2411/301
PHYSICAL CHEMISTRY
Oct./Nov. 2019
Time: 3 Hours

THE KENYA NATIONAL EXAMINATIONS COUNCIL

DIPLOMA IN ANALYTICAL CHEMISTRY

PHYSICAL CHEMISTRY

3 hours

INSTRUCTIONS TO CANDIDATES

You should have the following for this examination:
answer booklet;
battery operated scientific calculator.
*This paper consists of **TWO** sections; **A** and **B**.*
*Answer **ALL** the 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 a question are indicated.
Candidates should answer the questions in English.

This paper consists of 5 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. (a) (i) Define the term compressibility factor (z) of ideal gas. (1 mark)

$Z = \frac{PV}{nRT} = 1$ is the ratio of molar volume of the gas to the molar volume of ideal gas at the same temp & Pressure.

(ii) Calculate the compressibility factor of ammonia gas at standard contions. (2 marks)

(b) State **two** characteristics of an ideal gas. (1 mark)

2. (a) An aqueous solution of C_6H_5COONa turns red litmus paper blue. Use chemical equations to explain this observation. (2 marks)

(b) Calculate the pH of 0.3 M C_6H_5COONa (pka = 4.2). (2 marks)

3. Explain the applications of the study of reaction rates in industry. (4 marks)

4. (a) (i) State Hess's law. States that the heat change in a chemical rxn is independently of the pathways used as long as the initial & final stages are the same. (1 mark)

(ii) Explain the industrial application of Hess's law. (1 mark)

determination of heat of formation of ionic cpds using born-haber process

(b) Using an energy cycle diagram, explain why some ionic salts are soluble in water while others are not. (2 marks)

5. (a) State the second law of thermodynamics. States that the rxn is spontaneous when Gibb's free energy is negative. (1 mark)

(b) The enthalpy change for the reaction; A ⟶ products, is – 235.8 kJ/mol and the change in entropy is –358 J $mol^{-1}K^{-1}$. Estimate the lowest temperature at which the reaction takes place. (3 marks)

6. (a) Define the term common-ion effect as used in ionic equilibria. (1 mark)

(b) Starting with the fatty acid, describe how soap as sodium stearate is prepared. (3 marks)

7. (a) (i) Write down the ILKOVIC equation. (1 mark)

(ii) Describe quantitative polarographic analysis of a sample. (2 marks)

(b) Explain why the sample is purged with inert gas during polarographic analysis. (1 mark)

8. The equilibrium constant for the following reaction is 4:

$$CH_3COOH_{(aq)} + CH_3CH_2OH_{(aq)} \rightleftharpoons CH_3COOCH_2CH_{3(aq)} + H_2O_{(l)}$$

(a) Using this reaction, as an example, define the term equilibrium constant. (1 mark)

$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

(b) Calculate the equilibrium constant for the hydrolysis of ethyl acelate. (2 marks)

(c) State **one** factor that affects the equilibrium constant of a chemical reaction. (1 mark)

9. (a) Define the following terms as used in solid state chemistry:

(i) unit cell; (1 mark)
(ii) coordination number. (1 mark)

(b) Lithium chloride has a simple cubic structure. Use the following information about lithium chloride to calculate the Avogadro's number. (2 marks)

Density in g/m^3	=	2.56
Inter ionic distance in cm	=	2.4×10^{-8}
Relative atomic mass	=	Li = 7; Cl = 35.5

10. Draw a labelled phase diagram for a mixture of gold (M.pt = 1064°C) if a mixture of 70% Au and 30% Ag, cannot be separated by thermal methods of analysis and freezes at 451°C. (4 marks)

SECTION B (60 marks)

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

11. (a) Define the following terms as used in reaction kinetics:

(i) molecularity; (1 mark)
(ii) order; (1 mark)
(iii) rate determining step; (1 mark)
(iv) rate. (1 mark)

(b) The data in table I was obtained in a series of experiments for the reaction.

$$2NO + H_2 \longrightarrow N_2 + 2H_2O \text{ ; at } 904°C$$

Table I

Expt	Initial [NO]	Initial [H_2]	Rate of appearance of N_2 in mol $L^{-1}S^{-1}$
1	0.210	0.122	0.0339
2	0.210	0.244	0.0678
3	0.210	0.366	0.102
4	0.420	0.122	0.136
5	0.630	0.122	0.305

(i) Use this information to calculate order of the reaction with respect to NO. (3 marks)

(ii) Use the graphical method to determine the order of the reaction with respect to hydrogen by plotting a graph of rate against $[H_2]$. (10 marks)

(iii) Determine the rate law equation for this reaction. (3 marks)

12. Use the following equation to answer the questions that follow:

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

(a) The standard enthalpy change of combustion of hydrogen is $-286\ KJmol^{-1}$ and the standard enthalpy of formation of carbon monoxide is $-110\ KJmol^{-1}$ and the molar enthalpy of vapourization of water is $41\ KJmol^{-1}$.

(i) Define the following terms:

(I) standard molar enthalpy of combustion; (1 mark)

(II) standard molar enthalpy of formation. (1 mark)

(ii) Calculate the enthalpy change of the reaction. (5 marks)

(b) ΔH^{θ}_{298} for the reaction is a constant between 0 to 3500 K; while TDS varies linearly from 0 at 0 K to 500 $KJmol^{-1}$ at 3500 K.

(i) Plot these values on a graph of temperature against ΔH. (4 marks)

(ii) Use the graph to determine the temperature at which the reaction starts. (4 marks)

(c) ΔG^{θ} for the reaction is 633 $KJmol^{-1}$. Calculate K_p at 500 K. ($R = 0.00831\ L\ atm\ K^{-1}mol^{-1}$). (5 marks)

13. (a) (i) State the first law of thermodynamics. - states that the net energy change of a closed system is equal to the heat transfer to the system less the work done by the system. (1 mark)

(ii) State the limitations of the first law of thermodynamics. (2 marks)

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

(i) adiabatic change; - do not allow passage of energy as heat through its boundary even if there is a temp. difference (1 mark)

(ii) isolated systems; - is a system that allows (1 mark)

(iii) closed system. - is a system that does not allow passage of either matter or energy through its walls (1 mark)

(c) A fixed mass of a gas at standard conditions has a volume of 5 litres and undergoes an isobaric change to temperature of 360 K. (Cv = 12.61). Calculate:

(i) moles of the gas; (4 marks)

(ii) final volume of the gas; (4 marks)

(iii) change in entropy of the gas; (4 marks)

(iv) state the assumptions made in c(iii) above. (2 marks)

14. (a) Conductivities of solutions are measured by comparing the resistance of a cell filled with the sample to its resistance when filled with a standard solution such as $KCl_{(aq)}$. The conductivity of water is 7.6×10^{-4} sm^{-1} and that of 0.1 M KCl is $1.1639 \times 10^{-2} sm^{-1}$. A cell filled with acetic acid has a resistance of 300 Ω. Calculate the cell constant. (3 marks)

(b) The resistance of a series of solutions of acetic acid were measured using a conductivity cell and the values obtained are shown in table II.

Table II

Conc. in mol/dm^{-3}	0.00049	0.00099	0.00198	0.01581	0.06323
Resistance in Ω	6146	4210	2927	1004	497

Use these results to draw the appropriate graph and use the graph to obtain the values of K_a of the acid using the equation:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^{\infty}} + \frac{\Lambda_m C}{K_a(\Lambda_m^{\infty})^2}$$

(17 marks)

15. (a) Define the following terms:

(i) cryoscopic constant; (1 mark)

(ii) ebullioscopic constant. (1 mark)

(b) (i) Draw a labelled diagram of the apparatus used to determine the elevation of the boiling point of a solution. (8 marks)

(ii) Describe how the apparatus in b(ii) above functions. (4 marks)

(c) A 40% w/w solution of ribitol in water has the same boiling point as a 4.5% w/w solution of glucose (f. wt = 180) in water. Calculate the molecular mass of ribitol. (6 marks)

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