nAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH, NATURAL RESOURCES AND APPLIED SCIENCES

DEPARTMENT OF NATURAL AND APPLIED SCIENCES

QUALIFICATION: VARIOUS	
QUALIFICATION CODE: VARIOUS	LEVEL: 6
COURSE NAME: : PHYSICAL CHEMISTRY	COURSE CODE: PCH602S
SESSION: JANUARY 2023	PAPER: THEORY
DURATION: 3 HOURS	MARKS: 100

SUPPLEMENTARY/SECOND OPPORTUNITY EXAMINATION QUESTION PAPER	
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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 8 PAGES (Including this front page and list of useful constants and equation as an attachment)

SECTION A: MULTIPLE CHOICE QUESTIONS [20]

There are 10 questions in this section. Choose the correct answer. Each question carries 2 marks.

1. Which of the following statements is **not true** about the First Law of Thermodynamics?
   A. Although energy may be converted from one form to another, it cannot be created or destroyed.
   B. When a chemical system changes from one state to another, the net transfer of energy to its surroundings must be balanced by a corresponding change in the internal energy of the system.
   C. Energy U is a state function, meaning that its value is completely determined by the thermodynamic state of the system.
   D. Energy is not conserved in an isolated system, i.e. energy of an isolated system is not constant.
   E. There are 2 distinct ways to transport energy into or out of a closed system that is not isolated, through heat, q, and work, w

2. For a reversible adiabatic process, change in entropy is
   A. Maximum
   B. Minimum
   C. Zero
   D. Negative
   E. Unpredictable

3. Which of the following is a spontaneous process?
   A. Freezing water at 40°C
   B. Melting of ice at -273°C
   C. Freezing of water at -24°C
   D. Melting of ice at -24°C
   E. Melting of ice at 100°C

4. Which of the following processes is most likely to lead to an increase in the entropy of the system?
   A. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   B. $H_2O(l) \rightleftharpoons H_2O(s)$
   C. $SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(g)$
   D. $NH_4NO_3(s) + H_2O(l) \rightarrow NH_4^+ (aq) + NO_3^- (aq)$
   E. $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

5. The equilibrium constant for a reaction is 0.48 at 25°C. What is the value of ΔG° at this temperature?
   A. 1.8 kJ
   B. − 4.2 kJ
   C. 1.5×10^2 kJ
   D. 4.2 kJ
   E. More information is needed

6. Consider the reaction $A(g) + B(g) \rightarrow 2C(g)$. For this reaction, $\Delta H° = -116$ kJ mol^{-1} and the equilibrium constant K_p is 140 at 600 K. Calculate for this reaction (i) $\Delta G°$ and (ii) $\Delta S°$ at 600 K.

   A. (i) 24.7 kJmol^{-1} and   (ii) -60.4 kJ K^{-1}mol^{-1}
   B. (i) -60 kJmol^{-1} and   (ii) -24.7 kJ K^{-1}mol^{-1}
   C. (i) -24.7 kJmol^{-1} and   (ii) -152 J K^{-1}mol^{-1}
   D. (i) -24.7 kJmol^{-1} and   (ii) -60.4 kJ K^{-1}mol^{-1}
   E. None of the above

7. When the concentration of the reactants are measured in moldm^{-3} and time in seconds, what are the appropriate units for (i) rate and (ii) rate constant for the reaction associated with rate law, Rate = k[A][B]?

   A. (i) moldm^{-3}s^{-1} (ii) dm^{3}mol^{-1}s^{-1}
   B. (i) moldm^{-3}s^{-1} (ii) dm^{3}mol^{-1}s^{-1}
   C. (i) moldm^{-3} (ii) dm^{3}mol^{-1}s^{-1}
   D. (i) moldm^{-3}s^{-1} (ii) dm^{6}mol^{-1}s^{-1}
   E. (i) moldm^{-3}s^{-1} (ii) dm^{-3}mol^{-1}s^{-1}

8. When the concentration of A in a simple reaction $A \rightarrow B$ was changed from 0.51 moldm^{-3} to 1.03 moldm^{-3}, the half-life dropped from 150 seconds to 75 seconds at 25°C. What is the (i) order of the reaction and (ii) the value of the rate constant?

   A. (i) n = 0   and   (ii) k = 1.70 x 10^{-3} moldm^{-3}s^{-1}
   B. (i) n = 1   and   (ii) k = 1.31 x 10^{-2} s^{-1}
   C. (i) n = 2   and   (ii) k = 1.31 x 10^{-1} dm^{3}mol^{-1}s^{-1}
   D. (i) n = 1   and   (ii) k = 4.62 x 10^{-3} s^{-1}
   E. None of the above

9. The reaction of a tertiary haloalkane (represented by RX below) with hydroxide ions to follow the mechanism:

   Step 1: $RX \rightarrow R^+ + X^-$
   Step 2: $R^+ + OH^- \rightarrow ROH$

   If Step 1 is found to be a slow step in the mechanism, which of the following statements is true?

   (i)   The reaction will be found to be first order with respect to RX.
   (ii)   The reaction has an intermediate represented by R^+.
   (iii)   The reaction rate is independent of the concentration of the hydroxide ions.

   A. (i) only
   B. (ii) only
   C. (iii) only
   D. (ii) and (ii) only
   E. (i), (ii) and (iii)

10. If the activation energy in the forward direction of an elementary step is 52 kJ and the activation energy in the reverse direction is 74 kJ, what is the energy of reaction, ΔH, for this step?
    A. 22 kJ
    B. - 22 kJ
    C. 52 kJ
    D. - 52 kJ
    E. 126 kJ

SECTION B   [80]
There are **FOUR** questions in this section. Answer **all** Questions.

## QUESTION 1   [16]
   (a) Briefly state each of the following laws: (4)
       (i) Boyle's law
       (ii) Hess's law
       (iii) Zeroth law of thermodynamics
       (iv) Kirchhoff's law or equation
   (b) State whether q, w, ΔU and ΔS are negative, zero or positive for cooling of an ideal gas at constant volume.   (4)
   (c) The statements below are all **false**. For each statement either correct it or state briefly the reason for its being false.   (6)
       (i) Charles' law states that the volume of a given amount of gas is directly proportional to the absolute temperature on the Kelvin scale under any conditions.
       (ii) The total heat absorbed, q, for a cyclic process is equal to zero.
       (iii) The Second Law of Thermodynamics states that the entropy of the system. always increases during a spontaneous process.
       (iv) Every closed system is isolated and every isolated system is closed.
       (v) The work done for reversible process is greater than the work done for an irreversible process.
       (vi) $C_p = \left(\dfrac{\partial U}{\partial T}\right)_p$
   (d) For each of the following reactions, show or explain whether the heat evolved at constant pressure (ΔH) is smaller, larger than or the same as the heat evolved at constant volume (ΔU).   (2)
       (i) $C_2H_2(g) + 3H_2(g) \rightarrow 2CH_4(g)$
       (ii) $BaCl_2(s) + F_2(g) \rightarrow BaF_2(s) + Cl_2(g)$

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QUESTION 2 [24]

(a) If one mole of an ideal gas, $C_v = \frac{5}{2}R$, is expanded adiabatically until the temperature drops from 20°C to 10°C, calculate q, w, ΔU and ΔH. (8)

(b) In the figure below, if 17 moles of an ideal gas (, $C_v = \frac{3}{2}R$) go from point 1, $T_1 = 290$ K, to point 2, $T_2 = 358$ K, what is its change in internal energy (in kJ). (3)

(c) If $P_1 = 179$ kPa, $V_1 = 7.37$ dm^3 and $P_2 = 200$ kPa, $V_2 = 10$ dm^3, what is the heat absorbed or liberated (in kJ) for the path taken as shown by the arrows? Assume that the change in internal energy is the same as your answer in Problem (b). (4)
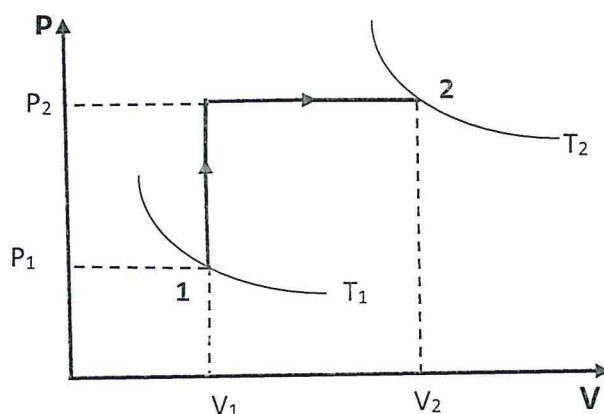
(d) The linear form of the Clausius–Clapeyron equation may be written as:

$$\ln P = -\frac{\Delta H_v}{R}\frac{1}{T} + C$$

(i) State the main assumptions in its derivation. (3)

(ii) The vapour pressure of chloromethane is represented by the equation

$$\ln\left(P/\text{mmHg}\right) = -\frac{2647}{T} + 17.23$$

where T is the temperature in Kelvins. Calculate the molar enthalpy of vaporization. Does the molar entropy of vaporization for chloromethane conform to Trouton's rule? Show clearly your answer. (Normal boiling point of chloroomethane is −23°C) (6)

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QUESTION 3 [16]

(a) Given the standard enthalpy of formation and heat capacity data below, estimate the enthalpy change at 100°C for the gas phase reaction: $3C_2H_2 \rightarrow C_6H_6$ (8)

Species	C_2H_2	C_6H_6
$\Delta H^\circ_{f,298}$/kJmol^{-1}	226.7	82.9

$$C_p(C_2H_2) = 30.7 + 5.28 \times 10^{-2}T \qquad JK^{-1}mol^{-1}$$
$$C_p(C_6H_6) = -1.7 + 32.5 \times 10^{-2}T \qquad JK^{-1}mol^{-1}$$

(b) Use the data below to calculate ΔH°, ΔS°, ΔG° and K_p for the reaction below at 298K.

$CH_3CH_2CH_2CH_3$ (g) $\leftrightharpoons$ $CH_3CH(CH_3)_2$ (g) (8)
Butane   2-Methylpropane

Compound	ΔH°_f / kJmol^{-1}	S° (298K)
Butane	-126 kJmol^{-1}	270 JK^{-1}mol^{-1}
2-Methylpropane	-125 kJmol^{-1}	295 JK^{-1} mol^{-1}

QUESTION 4 [24]

(a) The general expression for the integrated rate equations is of the form:

$$\frac{1}{n-1}\left(\frac{1}{[A]^{n-1}} - \frac{1}{[A]_o^{n-1}}\right) = kt \quad \text{for } n \neq 1$$

State the two requirements in order to derive such equations. (2)

(b) The reaction $H_2 + I_2 \rightarrow 2HI$ is first order with respect to $[H_2]$ and $[I_2]$. When $[H_2] = 1$ molL^{-1} and $[I_2] = 2$ molL^{-1}, the following kinetic are observed.

$$\frac{d[HI]}{dt} = 1.78 \times 10^{-4} \text{ molL}^{-1}s^{-1} \text{ at 556 K and } \frac{d[HI]}{dt} = 0.2572 \text{ molL}^{-1}s^{-1} \text{ at 700 K.}$$

Calculate the rate constant at each of the temperatures and evaluate the activation energy and the Arrhenius pre-exponential factor. [Assume that the pre-exponential factor is constant] (8)

(c) The reverse reaction, i.e. $2HI \rightarrow H_2 + I_2$, has an activation energy of 183 kJmol^{-1}. Does this make the reaction $H_2 + I_2 \rightarrow 2HI$ exothermic or endothermic? Explain your answer with a diagram of the energy profile of the reaction. (6)

(d) Hydrogen peroxide, H_2O_2, decomposes in water by a first order kinetics process. A 0.156 moldm^{-3} solution of H_2O_2 in water has an initial rate of 1.14×10^{-5} moldm^{3}s^{-1}. Calculate the rate constant, k, for the decomposition reaction and the half-life of the decomposition. (4)

(e) Explain the meaning of *intermediate* and *catalyst* using the following mechanism, which is thought to occur in the atmosphere: (2)

$$NO + O_3 \xrightarrow{k_1} NO_2 + O_2$$

$$O + NO_2 \xrightarrow{k_2} NO + O_2$$
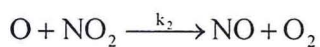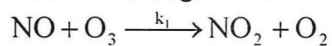
(f) The gas decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps

$$N_2O \xrightarrow{k_1} N_2 + O$$

$$N_2O + O \xrightarrow{k_2} N_2 + O_2$$
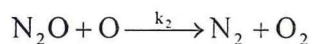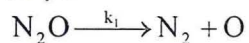
Experimentally, the rate is found to be rate = $k[N_2O]$.

(i)   Write the equation for the overall reaction. (1)

(ii)   What can you say about the relative rates of steps 1 and 2? (1)

END OF EXAM QUESTIONS

LIST OF USEFUL EQUATION AND CONSTANTS

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

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