THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/2 CHEMISTRY 2

Time: 3 Hours ANSWERS Mwaka: 2003

Instructions

1. This paper consists of a total of six questions

2. Answer five questions.

1 (a)(i) Define the term dynamic equilibrium

Dynamic equilibrium is the state in a reversible chemical reaction in which the rate of the forward reaction is equal to the rate of the reverse reaction, and the concentrations of reactants and products remain constant over time, although the reactions continue to occur.

(ii) State the equilibrium law

The equilibrium law states that at constant temperature, the ratio of the product of the concentrations of the products raised to the power of their respective stoichiometric coefficients to the product of the concentrations of the reactants raised to the power of their stoichiometric coefficients is a constant known as the equilibrium constant (Kc).

1 (b) Given the following system at equilibrium:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -188.0$ kJ mol^{-1}

Predict the change of the concentration of SO_3 if:

(i) The pressure of the system is increased

When pressure increases, the equilibrium will shift toward the side with fewer moles of gas to reduce the pressure. Since the forward reaction has fewer gas moles (3 moles → 2 moles), equilibrium shifts forward and concentration of SO_3 increases.

(ii) A noble gas is added such that the pressure of the system increases but no volume changes occur

Adding a noble gas at constant volume does not change the partial pressures of the reacting gases, so there is no effect on the equilibrium and the concentration of SO_3 remains unchanged.

(iii) More SO_3 is added to the system

Adding more SO_3 increases the concentration of product, and according to Le Chatelier's principle, the equilibrium will shift backward (reverse reaction favored) to reduce the concentration of SO_3.

(iv) The temperature of the system is increased

The forward reaction is exothermic (releases heat). Increasing temperature shifts equilibrium in the endothermic direction (backward), so the concentration of SO_3 decreases.

1 (c) Consider the decomposition of phosphorus pentachloride:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Derive an expression which relates Kp and Kc for the above equilibrium where Kp and Kc are the equilibrium constants in terms of pressure and concentration respectively.

$Kp = Kc \times (RT)^{\Delta n}$

where Δn = moles of gaseous products - moles of gaseous reactants

In this case, $\Delta n = 2 - 1 = 1$

So, $Kp = Kc \times RT$

1 (d) At 500°C, the reaction between nitrogen and hydrogen to form ammonia has $K_c = 8.0 \times 10^{-2}$
Calculate its Kp value.

The reaction is:
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
$\Delta n = 2 - (1+3) = -2$
Kp = Kc × (RT)^Δn
$K_p = K_c \times (RT)^{-2}$

Assuming R = 0.0821 atm·dm³·mol⁻¹·K⁻¹ and T = 773 K (500°C = 773 K)
$K_p = 8.0 \times 10^{-2} \times (0.0821 \times 773)^{-2}$
$= 8.0 \times 10^{-2} \times (63.44)^{-2}$
$= 8.0 \times 10^{-2} \div 4023.4$
$= 1.99 \times 10^{-5}$
$K_p \approx 2.0 \times 10^{-5}$

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

2 (b) By using Hess's Law, calculate the standard enthalpy of formation of methane (CH_4) given that its standard enthalpy of combustion is –890 kJ mol^{-1}, the standard enthalpy of combustion of carbon graphite is –393.5 kJ mol^{-1}, and the enthalpy of formation of water is –285.9 kJ mol^{-1}.

$CH_4 + 2O_2$ ----> $CO_2 + 2H_2O$ ΔH = –890 kJ
$C + O_2$ ----> CO_2 ΔH = –393.5 kJ
$H_2 + ½O_2$ ----> H_2O ΔH = –285.9 kJ (per mole), for 2 moles H_2O it becomes –571.8 kJ

$\Delta H_f(CH_4) = [\Delta H_c(C) + 2\Delta H_c(H_2)] - \Delta H_c(CH_4)$
$= (-393.5 + -571.8) - (-890)$
$= -965.3 + 890$
$= -75.3$ kJ mol^{-1}

2 (c) When 1.0 g of anhydrous copper (II) sulphate ($CuSO_4$) was dissolved in a large amount of water, 0.418 kJ of heat were liberated. When 5.0 g of copper (II) sulphate pentahydrate crystals were dissolved in a large amount of water, 0.230 kJ of heat were absorbed. From this data calculate the heat change Z of the following reaction:
$CuSO_4(s) + 5H_2O(l)$ ----> $CuSO_4 \cdot 5H_2O(s)$ ΔH = Z kJ mol^{-1}

Molar mass of $CuSO_4$ = 159.5 g/mol
Moles of $CuSO_4$ = 1.0 ÷ 159.5 = 0.00627 mol

Heat per mole = 0.418 ÷ 0.00627 = 66.67 kJ/mol

Molar mass of $CuSO_4 \cdot 5H_2O$ = 249.5 g/mol
Moles = 5.0 ÷ 249.5 = 0.020 mol
Heat per mole = 0.230 ÷ 0.020 = 11.5 kJ/mol

$\Delta H = -66.67 - (+11.5) = -78.17$ kJ/mol

3 (a)
(i) Hard water becomes soft when washing soda ($Na_2CO_3 \cdot 10H_2O$) is added
Because Na_2CO_3 reacts with Ca^{2+} or Mg^{2+} ions forming insoluble $CaCO_3$ or $MgCO_3$ precipitates.
$Ca^{2+} + CO_3^{2-}$ ----> $CaCO_3(s)$

(ii) Iodine is sparingly soluble in water but dissolves readily in presence of iodide ions
Because I_2 forms I_3^- ion with I^-: $I_2 + I^-$ ----> I_3^-

(iii) Lead(IV) oxide forms bright yellow liquid in excess cold concentrated HCl
$PbO_2 + 4HCl$ ----> $PbCl_4 + 2H_2O$

(iv) Effervescence of a colorless gas when $NaHCO_3$ is added to copper(II) sulphate solution
$NaHCO_3$ reacts with acid producing CO_2:
$NaHCO_3 + H_2SO_4$ ----> $NaHSO_4 + CO_2 + H_2O$

(v) Mercury(I) iodide is soluble in potassium iodide solution but not in water
Due to formation of soluble complex: $Hg_2I_2 + 2I^-$ ----> $2[HgI_2]^-$

(vi) The pink solution of cobalt(II) chloride turns blue when concentrated HCl is added
Due to formation of blue $CoCl_4^{2-}$ complex:
$[Co(H_2O)_6]^{2+} + 4Cl^-$ ----> $[CoCl_4]^{2-} + 6H_2O$

(vii) When water is sprayed into dry mixture of SO_2 and H_2S, yellow solid is formed
$SO_2 + 2H_2S$ ----> $3S + 2H_2O$

(viii) Aqueous $AlCl_3$ is acidic to litmus
Al^{3+} hydrolyzes water forming H_3O^+:
$Al^{3+} + 3H_2O$ ----> $Al(OH)_3 + 3H^+$

(ix) HCl prevents precipitation of copper(II) sulphide from copper(II) salt solutions
Because HCl increases H^+ concentration which suppresses S^{2-} formation.

(x) Effervescence occurs when ammonium chloride is added to warm sodium nitrite
$NH_4Cl + NaNO_2$ ----> $N_2 + 2H_2O + NaCl$

4 (a)
(i) Electrochemical series: Arrangement of elements according to standard electrode potentials.
(ii) Electrochemical equivalent: Mass of substance deposited by unit electric charge.
(iii) Redox series: Arrangement of substances based on ease of oxidation or reduction.
(iv) Redox reaction: Chemical reaction involving transfer of electrons.

4 (b) Given:
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ E° = –0.76 V
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$ E° = –0.25 V

(i) Feasible reaction: Zn reduces Ni^{2+} because Zn has lower E° value.
(ii) Zn + Ni^{2+} ----> Zn^{2+} + Ni
(iii) Cell diagram: Zn(s) | Zn^{2+} || Ni^{2+} | Ni(s)
(iv) E°cell = E°cathode – E°anode = –0.25 – (–0.76) = +0.51 V

4 (c) Sodium chlorate(I) is converted by heat to sodium chlorate(V) and sodium chloride:
3NaOCl ----> $NaClO_3$ + 2NaCl
Oxidation: Cl from +1 to +5 ($NaClO_3$)
Reduction: Cl from +1 to –1 (NaCl)

5 (a) Give the meaning of volumetric analysis
Volumetric analysis is a quantitative method to determine concentration of solutions using titration based on volume measurements.

5 (b) Differentiate between:
(i) Molar solution = contains 1 mole of solute per litre
Normal solution = contains 1 equivalent per litre
(ii) Standard solution = known concentration
Primary standard = substance of high purity used to prepare standard solution

5 (c) Oxidation number of Cl:
(i) In ClO^- → Cl = +1
(ii) In ClO_3^- → Cl = +5

5 (d) Titration reaction:
$Cr_2O_7^{2-} + 6I^- + 14H^+$ ----> $3I_2 + 2Cr^{3+} + 7H_2O$
$I_2 + 2S_2O_3^{2-}$ ----> $2I^- + S_4O_6^{2-}$

Moles of $K_2Cr_2O_7$ = 1.85 ÷ 294 = 0.00629 mol
Concentration = 0.00629 ÷ 0.25 = 0.0252 mol/L

Moles thiosulphate = 0.0175 × x
Using stoichiometry: 1 mol $Cr_2O_7^{2-}$ requires 6 mol $S_2O_3^{2-}$

0.00629 mol $Cr_2O_7^{2-}$ needs 0.03774 mol thiosulphate
x = 0.03774 ÷ 0.0175 = 2.156 mol/L

Electrons accepted = 6 per mole $Cr_2O_7^{2-}$ × 0.00629 = 0.03774 mol

6 (a)
(i) Al is more metallic than B due to lower ionization energy and larger atomic radius.
(ii) HI cannot be prepared from KI and H_2SO_4 because H_2SO_4 oxidizes I^- to I_2.
(iii) Simple salts of Cu^+ disproportionate to Cu and Cu^{2+} in aqueous solution.
(iv) Carbon forms more stable hydrides due to small size and effective orbital overlap.
(v) Li compounds have partial covalent character due to high polarizing power of Li^+ ion.

6 (b) Group I elements have similar properties:
- React vigorously with water
- Form colorless solutions and hydroxides
- Show +1 oxidation state
- Have low ionization energy

7 (a)(i) What do you understand by the following terms?
Heat of reaction: It is the amount of heat evolved or absorbed during a chemical reaction under standard conditions.

(ii) Thermochemical equations: These are balanced chemical equations that include the enthalpy change (ΔH) of the reaction, showing whether the process is exothermic or endothermic.

7 (b) Given the following reactions:
Cd(s) ----> Cd(g) $\Delta H_1°$
Cd(g) ----> Cd^{2+}(g) + $2e^-$ $\Delta H_2°$
I_2(s) ----> I_2(g) $\Delta H_3°$
I_2(g) ----> 2I(g) $\Delta H_4°$
I(g) + e^- ----> I^-(g) $\Delta H_5°$
Cd(s) + I_2(s) ----> CdI_2(s) ΔHf°

(i) What do the symbols $\Delta H_1°$ to ΔHf° above refer to?
$\Delta H_1°$: Enthalpy of atomization of Cd
$\Delta H_2°$: Enthalpy of ionization of Cd
$\Delta H_3°$: Enthalpy of sublimation of I_2
$\Delta H_4°$: Bond dissociation enthalpy of I_2
$\Delta H_5°$: Electron affinity of iodine
ΔHf°: Enthalpy of formation of CdI_2(s)

(ii) What is the sign for the enthalpy change corresponding to $\Delta H_5°$ above?
It is negative (–), since electron affinity is exothermic.

(iii) Define the standard enthalpy change corresponding to the following symbols:
$\Delta H_1°$: Enthalpy required to convert 1 mole of atoms in solid state to gaseous atoms.
$\Delta H_2°$: Enthalpy required to remove electrons from 1 mole of gaseous atoms.
$\Delta H_5°$: Enthalpy change when 1 mole of electrons is added to 1 mole of gaseous atoms.
$\Delta Hf°$: Enthalpy change when 1 mole of a compound is formed from its elements in standard states.

(iv) Calculate the value of $\Delta Hf°$ given:
$\Delta H_1° = +113$ kJ/mol
$\Delta H_2° = +2490$ kJ/mol
$\Delta H_3° = +199$ kJ/mol
$\Delta H_4° = +151$ kJ/mol
$\Delta H_5° = –314$ kJ/mol
ΔHl (lattice enthalpy) = –2014 kJ/mol

$\Delta Hf° = \Delta H_1° + \Delta H_2° + \Delta H_3° + \Delta H_4° + 2\Delta H_5° + \Delta Hl$
= 113 + 2490 + 199 + 151 + (2 × –314) + (–2014)
= 113 + 2490 + 199 + 151 – 628 – 2014
= 3113 – 2642 = 471 kJ/mol

8 (a) The members of the following pairs of isomeric compounds have different melting/boiling points. Indicate which member has the higher value and suggest reasons:

(i)Compound with –OH and $–NO_2$ in para-position has higher melting point than ortho-isomer due to better packing in the lattice structure and symmetry.

(ii)
$CH_3–C(OH)(CH_3)–CH_3$ has higher boiling point than $CH_3CH_2CH_2CH_2OH$ due to stronger hydrogen bonding and higher branching leading to less surface area contact.

(iii)
CH_3CH_2OH has higher boiling point than CH_3OCH_3 due to hydrogen bonding in alcohols compared to weaker dipole interactions in ethers.

8 (b) From mass spectrum:
Molecular mass = 58
Empirical formula = C_3H_6O
(i) Molecular formula = C_3H_6O
(ii) Two possible structures:
Propanal (CH_3CH_2CHO), Propanone (CH_3COCH_3)

8 (c) Liquid X tests:

TEST	REAGENT	OBSERVATION
A	Sodium metal	No reaction
B	Bromine water	No reaction
C	2,4-Dinitrophenylhydrazine	Orange precipitate (positive test)
D	Tollen's reagent	No reaction

(i) Interpretation:
- Test A: no acidic H → not alcohol
- Test B: no unsaturation → not alkene
- Test C: carbonyl group present → aldehyde or ketone
- Test D: negative → not aldehyde → hence ketone

(ii) Structure of X = Propanone (CH_3COCH_3)

9 (a) Explain briefly how the following conversions can be affected:

(i) A ----> $CH_3CH_2CH_3$
Alkylation reaction with suitable reagent like $CH_3CH_2Cl + AlCl_3$

(ii)
Aniline ----> Bromoaniline
Electrophilic substitution using Br_2

(iii) $(CH_3)_3N$ ----> $[(CH_3)_3N]^+OH^-$
Reaction with CH_3I followed by aqueous silver oxide

9 (b) Distinguish between the following by chemical means:

(i) Phenol and Benzyl alcohol
Phenol reacts with $FeCl_3$ to give violet complex; alcohol does not.

(ii) $CHCl_3$ and CH_3CCl_3
$CHCl_3$ gives isocyanide odor on reaction with NaOH and acetone; CH_3CCl_3 does not.
(iii) CH_3COCH_3 and CH_3CH_2CHO
CH_3CH_2CHO gives silver mirror with Tollen's reagent; CH_3COCH_3 does not.

9 (c) Explain the following:
(i) Phenol is more acidic than ethanol due to resonance stabilization of phenoxide ion.
(ii) Trichloroethanoic acid is stronger than ethanoic acid due to inductive effect of Cl atoms.

(iii) Aniline is a weaker base than ethylamine due to delocalization of lone pair of nitrogen over the benzene ring.

10 (a) Give the products when ethyl alcohol reacts with concentrated sulphuric acid under the following conditions:

(i) 180°C
At 180°C, ethyl alcohol undergoes dehydration to form ethene:
C_2H_5OH ----> $CH_2{=}CH_2 + H_2O$

(ii) 140°C
At 140°C, two molecules of ethyl alcohol condense to form diethyl ether:
$C_2H_5OH + C_2H_5OH$ ----> $C_2H_5–O–C_2H_5 + H_2O$

10 (b) The following is part of a protein chain:

  CH_3 H CH_3
–N–C–C–N–C–C–N–C–C–N–C–
      H O   H O   H O

Draw the structure of two amino acids obtained on hydrolysis of this protein:

Amino acids on hydrolysis:
1. $CH_3–CH(NH_2)–COOH$ ---->Alanine
2. $CH_3CH_2–CH(NH_2)–COOH$ ----> Valine

10 (c)
1. Combustion data:
CO_2 from 1.173 g
Moles of C = 1.173 ÷ 44 = 0.02666 mol
mass of C = 0.02666 × 12 = 0.3199 g
H_2O from 0.240 g
Moles of H = 0.240 ÷ 18 = 0.01333 mol
mass of H = 0.01333 × 2 = 0.02666 g
Mass of O = 1.1 – (0.3199 + 0.02666) = 0.7534 g
Moles of O = 0.7534 ÷ 16 = 0.0471 mol

Divide by smallest:
C = 0.02666 ÷ 0.02666 = 1
H = 0.01333 ÷ 0.02666 = 0.5
multiply by 2 ----->1
O = 0.0471 ÷ 0.02666 ≈ 1.77 ≈ 3.5
multiply by 2 ---->7

Empirical formula = $C_2H_2O_7$
empirical mass ≈ 106

2. Freezing point depression:
$\Delta T = Kf \times m$
$0.186 = 1.86 \times (1.125 \div M) \times (1000 \div 125)$
$0.186 = 14.88 \div M$
$M = 14.88 \div 0.186 \approx 80$ g/mol

Approximate molecular mass = 80
Thus, molecular formula = $C_2H_4O_3$ (most probable adjustment from empirical formula)