THE UNITED REPUBLIC OF TANZANIA

NATIONAL EXAMINATIONS COUNCIL OF TANZANIA

ADVANCED CERTIFICATE OF SECONDARY EDUCATION EXAMINATION

132/1 **CHEMISTRY 1**

(For Both School and Private Candidates)

Time: 3 Hours **ANSWERS** **Year: 2014**

Instructions

1. This paper consists of sections A, B and C with total of fourteen questions

2. Each question carries ten marks.

1. (a) Nitrogen and oxygen combine endothermically at elevated temperature according to the equation

$2N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

If the equilibrium constant for the reaction is 4.3×10^{-3} at 3000°C and 1 atm, calculate the composition of each in the equilibrium if 2 moles of each nitrogen and oxygen were heated.

Let x be the number of moles of NO formed at equilibrium.

Initial moles:
$N_2 = 2$, $O_2 = 2$, $NO = 0$

Change in moles:
$N_2 = 2 - x/2$, $O_2 = 2 - x$, $NO = x$

Total moles at equilibrium = $(2 - x/2) + (2 - x) + x = 4 - x/2$

Equilibrium constant:

$K_c = [NO]^2 / ([N_2][O_2])$

$K_c = 4.3 \times 10^{-3} = (x^2) / ((2 - x/2)(2 - x))$

Solving for x gives $x \approx 0.52$

Moles at equilibrium:
$N_2 = 1.74$
$O_2 = 1.48$
$NO = 0.52$

(b) When 20.85 g of PCl_5 was heated in a sealed tube of 4 dm^3 volume, the pressure in the vessel was found to be 1.5 atm. At this pressure it was found that PCl_5 dissociated to 80%. Calculate the partial pressure of each gas.

Moles of $PCl_5 = 20.85 / 208.5 = 0.1$ mol

Dissociation:

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

At equilibrium:
$PCl_5 = 0.1 \times (1 - 0.8) = 0.02$ mol
$PCl_3 = 0.1 \times 0.8 = 0.08$ mol

Cl_2 = 0.08 mol

Total moles = 0.02 + 0.08 + 0.08 = 0.18 mol

P_total = 1.5 atm

Partial pressures:
$P\_PCl_5 = (0.02 / 0.18) \times 1.5 = 0.167$ atm
$P\_PCl_3 = (0.08 / 0.18) \times 1.5 = 0.667$ atm
$P\_Cl_2 = (0.08 / 0.18) \times 1.5 = 0.667$ atm

2. (a) State the following laws:

(i) Graham's law of gas diffusion: The rate of diffusion of a gas is inversely proportional to the square root of its molar mass.

(ii) Charles' law: The volume of a gas is directly proportional to its temperature at constant pressure.

(iii) Boyle's law: The volume of a gas is inversely proportional to its pressure at constant temperature.

(b) Identify two laws in 2(a) above and show how they can be combined to give a single gas equation.

Boyle's law and Charles' law can be combined into the ideal gas equation:

PV = nRT

(c) A chloride of phosphorus is found to diffuse in the gaseous state more slowly by a factor of 2.216 than nitrogen under the same conditions.

(i) Calculate the relative molecular mass of chloride.

$Rate\_N_2 / Rate\_PCl\_x = \sqrt{(M\_PCl\_x / M\_N_2)}$

$2.216 = \sqrt{(M\_PCl\_x / 28)}$

M_PCl_x = 138 g/mol

(ii) Given that chloride molecule contains one atom of phosphorus, write down its formula.

PCl_3

3. (a) Define colligative properties and give four examples of those properties.

Colligative properties are properties that depend only on the number of solute particles in a solution and not on their identity. Examples:
- Boiling point elevation
- Freezing point depression
- Osmotic pressure
- Vapor pressure lowering

(b) Nicotine, extracted from tobacco leaves, is immiscible with water at low temperature.

(i) What is the molality of nicotine in an aqueous solution that starts to freeze at -0.45°C given that $K_f = 1.86°C \cdot m^{-1}$?

$\Delta T_f = K_f \times m$
$m = 0.45 / 1.86 = 0.242$ m

(ii) If this solution is obtained by dissolving 1.921 g of nicotine in 48.92 g of water, what must be the molar mass of nicotine?

Molality = moles of solute / kg of solvent
Moles of nicotine = $0.242 \times 0.04892 = 0.01183$ mol
Molar mass = $1.921 / 0.01183 = 162.4$ g/mol

(iii) Combustion analysis shows nicotine consists of 74.03% C, 8.70% H, and 17.27% N by mass. What is the molecular formula of nicotine?

Empirical formula: C_5H_8N

Molecular formula = empirical formula × (162.4 / 81) = $C_{10}H_{16}N_2$

4. (a) (i) Write the atomic number of an atom with electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$.

Atomic number = 17 (chlorine).

(ii) X occurs naturally as ^{37}X and ^{35}X. Given the relative atomic mass of X is 35.5, determine the percentage of ^{35}X and ^{37}X in the sample of element X.

Let x be the percentage of ^{35}X.

$35x + 37(100 - x) = 35.5 \times 100$

Solving, x = 75%

So, ^{35}X = 75%, ^{37}X = 25%.

(b) The motion of the electron in an atom is not a simple rotation around an orbit but rather a three-dimensional standing wave which obeys Schrödinger equation.

(i) In which atomic model is this statement based?

Quantum mechanical model.

(ii) Name other two atomic models that attempt to explain the structure of the atom.

- Bohr model
- Rutherford model

(c) Describe the dual nature of electromagnetic radiation and wave-particle duality.

Electromagnetic radiation exhibits both wave-like and particle-like behavior. Light shows interference (wave-like) and photoelectric effect (particle-like).

5. (a) Arrange the following colored lights in order of increasing wavelength:

Blue < Green < Yellow < Red < Violet

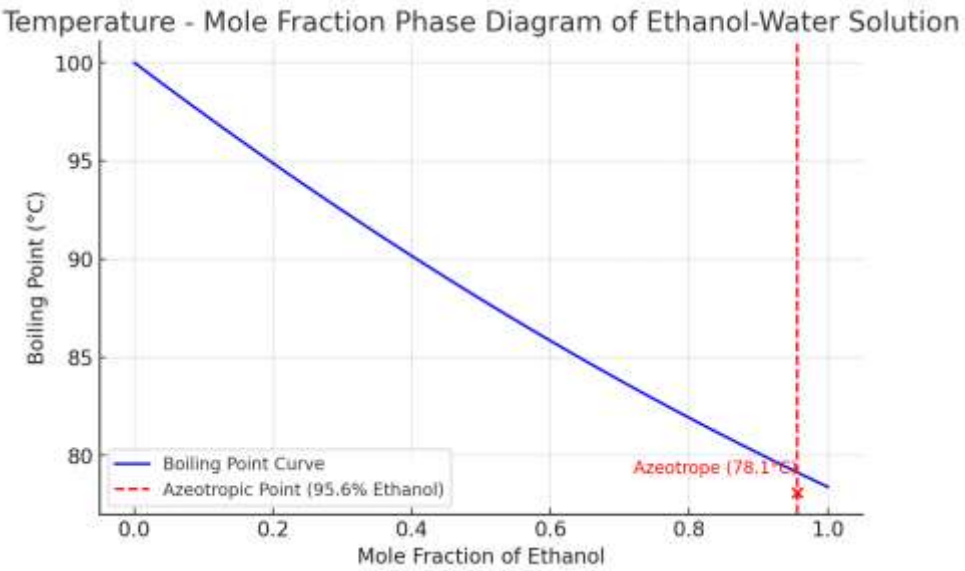
(b) With reference to krypton at ground state, how many electrons have the following quantum numbers?
(i) n = 3 → 18 electrons
(ii) n = 3, l = 2 → 10 electrons
(iii) n = 2, l = 1, ml = -1, s = ½ → 2 electrons

(c) Briefly explain in molecular orbital terms, the bonding in silane (SiH_4).
SiH_4 forms sp^3 hybrid orbitals, leading to four sigma bonds with hydrogen.

6. (a) A solution is prepared from 90 g of water and 10.6 g of a non-volatile solute. The vapour pressure of the solution at 60°C is found to be 18.91 × 10^3 Nm^{-2}. Calculate the approximate molecular mass of the solute given that the vapour pressure of water at 60°C is 19.92 × 10^3 Nm^{-2}.

Raoult's law: $P_1 = X_1 \times P_0$
$X_2 = 1 - (18.91 \times 10^3 / 19.92 \times 10^3) = 0.0507$
Moles of water = 90 / 18 = 5 moles
Moles of solute = 5 × 0.0507 = 0.2535 mol
Molar mass = 10.6 / 0.2535 = 41.8 g/mol

(b) i



(ii) When a solution of less than 50% ethanol is boiled, the more volatile component (ethanol) vaporizes first. As boiling continues, the composition of the remaining liquid shifts towards water, and the boiling point gradually increases. Eventually, the solution reaches the azeotropic composition (95.6% ethanol), where further boiling results in both ethanol and water vaporizing in a constant ratio, preventing further separation by simple distillation.

7. (a) Calculate the standard heat of formation of the reaction

$C(graphite) + 2H_2(g) \text{------>} CH_4(g)$

from the following sets of data:

(i) $CH_4(g) + 2O_2(g) \text{------>} CO_2(g) + 2H_2O(l)$ $\Delta H = -890\ kJmol^{-1}$
(ii) $C(graphite) + O_2(g) \text{------>} CO_2(g)$ $\Delta H = -394\ kJmol^{-1}$
(iii) $H_2O(l) + \frac{1}{2}O_2(g) \text{------>} H_2O(l)$ $\Delta H = -286\ kJmol^{-1}$

Reversing reaction (i):

$CO_2(g) + 2H_2O(l) \text{------>} CH_4(g) + 2O_2(g)$ $\Delta H = +890\ kJmol^{-1}$

Reaction (ii) remains unchanged:

$C(graphite) + O_2(g) \text{------>} CO_2(g)$ $\Delta H = -394\ kJmol^{-1}$

Reversing reaction (iii) and multiplying by 2:

$2H_2O(l) \text{------>} 2H_2(g) + O_2(g)$ $\Delta H = +572\ kJmol^{-1}$

Summing the three reactions:

$C(graphite) + 2H_2(g) \text{------>} CH_4(g)$

$\Delta H = 890 - 394 + 572 = +108\ kJmol^{-1}$

(b) $NaCl_4$ can be formed directly from sodium and chlorine elements via the reaction:

$Na(s) + \frac{1}{2}Cl_2(g) \text{------>} NaCl_4(s) \quad \Delta H = -411\ kJmol^{-1}$

Construct a well-labeled Born-Haber cycle for the formation of $NaCl_4$.

The cycle includes:
- Sublimation energy of Na
- Ionization energy of Na
- Bond dissociation energy of Cl_2
- Electron affinity of Cl
- Lattice energy of $NaCl_4$

8. (a) For the equilibrium:

$2NO_2(g) + O_2(g) \rightleftharpoons 2NO_3(g) \quad \Delta H = -115\ kJ$

(i) Expression for the equilibrium constant K:

$K = [NO_3]^2 / ([NO_2]^2[O_2])$

(ii) Magnitude of K indicates the reaction strongly favors product formation.

(iii) Effect of increasing temperature: Since the reaction is exothermic, increasing temperature shifts equilibrium towards reactants, decreasing K.

(iv) Equilibrium concentration of NO_2 when equilibrium concentrations of NO_3 and O_2 are both 0.1 mol l^{-1}.

Using K = 15,

$15 = (0.1)^2 / ([NO_2]^2 \times 0.1)$

$[NO_2]^2 = (0.01) / (15 \times 0.1)$

$[NO_2] = \sqrt{(0.01 / 1.5)} = 0.08\ M$

(b) The value for equilibrium constant, K, for the reaction

acid + alcohol ⇌ ester + water

(i) Predict the maximum yield of ester and why it may not be achieved in practice.
Maximum yield is achieved when water is continuously removed, but side reactions and incomplete conversions lower the yield.

(ii) Will the addition of a catalyst increase the yield of ester?
No, a catalyst only speeds up the reaction without shifting equilibrium.

(iii) Increasing the concentration of alcohol increases ester yield but does not alter K.

9. (a) Four postulates of the kinetic theory of gases.

- Gas molecules are in constant random motion.
- Volume of gas molecules is negligible compared to the container.
- No intermolecular forces exist between gas molecules.
- Collisions between gas molecules are perfectly elastic.

(b) Define root mean square speed of gas molecules.

It is the square root of the average of the squares of the velocities of gas molecules.

(c) The root mean square speed of hydrogen molecules at a fixed temperature is 1600 m/s. What is the root mean square speed of oxygen molecules at the same temperature?

Using $\sqrt{(M_2/M_1)} = u_1/u_2$:

$\sqrt{(32/2)} = 1600/u_2$

$u_2 = 1600 / \sqrt{16} = 400$ m/s

10. (a) Giving reason; explain for each of the following observations:

(i) Boiling points of water, ethanol, and ethoxyethane are in reverse order of their molecular masses compared to H_2S, C_2H_5SH, and $C_2H_5SC_2H_5$.
Water and ethanol form hydrogen bonds, increasing boiling points, whereas sulfur compounds lack strong hydrogen bonds.

(ii) BF_3 is non-polar, but NF_3 is polar.
BF_3 has symmetrical trigonal planar structure, whereas NF_3 has a lone pair causing polarity.

(iii) Aluminium fluoride has a much higher melting point than aluminium chloride.
AlF_3 is ionic with strong electrostatic forces, whereas $AlCl_3$ has covalent character due to polarization.

(b) Given that X, Y, and Z represent elements of atomic numbers 9, 19, and 34,

(i) Electronic configurations:
X = $1s^2\ 2s^2\ 2p^5$
Y = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
Z = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^4$

(ii) Type of bonding:
X and Y - Ionic
Y and Z - Metallic
X and Z - Covalent

(iii) Relative volatility, electrical conductance, and solubility in water:
X and Z form covalent compounds with higher volatility.
Y and X form ionic compounds with high conductance in solution.
Ionic compounds are more soluble than covalent compounds.

11. (a) Briefly explain the following:

(i) Chain reaction: A reaction in which the products of one step initiate further reactions.

(ii) Chain initiating step: The step where free radicals are first generated.

(iii) Chain propagation step: Steps where radicals react to form new radicals, sustaining the reaction.

(iv) Chain terminating step: Steps where radicals combine to form stable molecules, ending the reaction.

(b) Why does benzene show extra stability?
Benzene has resonance, with delocalized π-electrons reducing reactivity and increasing stability.

(c) Chemical tests to distinguish the following:

(i) Hexane and 2-hexene: Bromine water test; 2-hexene decolorizes bromine, hexane does not.

(ii) Propyne and propene: Baeyer's test with $KMnO_4$; propyne gives a precipitate, propene does not.

(iii) 1-pentyne and 2-pentyne: Ammoniacal silver nitrate test; 1-pentyne forms a white precipitate, 2-pentyne does not.

12. (a) Give the organic product in each of the following:

(i)

$C_6H_5Br + CH_3I + 2Ni/dry\ ether$ ------> $C_6H_5CH_3$

(ii)

$C_6H_5Br + 3H_2/Pt, 200°C$ ------> C_6H_6

(iii)

C_6H_5Cl + Aq.NaOH, 360°C, 150 atm, then dil. HCl ------> C_6H_5OH

(b) Show the mechanism for the nitration of benzene.

Step 1: Generation of nitronium ion
$HNO_3 + H_2SO_4$ ------> $NO_2^+ + HSO_4^- + H_2O$

Step 2: Electrophilic attack
Benzene + NO_2^+ ------> Arenium ion

Step 3: Loss of H^+ to regenerate aromaticity
Arenium ion ------> Nitrobenzene + H^+

(c) With the help of chemical equations, show how you can prepare the following:

(i) Toluene from benzene
$C_6H_6 + CH_3Cl + AlCl_3$ ------> $C_6H_5CH_3 + HCl$

(ii) Butane from methane
$CH_4 + Cl_2$ ------> CH_3Cl
$CH_3Cl + Na$ ------> C_2H_6
$C_2H_6 + Cl_2$ ------> C_2H_5Cl
$C_2H_5Cl + Na$ ------> C_4H_{10}

(iii) Toluene from ethyne
$CH{\equiv}CH + HCl$ ------> $CH_2{=}CHCl$
$CH_2{=}CHCl + H_2$ ------> CH_3CH_2Cl
$CH_3CH_2Cl + AlCl_3$ ------> $C_6H_5CH_3$

(iv) Pentane from propyne
$CH_3CH_2C{\equiv}CH + H_2$ ------> $CH_3CH_2CH{=}CH_2$
$CH_3CH_2CH{=}CH_2 + H_2$ ------> $CH_3CH_2CH_2CH_3$

13. (a) Briefly explain why $(CH_3)_3CBr$ reacts by SN1 mechanism while CH_3CH_2Br reacts by SN2 mechanism.

$(CH_3)_3CBr$ forms a stable tertiary carbocation, favoring SN1. CH_3CH_2Br is primary, so it undergoes backside attack (SN2).

(b) The ease of nucleophilic substitution reaction of alkyl halide R-X with OH^- is:
C-I > C-Br > C-Cl > C-F

Explain this trend.

Bond strength decreases down the group. C-I is weakest and easiest to break, while C-F is strongest and hardest to break.

(c) Give all possible isomers of the compound $C_5H_{10}Br_2$ and their corresponding IUPAC names.

1. 1,1-dibromopentane
2. 1,2-dibromopentane
3. 1,3-dibromopentane
4. 1,4-dibromopentane
5. 2,2-dibromopentane

14. (a) What is ozonolysis?

Ozonolysis is the cleavage of alkenes or alkynes using ozone (O_3), forming carbonyl compounds.

(b) A hydrocarbon with molar mass 96 g/mol and molecular formula C_7H_{12} was ozonized and hydrolyzed in the presence of zinc, yielding ethanol and glyoxal (H-C-C-H). Determine its structure and show ozonolysis mechanism.

Structure: 3-heptene ($CH_3CH_2CH=CHCH_2CH_3$)

Ozonolysis:

$CH_3CH_2CH=CHCH_2CH_3 + O_3$ ------> $CH_3CH_2CHO + O=CH-CH=O$

(c) Two isomeric hydrocarbons P and Q have molecular formula C_8H_{12}.

(i) Structural formula of P and Q:
P = o-xylene
Q = mesitylene

(ii) Oxidation of Q to tricarboxylic acid:
$C_6H_3(CH_3)_3 + 3[O]$ ------> $C_6H_3(COOH)_3$

(iii) Name the compound formed when P undergoes oxidation.
Phthalic acid ($C_6H_4(COOH)_2$)