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: NOVEMBER 2022	**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 8 PAGES (Including this front page and a 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. An ideal gas at 27°C is heated at constant pressure until its volume is doubled. The final temperature is:
   A. 54°C
   B. 327°C
   C. 108°C
   D. 654°C
   E. 600°C

2. Which of the following **is not** an intensive property?
   A. Pressure
   B. Temperature
   C. Density
   D. Heat
   E. Molar volume

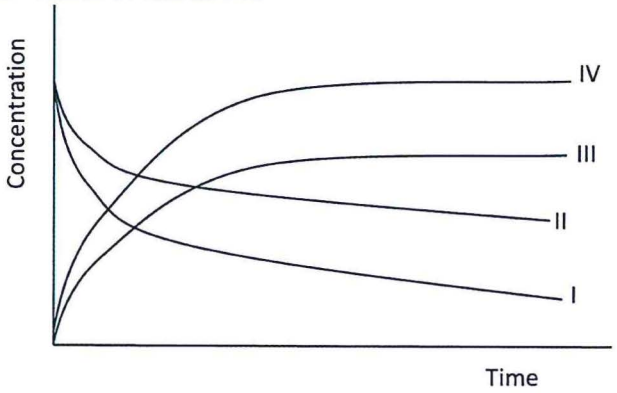
3. For a reversible power cycle, the operating temperature limits are 800 K and 300 K. It takes in 400 kJ of heat. The unavailable work will be:
   A. 250 kJ
   B. 150 kJ
   C. 120 kJ
   D. 100 kJ
   E. Zero

4. If $\Delta G^\circ < 0$, then K is _____. If $\Delta G^\circ > 0$, then K is _____. If $\Delta G^\circ = 0$, then K is _____.
   A. $> 1, < 1, = 1$
   B. $< 1, > 1, = 1$
   C. $< 0, > 0, = 0$
   D. $> 0, < 0, = 0$
   E. $< 1, > 1, = 0$

5. Which of the following **is not** one of the assumptions in the derivation of the Clausius-Clapeyron equation?
   A. $V_{gas} >>> V_{liquid}$
   B. Gas behaves as ideal gas, i.e. $V = RT/P$ for 1 mole
   C. $\Delta H_{vaporisation}$ is independent of temperature in a given range
   D. Solid $\rightleftharpoons$ Liquid
   E. None of the above

6. A schematic diagram of the variation of concentration of the reactants and products with time for the reaction $3W + X \rightarrow Y + 2Z$ is shown below. Which of the following is the most likely representation of the variation of the concentration of the reactants and products with time?

A. I = W; II = X; III = Z; IV = Y
B. I = X; II = W; III = Y; IV = Z
C. I = W; II = X; III = Y; IV = Z
D. I = X; II = W; III = Z; IV = Y
E. None of the above



7. Write a balanced reaction for which the following rate relationships are true.

$$\text{Rate} = \frac{1}{2}\frac{d[N_2]}{dt} = \frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[N_2O]}{dt}$$

A. $2N_2O \rightarrow 2N_2 + O_2$
B. $N_2O \rightarrow N_2 + 2O_2$
C. $2N_2 + O_2 \rightarrow 2N_2O$
D. $\frac{1}{2}N_2O \rightarrow \frac{1}{2}N_2 + O_2$
E. Insufficient information

8. The decomposition of $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$ proceeds as a first order reaction. Which equation below best gives the concentration of N_2O_5 versus time profile?

A. $[N_2O_5] = \frac{[N_2O_5]_o}{t_{0.5}}$
B. $[N_2O_5] = kt$
C. $[N_2O_5] = [N_2O_5]_o e^{-kt}$
D. $\frac{1}{[N_2O_5]} = \frac{1}{[N_2O_5]_o} + kt$
E. None of the above

9. The values for the change in enthalpy, ΔH, and the activation energy, E_A, for a given reaction are known. The value of E_A for the reverse reaction equals
   A. E_A for the forward reaction
   B. $-(E_A)$ for the forward reaction
   C. the sum of $-(\Delta H)$ and E_A
   D. the sum of E_A and ΔH
   E. the difference between ΔH and E_A

10. The balanced equation for the reaction of nitrogen dioxide and fluorine is
    $2NO_2 + F_2 \rightarrow 2NO_2F$
    The proposed mechanism is

Step 1:	$NO_2 + F_2 \rightarrow NO_2F + F$	slow
Step 2:	$F + NO_2 \rightarrow NO_2F$	fast

    Which of the following are correct?
    (i) The mechanism supports an experimentally determined rate law of rate = $k[NO_2]^2[F_2]$
    (ii) F is an intermediate
    (iii) The reaction is first order with respect to F_2.
    A. (i) only
    B. (i) and (ii) only
    C. (i) and (iii) only
    D. (ii) and (iii) only
    E. (i), (ii) and (iii)

SECTION B **[80]**

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

QUESTION 1 **[12]**

State whether each of the following statements is **true** or **false**. If false either correct it or state briefly the reason for its being false.

(a) $q = \oint dq = 0$ and $\Delta T = \oint dT = 0$, where q and T is the heat absorbed and temperature, respectively. (2)

(b) The compressibility factor, $Z > 1$ for many gases at high pressures is attributed to finite size of gas molecules and repulsive forces. (2)

(c) $\Delta H_{combustion} = \Delta U_{combustion}$ for the combustion reaction (2)
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ (2)

(d) For the reaction $2C(g) + O_2(g) \rightarrow 2CO(g)$, $\Delta H^{\circ}_{reaction} = \Delta H^{\circ}_{f}\left(CO(g)\right)$ (2)

(e) For a perfect crystalline substance, $S_{0^{\circ}C} = 0$. (2)

(f) $\left(\frac{\partial G}{\partial T}\right)_P = S$ and $\left(\frac{\partial U}{\partial T}\right)_V = C_V$ (2)

QUESTION 2 **[13]**

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

(b) A sample consisting of 2.00 mol argon (assume to behave as ideal gas) is expanded reversibly and isothermally at 0°C from 22.4 dm^3 to 44.8 dm^3. For this process, calculate q, w ΔU and ΔH. (8)

QUESTION 3 **[13]**

(a) Estimate the enthalpy change of formation for $NH_3(g)$ at 100°C given: (3)

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightleftharpoons NH_3(g),\ \Delta H_f^\circ(25°C) = -46.11\ kJmol^{-1}$$

$C_p(N_2, g) = 29.12\ JK^{-1}mol^{-1}$

$C_p(H_2, g) = 28.82\ JK^{-1}mol^{-1}$

$C_p(NH_3, g) = 35.06\ JK^{-1}mol^{-1}$

(b) Calculate ΔG° for 1 mole of N_2O_4 decomposition at 298 K, given $K_p = 0.163$. If ΔS° for the reaction is 184.2 $JK^{-1}mol^{-1}$ at 298 K, calculate ΔH° at 298 K. (3)

(c) The equilibrium constant of the reaction

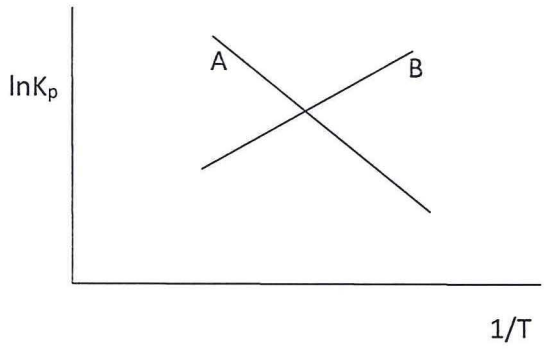
$COCl_2(g) \rightleftharpoons CO)g) + Cl_2(g)$

was determined as a function of temperature and the data was fitted using the linear form of the van't Hoff isochore and the result was:

$$\ln K_p = \frac{14080}{T} + 17.85$$

Use these results to obtain ΔH°, ΔS° and ΔG°. (4)

(d) Is the reaction in (c) above endothermic or exothermic? Give a reason for you answer. Which linear plot A or B in the diagram below best represents this reaction? (3)



QUESTION 4 **[11]**

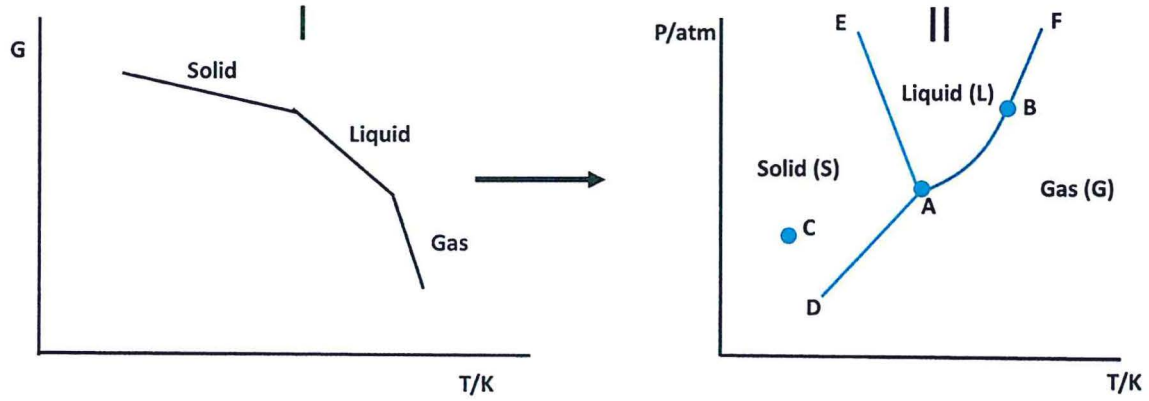
Using the diagrams **I** and **II** below for a given pure liquid, answer the following questions:

(a) Sketch diagram **I** and on the same diagram show the effect of solute and label the positions of the melting point and boiling point of both the liquid and solution. (3)

(b) Calculate the degrees of freedom at A, B and C in diagram **II**. (3)

(c) The $\Delta H_{sublimation}$ of pure liquid is 60.5 kJ/mol, while its $\Delta H_{vaporization}$ is 48.0 kJ/mol. What is the ΔH_{fusion} of the pure liquid? (2)

(d) If the boiling point of the pure liquid in (c) is 184.3°C, calculate the entropy of vaporisation (ΔS_V) and comment on the result. (3)



QUESTION 5 **[31]**

(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 = $k\dfrac{[A]^{1.5}}{[B]^{1.5}}$ (ii) Rate = $k[A][B]^{0.5}[C]^{1.5}$ (4)

(b) Nitrogen pentoxide (N_2O_5) gas decomposes according to the reaction

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

At 328 K, the rate of the reaction under certain conditions is 0.75×10^{-4} $molL^{-1}s^{-1}$. Assuming that none of the intermediates have appreciable concentrations, determine the values of:

(i) $\dfrac{d[N_2O_5]}{dt}$ (ii) $\dfrac{d[NO_2]}{dt}$ (iii) $\dfrac{d[O_2]}{dt}$ (6)

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

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

(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)

(d) 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 three reactions. (6)

	$t_{0.5}$ / min		
C_o / moldm^{-3}	Reaction 1	Reaction 2	Reaction 3
2	2	120	20
1	2	60	40

(e) 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)

(v) For majority of the reactions, a catalyst speeds up the reaction by decreasing the energy of activation but for a few reactions, a catalyst speeds up the reaction but the energy of activation increases. Give a brief plausible reason. (1)

END OF EXAM

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