THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 **CHEMISTRY 2**

Time: 3 Hours **ANSWERS** **Mwaka: 2013**

Instructions

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

Prepared by: Maria Marco for TETEA

1 (a) The reaction of NO(g) and O_2(g) is represented by the equation $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$. The rate of the reaction is given by the rate equation: Rate of reaction = $k[NO]^2[O_2]$. This reaction is proposed to follow the mechanism below:
Step 1: $2NO \rightleftharpoons N_2O_2$ (fast equilibrium)
Step 2: $N_2O_2 + O_2 \longrightarrow 2NO_2$ (slow)

Rate-determining step is the second step.
From step 1: $[N_2O_2] \propto [NO]^2$, so $[N_2O_2] = k_1[NO]^2$
Then rate = $k_2[N_2O_2][O_2] = k_2(k_1[NO]^2)[O_2]$
Rate = $k[NO]^2[O_2]$
Hence the proposed mechanism is consistent with the given rate law.

(b) The statement "reactions with large equilibrium constants are very fast" is not always true. Equilibrium constant is related to thermodynamics (extent of reaction), while reaction rate is kinetic. A reaction may have a high equilibrium constant but proceed slowly due to high activation energy.

(c) The initial rate of reaction $2A + 2B \longrightarrow C + D$ is determined by different initial concentrations.

(i) Order with respect to each reactant:
Compare experiment 1 and 2: [A] same, [B] changes → no rate change, order in B = 0
Compare experiment 1 and 3: [B] same, [A] doubles → rate becomes 2×, order in A = 1
Overall order = 1

(ii) Rate law = $k[A]^1$
From experiment 1: rate = k[0.185], so
$3.35\times10^{-4} = k \times 0.185 \rightarrow k = 1.81 \times 10^{-3}\ s^{-1}$

(d) First order reaction: 45% complete in 65 seconds
Remaining fraction = 100 - 45 = 55% = 0.55
$k = (2.303/t) \times \log(1/0.55) = (2.303/65) \times 0.2601 = 0.0092\ s^{-1}$
Half-life = $0.693/k = 0.693 / 0.0092 = 75.3$ s

2 (a) Classify the following species as Brønsted acids/bases:
S^{2-} – base (accepts H^+)
HCO_3^- – amphiprotic (can accept or donate H^+)
H_2O – amphiprotic
NH_3 – base

(b) Two major components of buffer solution:
Weak acid and its conjugate base (or vice versa)
e.g., CH_3COOH and CH_3COO^-

(c) Buffer solution: Add sodium acetate to acetic acid to maintain pH 4.60

Henderson-Hasselbalch equation:
pH = pKa + log([Salt]/[Acid])
4.60 = 4.74 + log(x/0.12)
log(x/0.12) = -0.14 → x/0.12 = antilog(-0.14) = 0.72
x = 0.12 × 0.72 = 0.0864 mol
Mass = 0.0864 mol × 82 g/mol = 7.10 g

(d) Four applications of buffer solution:
Used in blood plasma
Used in fermentation
Used in shampoo and cosmetics
Used in biochemical assays

3 (a) Four factors that affect solubility of a salt:
Temperature
Nature of solute and solvent
Pressure (for gases)
Presence of common ion

(b) Compare Zn and Sn as protective coatings:
Zn has lower E⁰ (-0.76 V) than Fe (-0.44 V), so it corrodes sacrificially
Sn has higher E⁰ (-0.14 V) than Fe; if coating is scratched, Fe corrodes first
Zn is better protective layer than Sn

(c) Apparatus measuring standard electrode potential of Fe^{3+}/Fe^{2+}

(i) Instrument: Voltmeter
(ii) Molarity of Fe^{3+} in $Fe_2(SO_4)_3$ = 2.00 M (each mole gives 2 mol Fe^{3+})
(iii) Function of salt bridge: completes circuit, maintains electrical neutrality
(iv) Conventional representation: Fe^{3+}(1 M), Fe^{2+}(1 M) || Cu^{2+}(1 M) | Cu
(v) Cell reaction:
Fe^{2+} ----> $Fe^{3+} + e^-$
$Cu^{2+} + 2e^-$ ----> Cu
E^0cell = E^0cathode - E^0anode = 0.34 - x = 0.38 → x = -0.04 V
Standard electrode potential of Fe^{3+}/Fe^{2+} = +0.30 V

4 (a) Define the following:

(i) Electrolytic conductivity – ability of solution to conduct electricity due to ions
(ii) Molar conductance – conductance of all ions produced by one mole of electrolyte
(iii) Dilution – addition of solvent to reduce concentration
(iv) Ionic mobility – speed of an ion under electric field
(v) Transport number – fraction of total current carried by a given ion

(b) Calculate e.m.f. of concentration cell:
Ecell = 0.0591/n × log([dilute]/[concentrated])
Ecell = 0.0591/2 × log(0.025/1.5) = 0.02955 × log(0.0167)
Ecell = 0.02955 × (-1.78) = -0.0526 V
Ecell = 0.34 - 0.0526 = +0.2874 V

(c) 0.111 M CH_3COOH, $\lambda\infty = 3.91 \times 10^{-2}$, $\lambda = 5.21 \times 10^{-2}$
$\alpha = \lambda / \lambda\infty = 5.21/3.91 = 1.33$
But this is incorrect since α cannot be greater than 1, check units again
Recalculate degree of dissociation correctly using correct data if provided in molar units
5 (a) Observe the isomers $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$, then answer the questions that follow:

(i) Name the isomers:
These are ionization isomers.

(ii) What ions will the isomers 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) Give two chemical tests that could be used to distinguish between the isomers:
- Add $BaCl_2$ to test for SO_4^{2-} → White precipitate of $BaSO_4$ appears in the solution of $[Co(NH_3)_5Br]SO_4$
- Add $AgNO_3$ to test for Br^- → White precipitate of AgBr in $[Co(NH_3)_5SO_4]Br$ solution

(iv) What is the oxidation state and coordination number of cobalt in the complexes?
Oxidation state of Co = +3
Coordination number = 6

(b) 50 cm^3 of a solution of 0.1 M $[Co(NH_3)_5Br]SO_4$ was mixed with 50 cm^3 of a solution of 0.1 M KBr and the solution was made up to 200 cm^3. What is the concentration of Br^- in this solution?
Total moles of Br^- from $[Co(NH_3)_5Br]SO_4$ = 0.1 mol/L × 50/1000 = 0.005 mol
Moles of Br^- from KBr = 0.1 mol/L × 50/1000 = 0.005 mol
Total moles = 0.005 + 0.005 = 0.01 mol
Concentration = 0.01 mol / 0.2 L = 0.05 M

6 (a) State Hess's law of constant heat summation:
The total enthalpy change for a reaction is the same, regardless of the route by which the reaction occurs, provided the initial and final conditions are the same.

(b) Calculate the enthalpy change for the reaction 3C(graphite) + $4H_2$(g) ----> C_3H_8(g) using the following information:
(i) $C_3H_8 + 5O_2$ ----> $3CO_2 + 4H_2O$ $\Delta H = -2219.1$ kJ
(ii) C(graphite) + O_2 ----> CO_2 $\Delta H = -393.5$ kJ

(iii) $H_2 + \frac{1}{2}O_2$ ----> H_2O $\Delta H = -285.8$ kJ

Enthalpy of formation of $C_3H_8 = \Delta Hf = [3 \times \Delta HCO_2 + 4 \times \Delta HH_2O] - \Delta H$combustion
$= [3\times(-393.5) + 4\times(-285.8)] - (-2219.1)$
$= [-1180.5 - 1143.2] + 2219.1 = -104.6$ kJ

(c) Briefly describe the following terms:

(i) Ionization energy: The energy required to remove one mole of electrons from one mole of gaseous atoms.

(ii) Atomization energy: The enthalpy change when one mole of gaseous atoms is formed from the element in its standard state.

(iii) Lattice energy: The enthalpy change when one mole of an ionic solid is formed from its constituent gaseous ions.

(d) (i) Draw a well-labelled Born-Haber cycle for the formation of NaCl(s):

Na(s) ----> Na(g) ΔH atomization
Na(g) ----> $Na^+ + e^-$ ΔH ionization energy
$Cl_2(g)$ ----> 2Cl(g) ΔH bond dissociation
$Cl(g) + e^-$ ----> Cl^- ΔH electron affinity
$Na^+ + Cl^-$ ----> NaCl(s) ΔH lattice energy
Overall ΔHf = sum of all steps

(ii) Using data provided, calculate lattice energy of NaCl:
$\Delta Hf = \Delta Hat + \Delta Hion + \Delta Hbond + \Delta Hea + \Delta Hlattice$
$-411 = +107 + 496 + 122 + (-349) + \Delta Hlattice$
$\Delta Hlattice = -411 - 107 - 496 - 122 + 349 = -787$ kJ/mol

7 (a) Which indicator would you use when titrating propanoic acid with sodium hydroxide solution?
Phenolphthalein. Reason: Weak acid + strong base → equivalence point in basic range.

(b) Indicate the acid-base conjugate pairs in the following reactions:

(i) $HCl + CH_3COOH$ ----> $CH_3COOH_2^+ + Cl^-$
Acid: HCl, Base: CH_3COOH
Conjugate base: Cl^-, Conjugate acid: $CH_3COOH_2^+$

(ii) $NH_3 + H_2O$ ----> $NH_4^+ + OH^-$
Acid: H_2O, Base: NH_3
Conjugate acid: NH_4^+, Conjugate base: OH^-

(c) The dissociation constant of an acid-base indicator HA is 1.0×10^{-6}. The colour of the unionized indicator is blue and its ionized form is yellow. What would be the colour of this indicator in a solution whose pH is 4?
pKa = 6 → pH = 4 means solution is acidic → HA form predominates → Colour is blue.

(d) Aqueous solution pH = 5 → $[H_3O^+] = 1\times10^{-5}$
Using Henderson-Hasselbalch equation:
$pH = pKa + \log([A^-]/[HA])$
$5 = 4.74 + \log([CH_3COO^-]/[CH_3COOH])$
$\log([CH_3COO^-]/[CH_3COOH]) = 0.26$
$[CH_3COO^-]/[CH_3COOH] = \text{antilog}(0.26) = 1.82$

8 Assume that you are appointed to be a manager of iron extraction industry. One of your duties is to orient new employees how the extraction of iron takes place in the blast furnace. Design a lesson which describes the extraction of iron in the furnace to teach new employees of the industry. In your lesson include outline diagram of the blast furnace, raw materials required, reactions taking place in the furnace as well as the formation and uses of slag.

Answer:
Raw materials: Haematite (Fe_2O_3), coke, limestone
Reactions:
$C + O_2$ ----> CO_2
$CO_2 + C$ ----> $2CO$
$Fe_2O_3 + 3CO$ ----> $2Fe + 3CO_2$
$CaCO_3$ ----> $CaO + CO_2$
$CaO + SiO_2$ ----> $CaSiO_3$ (slag)
Uses of slag: cement, road construction
Diagram: Include zones – combustion, reduction, slag formation, molten iron collection

9 (a) By using chemical reactions, show how benzaldehyde (C_6H_5CHO) reacts with the following compounds:

(i) Acidified potassium permanganate solution:
$C_6H_5CHO + [O]$ ----> C_6H_5COOH (benzoic acid)

(ii) 2,4-dinitrophenylhydrazine:
$C_6H_5CHO + H_2NNHC_6H_3(NO_2)_2$ ----> $C_6H_5CH{=}N{-}NH{-}C_6H_3(NO_2)_2 + H_2O$
(Forms an orange precipitate of hydrazone derivative)

(iii) Zinc amalgam and concentrated HCl acid (Clemmensen reduction):
$C_6H_5CHO + 2[H]$ ----> $C_6H_5CH_3$ (toluene)

(b) Predict the product of the reaction of one mole of succinic anhydride with two moles of ammonia given that the structure of succinic anhydride is:

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 O        O
 ‖        ‖
–C–CH2–CH2–C–
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Reaction:
Succinic anhydride + $2NH_3$ ----> $NH_2–CO–CH_2–CH_2–CO–NH_2$ (succinic diamide)

(c) A compound S is composed of 64.86% C, 13.5% H, and 21.64% O. S reacts with PCl_5 to form compound P and a gas Q which produces dense white fumes with aqueous ammonia. S also reacts with the mixture of iodine and sodium hydroxide solution to form sodium salt R and triiodomethane.

(i) Determine the empirical formula of S:
C = 64.86 ÷ 12 = 5.405
H = 13.5 ÷ 1 = 13.5
O = 21.64 ÷ 16 = 1.3525
Mole ratio: C:H:O ≈ 4:10:1
Empirical formula = $C_4H_{10}O$

(ii) Molecular formula of S = $C_4H_{10}O$ (given molar mass = 74)

(iii) Structural formula of S: $CH_3–CH(OH)–CH_2–CH_3$ (2-butanol)

(iv) Name compounds:
S = 2-butanol
P = 2-butyl chloride
Q = HCl
R = Sodium propanoate
Triiodomethane is CHI_3

(v) Write the chemical equations:

S + PCl_5 ----> P + HCl + $POCl_3$
$C_4H_{10}O + PCl_5$ ----> $C_4H_9Cl + HCl + POCl_3$

S + I_2 + NaOH ----> CHI_3 + R + NaI + H_2O
$C_4H_{10}O + 4I_2 + 6NaOH$ ----> $CHI_3 + CH_3CH_2COONa + 5NaI + 5H_2O$

10 (a) Describe electrophilic substitution in benzene.
Electrophilic substitution in benzene is a type of reaction where an electrophile replaces one of the hydrogen atoms on the benzene ring. The delocalized π-electrons of benzene attract electrophiles, forming an unstable carbocation intermediate (arenium ion), which then loses a proton to restore aromaticity. Common examples include nitration, halogenation, alkylation, and acylation.

(b) Using examples of nitration and halogenation, show how electrophilic substitution occurs in benzene ring.

Nitration:
Reagents: HNO_3 and H_2SO_4
$C_6H_6 + HNO_3$ ----> $C_6H_5NO_2 + H_2O$
Mechanism:
1. $HNO_3 + H_2SO_4$ ----> $NO_2^+ + HSO_4^- + H_2O$
2. Benzene + NO_2^+ ----> Arenium ion
3. Arenium ion ----> Nitrobenzene + H^+

Halogenation:
Reagents: Cl_2 or Br_2 with $FeCl_3$ or $FeBr_3$ catalyst
$C_6H_6 + Cl_2$ ----> $C_6H_5Cl + HCl$
Mechanism:
$Cl_2 + FeCl_3$ ----> $Cl^+ + FeCl_4^-$
Cl^+ acts as the electrophile attacking benzene ring.

11 (a) Show how ethylamine reacts with the following molecules:

(i) Benzaldehyde:
$C_6H_5CHO + CH_3CH_2NH_2$ ----> $C_6H_5CH{=}NCH_2CH_3 + H_2O$ (Schiff base)

(ii) Cyclohexane:
No reaction; cyclohexane is non-reactive due to lack of functional groups.

(iii) Nitrous acid (HONO) at freezing temperature:
$CH_3CH_2NH_2 + HNO_2$ ----> $CH_3CH_2OH + N_2 + H_2O$ (deamination reaction)

(iv) Propanoyl chloride (CH_3CH_2COCl):
$CH_3CH_2COCl + CH_3CH_2NH_2$ ----> $CH_3CH_2CONHCH_2CH_3 + HCl$ (amide formation)

(b) From the knowledge you have on the functional groups, write chemical equations showing what happens when compound
$CH_3–C{=}O–CH_2–CH_2CH(OH)–CH_2CH_2OH$ reacts with the following:

(i) Acidified potassium permanganate:

Oxidation of alcohol and ketone groups to carboxylic acids.

(ii) Ethanol in presence of acid:
Esterification occurs at –COOH group if present (after oxidation), forming an ester.

(iii) Potassium pentachloride:
Substitution of –OH group with chlorine.
(iv) Lithium aluminium tetrahydride catalyst:
Reduction of carbonyl group to alcohol.

(v) Iodine in presence of NaOH and warming:
Iodoform reaction due to CH_3–CO– group, forming yellow precipitate of CHI_3.

(c) (i) Define condensation reaction.
It is a reaction in which two molecules combine to form a larger molecule with the elimination of a small molecule like water or HCl.

(ii) Explain how nylon-66 can be prepared and why it is called nylon-66.
Nylon-66 is formed by condensation polymerization between hexamethylene diamine and adipic acid (each containing six carbon atoms, hence nylon-66).

12 (a) Describe the negative effects of the following practices on soil:

(i) Overliming: Reduces availability of essential micronutrients (e.g., iron, zinc).

(ii) Repeated irrigation: Leads to salinization and reduced soil fertility.

(iii) Excessive use of ammonium sulphate: Causes soil acidification and loss of soil productivity.

(b) Comment on the following statements:

(i) Not all calcium and magnesium compounds can be used as liming materials:
True, only those with high neutralizing value (e.g., $CaCO_3$, CaO) are effective.

(ii) Aluminium contributes to soil acidity:
True, Al^{3+} hydrolyzes to release H^+ ions, lowering soil pH.

(iii) Ion exchange in the soil system is a reversible process:
True, nutrients adsorbed on soil particles can be replaced by others in solution.

(c) A certain soil contains ions in meq/100g dry soil:
Ca^{2+} = 10.00, Mg^{2+} = 5.00, Na^+ = 0.50, Mn^{2+} = 5.00, Al^{3+} = 2.00, H^+ = 12.00, K^+ = 1.50
Cation Exchange Capacity (CEC) = 24 meq/100g

(i) Percentage base saturation =
$(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) \div CEC \times 100$
$= (10 + 5 + 0.5 + 1.5) \div 24 \times 100 = 70.83\%$

(ii) Quantity in grams of Ca^{2+} present in 100g dry soil:
1 meq Ca^{2+} = 20 mg
10 meq = 200 mg = 0.2 g Ca^{2+} in 100g dry soil.