH upon addition of small amounts of acid or base.
(ii) Standard solution – A solution of known concentration.
(iii) Molarity – Moles of solute per liter of solution.

(b) A standard solution is made by dissolving 1.185 g of potassium dichromate (VI) in 250 cm^3 solution. A 25 cm^3 aliquot of oxidant is titrated against sodium thiosulphate.
Balanced equation:
$Cr_2O_7^{2-} + 6 I^- + 14 H^+$ ----> $3 I_2 + 2 Cr^{3+} + 7 H_2O$
$I_2 + 2 S_2O_3^{2-}$ ----> $2 I^- + S_4O_6^{2-}$
Molar mass of $K_2Cr_2O_7$ = 294 g/mol
Moles = 1.185 / 294 = 0.00403 mol
Molarity = 0.00403 mol / 0.250 L = 0.0161 mol/L
25 cm^3 = 0.025 L → moles = $0.0161 \times 0.025 = 4.03 \times 10^{-4}$ mol
Moles of $I_2 = 3 \times 4.03 \times 10^{-4} = 1.209 \times 10^{-3}$ mol
Moles of $S_2O_3^{2-} = 2 \times$ moles $I_2 = 2.418 \times 10^{-3}$ mol
Concentration = 2.418×10^{-3} mol / 0.020 L = 0.121 mol/L

(c) A chemist prepares 1 L buffer solution at pH 9.0.
Using Henderson-Hasselbalch equation:
pH = pKa + log([salt]/[acid])
9.0 = 4.74 + log(x / 0.20)
log(x / 0.20) = 4.26
x / 0.20 = $10^{4.26} \approx 1.82 \times 10^4$
x = 3640 mol not practical. Possibly a calculation error; this pH is too high for NH_4^+/NH_3 buffer system. Likely requires reconsideration or stronger base.

8. (a) Name the following compounds according to IUPAC system:
(i) CH_3-CH_2-CH_2Br
Name: 1-Bromopropane

(ii)
$(CH_3)_2CHCH_2Br$
Name: 1-Bromo-2-methylpropane

(iii)
$C_6H_5CH_2CH_2Br$
Name: 1-Phenylethyl bromide

(iv)
$C_6H_5NO_2$
Name: Nitrobenzene

(b) Write the products for the following reactions:

(i) $CH_3CH_2CH_2Br$ + NaOH(aq)
$CH_3CH_2CH_2OH$ + NaBr
Product: Propan-1-ol

(ii) $C_6H_5CH_2Cl + H_2O$
$C_6H_5CH_2OH$ + HCl
Product: Benzyl alcohol

(iii) $CH_3CH_2CH_2Br$ + NaSH
$CH_3CH_2CH_2SH$ + NaBr
Product: Propane-1-thiol

(iv) $CH_3CH_2Br + Na^+C{\equiv}C^-$
$CH_3CH_2C{\equiv}CH$ + NaBr
Product: But-1-yne

(v) $CH_3CH_2Br + Na^+OCH_2CH_3^-$
$CH_3CH_2OCH_2CH_3 + NaBr$
Product: Ethoxyethane (Diethyl ether)
9. (a) An unknown compound C ($C_5H_{10}O$) is insoluble in water. Compound C reacts with excess HI to give acidic compound D ($C_5H_{10}O$) and ethyl iodide. Give the structural formulae of compounds C and D and the equation of the reaction.

Since compound C gives ethyl iodide upon reaction with excess HI, it indicates that C contains an ethoxy group ($-OCH_2CH_3$), hence C is ethoxypropane ($CH_3CH_2OCH_2CH_2CH_3$).
Compound D is pentanoic acid ($CH_3CH_2CH_2CH_2COOH$).

Reaction:
$CH_3CH_2OCH_2CH_2CH_3$ + HI ----> $CH_3CH_2I + CH_3CH_2CH_2CH_2COOH$

(b) Show the mechanism of each of the following reactions:

(i) Friedel–Crafts acylation to form acetophenone:
$C_6H_6 + CH_3COCl$ (in presence of $AlCl_3$) ----> $C_6H_5COCH_3 + HCl$
Mechanism involves generation of acylium ion ($CH_3C^+{=}O$) which acts as electrophile attacking benzene ring.

(ii) Formation of nitronium ion when concentrated nitric acid and concentrated sulphuric acid react together:
$HNO_3 + H_2SO_4$ ----> $NO_2^+ + HSO_4^- + H_2O$
Mechanism involves protonation of nitric acid by sulphuric acid followed by loss of water forming NO_2^+.

(iii) Reaction between methylmagnesium bromide and carbon dioxide to form ethanoic acid:
$CH_3MgBr + CO_2$ ----> $CH_3COOMgBr$
$CH_3COOMgBr + H_2O$ ----> $CH_3COOH + Mg(OH)Br$

(iv) Stabilization of phenoxide ion by mesomerism:
Phenoxide ion shows delocalization of negative charge over ortho and para positions of benzene ring via resonance, increasing its stability.

10. (a) Write the structural formula for each of the following compounds:

(i) 2,4-dichloro-1-hexanol:
$CH_3CH(Cl)CH_2CH(Cl)CH_2CH_2OH$

(ii) 1,2-dimethoxyethane:
$CH_3OCH_2CH_2OCH_3$

(iii) 2-chlorobutanal:

$CH_3CH(Cl)CH_2CHO$

(iv) Cyclobutanone:
A four-membered cyclic ketone, represented as a square with a carbonyl (C=O) group attached.
(b) Indicate the monomers and the polymerization method which are likely used in making each of the following commercial polymers.

(i) Structure corresponds to polystyrene, formed from styrene ($C_6H_5CH=CH_2$) via addition polymerization.

(ii) Structure corresponds to polytetrafluoroethylene (PTFE), formed from tetrafluoroethylene ($CF_2=CF_2$) via addition polymerization.

(iii) Structure corresponds to Nylon-6,10, formed from hexamethylenediamine ($NH_2(CH_2)_6NH_2$) and sebacoyl chloride ($ClOC(CH_2)_8COCl$) via condensation polymerization.

(c) Describe the reaction which takes place during vulcanization of raw rubber. What changes in physical properties accompany this process? What would happen if the proportion of sulfur used in vulcanization is very large?

Vulcanization is the process of cross-linking rubber molecules with sulfur to improve elasticity, strength, and durability. The reaction involves forming disulfide (S-S) bonds between polymer chains of natural rubber (polyisoprene), which enhances its resilience and heat resistance.

Changes in physical properties:
- Increased elasticity and tensile strength.
- Improved resistance to wear, heat, and oxidation.
- Reduced stickiness and increased durability.

If too much sulfur is used, the rubber becomes excessively hard and brittle, losing its flexibility and resilience.