



**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
<ol style="list-style-type: none">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 dm³
 - B. 48.8 dm³
 - C. 67.2 dm³
 - D. 44.8 dm³
 - 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:
- Positive
 - Negative
 - Zero
 - Pressure x Volume
 - 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 $1 \times 10^6 \text{ Pa}$ and the change in internal energy is 54 kJ during the process. The heat absorbed by the mixture is
- 30 kJ
 - 54 kJ
 - 84 kJ
 - 100 kJ
 - Insufficient information
9. The heat absorbed or given out by a reaction at constant pressure is known as:
- Entropy change
 - Work
 - Enthalpy change
 - Internal energy change
 - 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?
- 900 J
 - 250 J
 - 1450 J
 - -1459 J
 - -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.
- 61.1 kJmol^{-1}
 - 16.1 kJmol^{-1}
 - 25.0 kJmol^{-1}
 - 28.9 kJmol^{-1}
 - Insufficient information
12. The conductivity for an acid HA solution of 0.0316 M concentration is $9.260 \text{ } \Omega^{-1}\text{m}^{-1}$. Calculate the molar conductivity (in $\Omega^{-1}\text{m}^2\text{mol}^{-1}$) of the solution.
- 2.93
 - 2.93×10^2
 - 0.293
 - 2.93×10^{-2}
 - None of the above

13. The degree of dissociation of an acid HX in aqueous solution of concentration $0.025 \text{ mol dm}^{-3}$ is 0.028. What is the K_a for the acid?
- 7.2×10^{-4}
 - 2.0×10^{-5}
 - 8.1×10^{-4}
 - 1.8×10^{-5}
 - 2.0×10^{-4}
14. The molar conductivities of Cs^+ and SO_4^{2-} are 0.772×10^{-2} and $1.600 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$, respectively. What is the molar conductivity of Cs_2SO_4 ?
- $3.972 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$
 - $3.144 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$
 - $0.828 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$
 - $2.372 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$
 - Insufficient information
15. The molar conductivity of $\text{Mg}(\text{NO}_3)_2$ is $2.488 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$. If the molar conductivity of Mg^{2+} is $1.060 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$, what is the molar conductivity of NO_3^- ?
- $0.368 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$
 - $1.428 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$
 - $0.714 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$
 - $0.184 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$
 - Insufficient information
16. The molar conductivities at infinite dilution, Λ_o , for $\text{HCl}(\text{aq})$, $\text{NaB}(\text{aq})$ (sodium benzoate) and $\text{NaCl}(\text{aq})$ are 426.2, 82.4 and $126.5 \text{ Scm}^2\text{mol}^{-1}$, respectively, at 25°C . What is Λ_o for HB (benzoic acid) in $\text{Sm}^2\text{mol}^{-1}$?
- 0.382
 - 3.82×10^2
 - 3.82
 - 3.82×10^{-2}
 - None of the above
17. What are the units of k for the rate law, $\text{Rate} = k \frac{[\text{A}]^2}{[\text{B}]}$, when the concentration and time units are mol/L and seconds, respectively?
- s^{-1}
 - $\text{L mol}^{-1} \text{ s}^{-1}$
 - $\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$
 - $\text{L}^2 \text{ s}^2 \text{ mol}^{-2}$
 - $\text{L}^{-2} \text{ s}^{-2} \text{ mol}^{-2}$

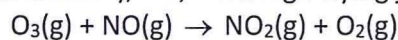
18. A reaction $A \rightarrow P$ displays first-order kinetics. It therefore follows that a plot of _____ versus time is linear, and that the slope of this plot = _____.

- 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.



The rate expression is $\text{rate} = k[O_3][NO]$. 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) $\text{Cl(g)} \rightarrow \text{Cl}^{\text{-}}(\text{g})$
 - (iv) Water frozen at 0°C and 1 atm
 - (v) $\text{CH}_3\text{CH}_2\text{CH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$
 - (vi) $\text{H}_2(\text{g}, 300\text{ K}, 1\text{ atm}) \rightarrow \text{H}_2(\text{g}, 100\text{ K}, 1\text{ atm})$
 - (vii) $\text{Cl}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$

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

- (a) The gas absorbs 234 J of heat and is compressed by 534 J of work. $\Delta U = ?$
- (b) The gas is cooled by removing 106 J of heat and expands doing 242 J of work. $\Delta U = ?$
- (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? $\Delta U = ?$
- (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 ($\kappa = 1.4087 \times 10^{-3} \text{ Scm}^{-1}$) in the cell, and the measured resistance was 688 Ω .
- (i) Find the cell constant. (3)
- (ii) A 0.010 M AgNO₃ solution in the same cell had a resistance of 777 Ω . What is the conductivity, κ , for the AgNO₃ solution? (3)
- (c) Given the standard reduction potentials – 0.403 V and 0.337 V at 298 K for the half cells Cd²⁺|Cd(s) and Cu²⁺|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]**

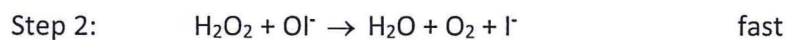
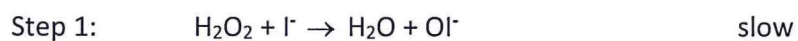
- (a) What is the overall order of the reaction described by each of the rate expressions below? State the units of the rate coefficient, k , if the rate is in $\text{mol dm}^{-3} \text{ s}^{-1}$.
- (i) Rate = $k[A]^2[B]$ (ii) Rate = $k[A]^{1.5}[B]^{0.5}$ (4)
- (b) Consider a reaction $A \xrightarrow{k} P$. The integrated rate law for the reaction is:
- $$[A] - [A]_0 = -kt$$
- (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 $\text{mol L}^{-1} \text{ min}^{-1}$? (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_0 . Determine the order of each of the two reactions. (4)

$C_0 / \text{mol dm}^{-3}$	$t_{0.5} / \text{seconds}$	
	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:



- (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
