

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.

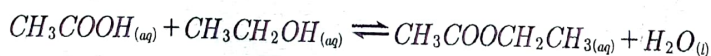
This paper consists of 5 printed pages.

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

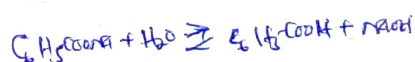
SECTION A (40 marks)

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 conditions. (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 ($pK_a = 4.2$). (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 reaction is independent of the pathway used as long as the initial & final states are the same. (1 mark)
- (ii) Explain the industrial application of Hess's law. (1 mark)
 Determination of heat of formation of ionic compounds 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 Gibbs free energy is negative. (1 mark)
- (b) The enthalpy change for the reaction; $A \rightarrow$ products, is -235.8 kJ/mol and the change in entropy is $-358 \text{ J mol}^{-1}\text{K}^{-1}$. 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:



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



- (b) Calculate the equilibrium constant for the hydrolysis of ethyl acetate. (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)

$$\begin{aligned} \text{Density in g/m}^3 &= 2.56 \\ \text{Inter ionic distance in cm} &= 2.4 \times 10^{-8} \\ \text{Relative atomic mass} &= \text{Li} = 7; \text{Cl} = 35.5 \end{aligned}$$

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; *Power to which concentration is raised to its half* (1 mark)
- (ii) order; *refers to the number of atoms or molecules taking part in the step that leads to a chemical reaction.* (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.

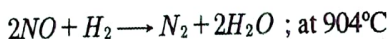
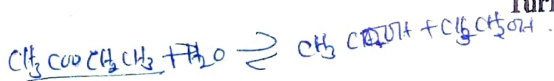


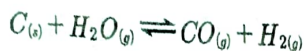
Table I

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 $[\text{H}_2]$. (10 marks)
- (iii) Determine the rate law equation for this reaction. (3 marks)

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



- (a) The standard enthalpy change of combustion of hydrogen is -286 kJ mol^{-1} and the standard enthalpy of formation of carbon monoxide is -110 kJ mol^{-1} and the molar enthalpy of vapourization of water is 41 kJ mol^{-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_{298}^θ for the reaction is a constant between 0 to 3500 K; while TDS varies linearly from 0 at 0 K to 500 kJ mol^{-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 kJ mol^{-1} . Calculate K_p at 500 K. ($R = 0.00831 \text{ L atm K}^{-1} \text{ mol}^{-1}$). (5 marks)

13. (a) (i) State the first law of thermodynamics. - states that the net change in energy 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 thru 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 thru 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. ($C_v = 12.61$). 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 $7.6 \times 10^{-4} \text{ sm}^{-1}$ and that of 0.1 M KCl is $1.1639 \times 10^{-2} \text{ sm}^{-1}$. 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:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\infty} + \frac{\Lambda_m C}{K_a (\Lambda_m^\infty)^2} \quad (17 \text{ marks})$$

15. (a) Define the following terms:

- (i) cryoscopic constant; *the molar constant shown by depression in freezing point when one mole of substance is added to a soln.* (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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