NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH, NATURAL RESOURCES AND APPLIED SCIENCES

SCHOOL OF NATURAL AND APPLIED SCIENCES

DEPARTMENT OF BIOLOGY, CHEMISTRY AND PHYSICS

QUALIFICATION: BACHELOR OF SCIENCE	
QUALIFICATION CODE: 07BOSC	**LEVEL:** 6
COURSE NAME: PHYSICAL CHEMISTRY	**COURSE CODE**: PCH602S
SESSION: JUNE 2023	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	**Prof Habauka M Kwaambwa**
MODERATOR:	**Dr Euodia Hess**

INSTRUCTIONS
1. Answer ALL the questions in Sections A and B. 2. Write clearly and neatly. 3. Number the answers clearly.

PERMISSIBLE MATERIALS

Non-programmable Calculators

ATTACHMENT

List of Useful Constants and Equation

THIS QUESTION PAPER CONSISTS OF 9 PAGES (Including this front page and a list of useful constants and equation as an attachment)

SECTION A: MULTIPLE CHOICE QUESTIONS [20]

There are **20 questions** in this section. Answer ALL questions by selecting the letter of the correct answer. Each question carries 2 marks.

1. The heating of a gas at constant pressure is governed by
   A. Boyle's law
   B. Charles' law
   C. Gay Lussac law
   D. Avogadro's law
   E. Ideal gas equation of state
2. An ideal gas is expanded to twice its original volume during an isothermal process. The final pressure of the gas
   A. Increases to less than twice its original value
   B. Decreases to twice its original value
   C. Increases to more than twice its original value
   D. Does not change
   E. Decreases to one-half its original value
3. A sample of an ideal gas in a rigid closed container at a temperature of 50°C and 1.5 atm is heated to 100°C. What is the pressure of the gas at the higher temperature?
   A. 3 atm
   B. 3.5 atm
   C. 1.7 atm
   D. 4.6 atm
   E. Insufficient information
4. What is the volume of 2 moles of a gas at STP?
   A. 22.4 dm^3
   B. 48.8 dm^3
   C. 67.2 dm^3
   D. 44.8 dm^3
   E. Insufficient information
5. A **closed** system is one in which
   A. Heat does not cross boundary of the system but mass may do so.
   B. Both mass and energy cross the boundary of the system
   C. Neither mass nor energy crosses the boundary of the system
   D. Mass crosses the boundary but not the energy
   E. Thermodynamic reactions do not occur
6. An **intensive property** of a system is one whose value
   A. depends on the mass of the system like volume.
   B. is not dependent on the path taken followed but on the state.
   C. is dependent on the path followed and not on the state.
   D. is always constant.
   E. does not depend on the mass of the system, like temperature, pressure, etc.

7. If a gas is compressed against a constant pressure, keeping the temperature constant, then work done will be equal to:
    A. Positive
    B. Negative
    C. Zero
    D. Pressure x Volume
    E. May be positive or negative depending on the temperature used
8. A mixture of gas expands from 0.06 m^3 to 0.09 m^3 at a constant pressure of 1 x 10^6 Pa and the change in internal energy is 54 kJ during the process. The heat absorbed by the mixture is
    A. 30 kJ
    B. 54 kJ
    C. 84 kJ
    D. 100 kJ
    E. Insufficient information
9. The heat absorbed or given out by a reaction at constant pressure is known as:
    A. Entropy change
    B. Work
    C. Enthalpy change
    D. Internal energy change
    E. None of the above
10. In a certain process, 900 J of work is done by the system which absorbs 550 J of heat. What is change in internal energy (ΔU) for the process?
    A. 900 J
    B. 250 J
    C. 1450 J
    D. – 1459 J
    E. – 350 J
11. For iodine, I_2, at 114°C, the standard enthalpy of fusion, ΔH_{fusion}, is 16.1 $kJmol^{-1}$ and the standard enthalpy of vaporization, ΔH_{vap}, is 45.0 $kJmol^{-1}$. Calculate the standard enthalpy of sublimation at this temperature.
    A. 61.1 $kJmol^{-1}$
    B. 16.1 $kJmol^{-1}$
    C. 25.0 $kJmol^{-1}$
    D. 28.9 $kJmol^{-1}$
    E. Insufficient information
12. The conductivity for an acid HA solution of 0.0316 M concentration is 9.260 $\Omega^{-1}m^{-1}$. Calculate the molar conductivity (in $\Omega^{-1}m^2mol^{-1}$) of the solution.
    A. 2.93
    B. 2.93 x 10^2
    C. 0.293
    D. 2.93 x 10^{-2}
    E. None of the above

13. The degree of dissociation of an acid HX in aqueous solution of concentration 0.025 $moldm^{-3}$ is 0.028. What is the K_a for the acid?
    A. 7.2×10^{-4}
    B. 2.0×10^{-5}
    C. 8.1×10^{-4}
    D. 1.8×10^{-5}
    E. 2.0×10^{-4}
14. The molar conductivities of Cs^+ and SO_4^{2-} are 0.772×10^{-2} and 1.600×10^{-2} Sm^2mol^{-1}, respectively. What is the molar conductivity of Cs_2SO_4?
    A. 3.972×10^{-2} Sm^2mol^{-1}
    B. 3.144×10^{-2} Sm^2mol^{-1}
    C. 0.828×10^{-2} Sm^2mol^{-1}
    D. 2.372×10^{-2} Sm^2mol^{-1}
    E. Insufficient information
15. The molar conductivity of $Mg(NO_3)_2$ is 2.488×10^{-2} Sm^2mol^{-1}. If the molar conductivity of Mg^{2+} is 1.060×10^{-2} Sm^2mol^{-1}, what is the molar conductivity of NO_3^-?
    A. 0.368×10^{-2} Sm^2mol^{-1}
    B. 1.428×10^{-2} Sm^2mol^{-1}
    C. 0.714×10^{-2} Sm^2mol^{-1}
    D. 0.184×10^{-2} Sm^2mol^{-1}
    E. Insufficient information
16. The molar conductivities at infinite dilution, Λ_o, for HCl(aq), NaB(aq) (sodium benzoate) and NaCl (aq) are 426.2, 82.4 and 126.5 Scm^2mol^{-1}, respectively, at 25°C. What is Λ_o for HB (benzoic acid) in Sm^2mol^{-1}?
    A. 0.382
    B. 3.82×10^2
    C. 3.82
    D. 3.82×10^{-2}
    E. None of the above
17. What are the units of k for the rate law, Rate = $k\frac{[A]^2}{[B]}$, when the concentration and time units are mol/L and seconds, respectively?
    A. s^{-1}
    B. $L\ mol^{-1}\ s^{-1}$
    C. $L^2\ mol^{-2}\ s^{-1}$
    D. $L^2\ s^2\ mol^{-2}$
    E. $L^{-2}\ s^{-2}\ mol^{-2}$

18. A reaction A $\rightarrow$P displays first-order kinetics. It therefore follows that a plot of _____ versus time is linear, and that the slope of this plot = _____.
    A. [A]; -k
    B. [A]; k
    C. 1/[A]; -k
    D. 1/[A]; k
    E. ln[A]; -k
19. The activation energy of a reaction can be determined from the slope of which of the following graphs?
    A. ln k vs T
    B. $\frac{\ln k}{T}$ vs $\frac{1}{T}$
    C. $\ln k$ vs $\frac{1}{T}$
    D. $\frac{T}{\ln k}$ vs $\frac{1}{T}$
    E. $\frac{\ln k}{T}$ vs $\frac{1}{T}$
20. The ozone, O_3, of the stratosphere can be decomposed by the reaction with nitrogen oxide (commonly called nitric oxide), NO, from high-flying jet aircraft.

$$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$$

The rate expression is rate = $k[O_3][NO]$. Which of the following mechanisms agree with observed rate expression?

Mechanism 1	$NO + O_3 \rightarrow NO_3 + O$	slow
	$NO_3 + O \rightarrow NO_2 + O_2$	fast
Mechanism 2	$NO + O_3 \rightarrow NO_2 + O_2$	one slow step
Mechanism 3	$O_3 \rightarrow O_2 + O$	slow
	$NO + O \rightarrow NO_2$	fast
Mechanism 4	$NO \rightarrow N + O$	slow
	$O_3 + O \rightarrow 2O_2$	fast
	$O_2 + N \rightarrow NO_2$	fast

    A. 1 only
    B. 1 and 2
    C. 2, 3 and 4
    D. 2 only
    E. All the 4 mechanisms

SECTION B **[60]**

There are **FOUR** questions in this section. Answer **all** Questions.

QUESTION 1 **[12]**

(a) State whether q, w, ΔU, ΔH and ΔS are positive, negative or zero for reversible adiabatic compression of an ideal gas. (5)

(b) Predict whether the entropy change, ΔS, is greater than zero, less than zero or zero for each of the following processes: (7)

(i) Dissolving a solute in a solvent to produce a solution

(ii) An ideal gas undergoing a Carnot cycle

(iii) $Cl(g) \rightarrow Cl^-(g)$

(iv) Water frozen at 0°C and 1 atm

(v) $CH_3CH_2CH_3\,(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

(vi) $H_2\,(g, 300\ K, 1\ atm) \rightarrow H_2\,(g, 100\ K, 1\ atm)$

(vii) $Cl_2(g) + H_2(g) \rightarrow 2HCl(g)$

QUESTION 2 **[12]**

Using the First Law of Thermodynamics, calculate the quantity listed in **bold**, in joules, for the system of one mole of gas in a cylinder with movable cylinder piston.

[Given: $C_v = 12.5\ JK^{-1}mol^{-1}$; $C_p = 20.8\ JK^{-1}mol^{-1}$]

(a) The gas absorbs 234 J of heat and is compressed by 534 J of work. **ΔU** = ?

(b) The gas is cooled by removing 106 J of heat and expands doing 242 J of work. **ΔU** = ?

(c) The gas is heated at constant pressure from 298 K to 398 K. **q** = ?

(d) The gas is heated at constant volume from 298 K to 398 K? **ΔU** = ?

(e) The gas expands from 0.250 L to 1.00 L against an external pressure of 2.50 atm. **w** = ?

(f) The change internal energy (ΔU) for a constant pressure process was – 407 J and the change in enthalpy was – 687 J. **w** = ?

QUESTION 3 **[14]**

(a) Define the terms **conductance, L**, and **resistivity,** ρ, as used in Electrochemistry and state the SI units. (4)

(b) A conductivity cell was calibrated using 0.01M KCl (κ =1.4087 x 10^{-3} Scm^{-1}) in the cell, and the measured resistance was 688 Ω.

(i) Find the cell constant. (3)

(ii) A 0.010 M $AgNO_3$ solution in the same cell had a resistance of 777 Ω. What is the conductivity, κ, for the $AgNO_3$ solution? (3)

(c) Given the standard reduction potentials – 0.403 V and 0.337 V at 298 K for the half cells $Cd^{2+}|Cd(s)$ and $Cu^{2+}|Cu(s)$, respectively. Deduce the overall reaction that will be spontaneous and write down the complete cell notation for this overall reaction. (4)

QUESTION 4 **[22]**

(a) What is the overall order of the reaction described by each of the rate expressions below? State the units of the rate coefficient, k, if the rate is in $moldm^{-3}s^{-1}$.

(i) Rate = $k[A]^2[B]$ (ii) Rate = $k[A]^{1.5}[B]^{0.5}$ (4)

(b) Consider a reaction A $\xrightarrow{k}$ P. The integrated rate law for the reaction is:

$$[A]-[A]_o = -kt$$

(i) State the two reaction requirements needed in order to derive the equation above. (2)

(ii) What is the order of the reaction? What are the units of the rate constant if the rate is in mol L^{-1} min^{-1}? (2)

(iii) What plot would you construct to determine the rate constant, k, for the reaction? Label the axes on diagram and sketch the graph that you would expect. (3)

(iv) Derive the half-life expression for this reaction. (3)

(c) The table below gives experimental data for the half-lives, $t_{0.5}$, of different reactions as a function of the initial reactant concentration, C_o. Determine the order of each of the two reactions. (4)

C_o / moldm^{-3}	$t_{0.5}$ / seconds	
	Reaction 1	Reaction 2
0.02	30	60
0.04	30	120

(d) The following questions refer to the popular demonstration called "Elephants Toothpaste" in which the mechanism is believed to be:

Step 1: $H_2O_2 + I^- \rightarrow H_2O + OI^-$ slow

Step 2: $H_2O_2 + OI^- \rightarrow H_2O + O_2 + I^-$ fast

(i) Identify the catalyst. (1)

(ii) Identify the intermediate. (1)

(iii) Devise the overall chemical equation consistent with the mechanism provided. (1)

(iv) Devise the rate law. (1)

END OF EXAM QUESTIONS

LIST OF USEFUL EQUATION AND CONSTANTS

Van der Waals eqⁿ. $P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$

Universal Gas constant	R	=	8.314 J K^{-1} mol^{-1}
Boltzmann's constant,	k	=	1.381 x 10^{-23} J K^{-1}
Planck's constant	h	=	6.626 x 10^{-34} J s
Debye-Hückel's constant,	A	=	0.509 $(mol\ dm^{-3})^{1/2}$ or $mol^{-0.5}kg^{0.5}$
Faraday's constant	F	=	96485 C mol^{-1}
Mass of electron	m_e	=	9.109 x 10^{-31} kg
Velocity of light	c	=	2.998 x 10^8 m s^{-1}
Avogadro's constant	N_A	=	6.022 x 10^{23}
1 electron volt (eV)		=	1.602 x 10^{-19} J