2915/305
PHYSICAL CHEMISTRY III
Oct./Nov. 2021
Time: 3 hours

THE KENYA NATIONAL EXAMINATIONS COUNCIL

DIPLOMA IN ANALYTICAL CHEMISTRY

MODULE III

PHYSICAL CHEMISTRY III

3 hours

INSTRUCTIONS TO CANDIDATES

You should have the following for this examination:
Answer booklet;
Non-programmable scientific calculator.
*This paper consists of **TWO** sections; **A** and **B**.*
*Answer **ALL** questions in section **A** and any **THREE** questions from section **B**.*
*Each question in section **A** carries **4** marks while each question in section **B** carries **20** marks.*
Maximum marks for each part of the question are indicated.
Candidates should answer the questions in English.

This paper consists of 6 printed pages.

Candidates should check the question paper to ascertain that all the pages are printed as indicated and that no questions are missing.

SECTION A (40 marks)

*Answer **ALL** the questions in this section.*

1. Given the following reaction:

$Ni_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$

where E° cell = 1.05, concentration of $2Ag^{+}$ (0.02 M) and Ni^{2+} (0.160 M).

(a) Calculate the EMF of the cell. (3 marks)

(b) Define the term *reference electrode*. (1 mark)

2. (a) State the **first** law of thermodynamics. (1 mark)

(b) State any **three** limitations of the first law of thermodynamics. (3 marks)

3. The unit cell of a face-centred cubic is 3.52 $\overset{0}{A}$. Given that the atomic mass of the compound X is 58.7 and its density is 8.94 g/m^3, calculate its avogado number. (4 marks)

4. (a) State Carnots principle. (1 mark)

(b) The heat supplied to a carnot engine is 453.6 Kcal. Calculation the work done by the engine between the temperatures 10°C to 100°C. (3 marks)

5. 0.025 mol/L of methanoic acid has a molar conductivity of 46.15 cm^2/mol. Given that λ^0 (H+) = 349.6 Scm^2/mol and λ^0 ($HCOO^-$) = 546 cm^2/mol. Calculate the:

(a) degree of dissociation; (2 marks)

(b) dissociaton constants. (2 marks)

6. Consider the cell below

$Zn/Zn^{2+}_{(aq)}$ (0.1M) // $Cu^{2+}_{(aq)}$ (0.1M) / Cu

Given that the standard potentials are:

$Cu^{2+} + 2\varepsilon \longrightarrow Cu_{(aq)}$ $E^0 = 0.350V$

$Zn^{2+} + 2\varepsilon \longrightarrow Zn_{(aq)}$ $E^0 = -0.763V$

(a) Write down the cell reaction. (2 marks)

(b) Calculate the EMF of the cell. (2 marks)

7. (a) Define a unit cell. (1 mark)

(b) Explain why solids are rigid. (3 marks)

8. For the reaction:

$(2X + Y \longrightarrow Z)$.

ΔH = 400 kJ/mol, T = 298 °K and Δ S= 0.2 kJ/mol. Calculate the temperature above which the reaction is considered spontaneous. (4 marks)

9. (a) Define the following terms:

(i) heat of formation;
(ii) standard heat of formation.

(2 marks)

(b) The $\Delta H^0 f$ for $CO_{2(g)}$, $CO_{(g)}$, $H_2O_{(g)}$ and H_2 are -393.5, –111.31, –241.8 and 0 Kj/mol respectively. Calculate the heat changes for the reaction :
$C_{(s)} + 2H_{2(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$ (2 marks)

10. Given the bond dissociation energies of H_2 = 104, Cl_2 = 58 and HCl = 103 Kcal/mol, calculate the enthalpy of formation of $HCl_{(g)}$. (4 marks)

SECTION B (60 marks)

*Answer **THREE** questions from this section.*

11. (a) Define the following terms:

(i) electrolytic conductivity; (2 marks)
(ii) molar conductivity. (2 marks)

(b) The conductivity of different concentrations of NaCl at T = 298 °K is as follows:

Con/M	1.0×10^{-3}	1.0×10^{-2}	2.0×10^{-2}	5.0×10^{-2}	1.0×10^{-1}
10^{-2} K/Sm^{-1}	1.237	11.85	23.15	55.53	106.74

(i) Calculate the λ_M for all the concentrations. (10 marks)

(ii) Plot a graph of λ u *Vs* $\sqrt{C}$. (5 marks)

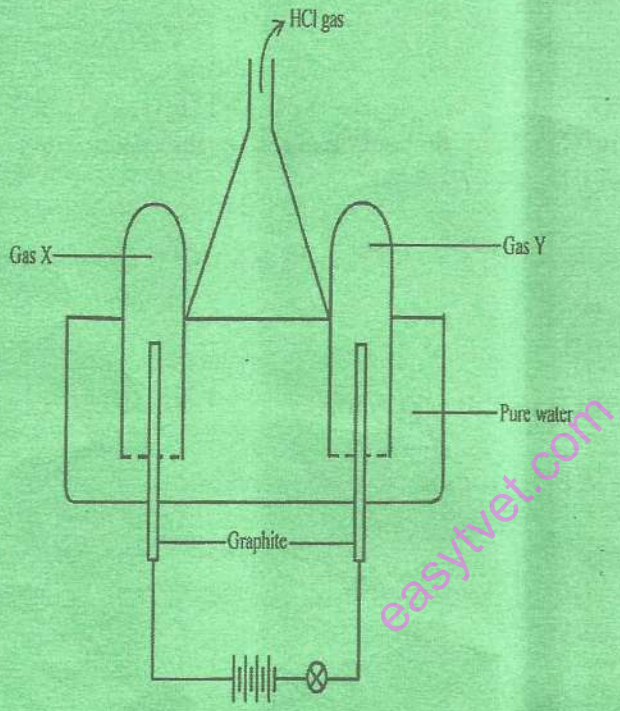
(iii) State the significance of the λ u *Vs* $\sqrt{C}$ graph. (1 mark)

12. (a) Using sketches, explain the following conductimetric titrations:

(i) Titration of CH_3COOH *Vs* NaOH. (3 marks)
(ii) HCl *Vs* NH_4OH. (3 marks)
(iii) Indicate the endpoints of the sketches. (2 marks)

(b) 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. Calculate electrochemical equivalent of copper. (4 marks)

(c) Study the diagram below and use it to answer the questions that follow.



When some hydrogen chloride gas is added to the water and mixed, the bulb lights and gases X and Y formed.

(i) Name gases X and Y. (2 marks)

(ii) Explain why the bulb does not light before the HCl is let into the solution. (3 marks)

(iii) Between gases X and Y, predict which one is lesser in volume. (1 mark)

(iv) Explain why one gas is lesser that the other. (2 marks)

13. (a) State **four** differences between reversible processes and irreversible processes in thermodynamics. (8 marks)

(b) The molar heat of formation of $NH_4NO_{3(s)}$ is -367.5 Kj and those of $N_2O_{(g)}$ and $H_2O_{(l)}$ are +81.46 Kj and –285.78 Kj respectively at 25°C and 1 atmospheric pressure. Calculate:

(i) ΔH for the reaction. (4 marks)

(ii) ΔE for the reaction. (3 marks)

(c) The bond dissociation of hydrogen (H_2) is 430 Kj/mol while that of nitrogen (N_2) is 941 Kj/mol. Given that the enthalpy of formation of ammonia (NH_3) is –46 Kj/mol, and $R = 8.314 \times 10^{-3}$ Kj/mol:

(i) Calculate the enthalpy of atomization of $NH_{3(g)}$. (4 marks)

(ii) Average bond enthalpy of N-H bond. (1 mark)

14. (a) Derive Ostwald's equation for a weak electrolyte. (12 marks)

(b) State the advantages of potentiometric titration. (2 marks)

(c) State and explain any **two** types of electrodes used in electrochemistry. (6 marks)

15. (a) (i) State Hess law. (2 marks)

(ii) Define the following terms as used in thermodynamics:

I. entropy; (2 marks)

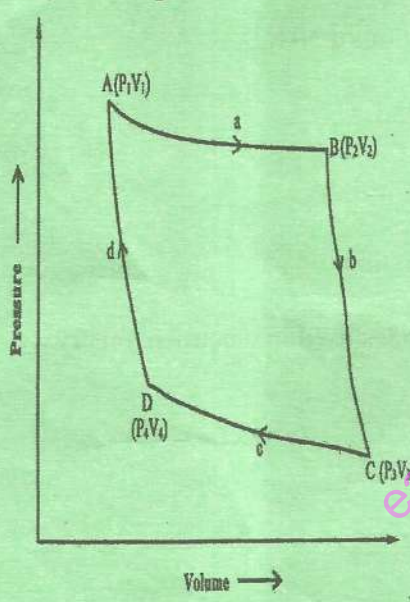
II. boundary; (2 marks)

III. cyclic process ; (2 marks)

IV. system. (2 marks)

(b) State **two** characteristics of entropy. (2 marks)

(c) Study the diagram below and use it to answer the questions that follow.



(i) State the processes:

I. a– (1 mark)

II. b– (1 mark)

III. c– (1 mark)

IV. d– (1 mark)

(ii) State the equations, for processes:

I. a– (2 marks)

II. b– (2 marks)

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