NAMIBIA UNIVERSITY
OF SCIENCE AND TECHNOLOGY

FACULTY OF HEALTH 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 2019	**PAPER:** THEORY
DURATION: 3 HOURS	**MARKS:** 100

FIRST OPPORTUNITY EXAMINATION QUESTION PAPER	
EXAMINER(S)	**Prof Habauka M Kwaambwa**
MODERATOR:	**Prof Rajaram Swaminathan**

INSTRUCTIONS
1. Answer ALL the questions. 2. Write clearly and neatly. 3. Number the answers clearly.

PERMISSIBLE MATERIALS

Non-programmable Calculators

ATTACHMENT

List of Useful Constants

THIS QUESTION PAPER CONSISTS OF 7 PAGES (Including this front page and 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 double. 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. If a gas is heated against a constant pressure, keeping the volume constant, then work done will be
   A. Positive
   B. Negative
   C. Zero
   D. Infinity
   E. Anywhere between zero and infinity

4. Which one of the following is always positive when a spontaneous process occurs?
   A. ΔS_{system}
   B. $\Delta S_{surrounding}$
   C. $\Delta S_{universe}$
   D. $\Delta H_{universe}$
   E. $\Delta H_{surrounding}$

5. The efficiency of a Carnot engine depends on
   A. Working substance
   B. Design of the engine
   C. Size of engine
   D. Type of fuel fired
   E. Temperatures of source and sink

6. 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. $< 1, > 1, = 0$

7. The $\Delta H_{sublimation}$ of I_2 is 60.46 kJ/mol, while its $\Delta H_{vaporization}$ is 41.71 kJ/mol. What is the ΔH_{fusion} of I_2?
   A. 102.17 kJ/mol
   B. – 102.17 kJ/mol
   C. 18.75 kJ/mol
   D. – 18.75 kJ/mol
   E. Insufficient information

8. When a conductance cell was filled with 0.0025 M solution of K_2SO_4, its resistance was 326 Ω. If the cell constant is 0.2281 cm^{-1}, the conductivity (in $\Omega^{-1}cm^{-1}$) of K_2SO_4 solution is
   A. 4.997×10^{-4}
   B. 5.997×10^{-4}
   C. 7.997×10^{-4}
   D. 3.997×10^{-4}
   E. 6.997×10^{-4}

9. Which of the following expressions is correct?
   A. $\Lambda_o\left(Al_2(SO_4)_3\right) = 3\lambda_o^+\left(Al^{3+}\right) + 2\lambda_o^-\left(SO_4^{2-}\right)$
   B. $\Lambda_o\left(Al_2(SO_4)_3\right) = \lambda_o^+\left(Al^{3+}\right) + \lambda_o^-\left(SO_4^{2-}\right)$
   C. $\Lambda_o\left(NH_4OH\right) = \Lambda_o\left(NH_4Cl\right) - \Lambda_o\left(NaCl\right) + \Lambda_o\left(NaOH\right)$
   D. $\Lambda_o\left(FeSO_4\right) = 2\lambda_o^+\left(Fe^{2+}\right) + 2\lambda_o^-\left(SO_4^{2-}\right)$
   E. $\Lambda_o\left(NH_4OH\right) = \Lambda_o\left(NH_4Cl\right) - \Lambda_o\left(NaOH\right) - \Lambda_o\left(NaCl\right)$

10. 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. Any of the above

SECTION B **[80]**

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

QUESTION 1 **[14]**

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) $w = \oint dw = 0$ and $\Delta H = \oint dH = 0$

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

(c) $\Delta H_{combustion} = \Delta U_{combustion}$ for the combustion reaction

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

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

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

(f) $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$

(g) According to Trouton's law, the entropy of vaporisation at normal boiling point of benzene (C_6H_6) and water is approximately equal to 88 $JK^{-1}mol^{-1}$.

QUESTION 2 **[13]**

(a) State whether q, w, ΔU, ΔH and ΔS are positive, negative or zero in adiabatic compression 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

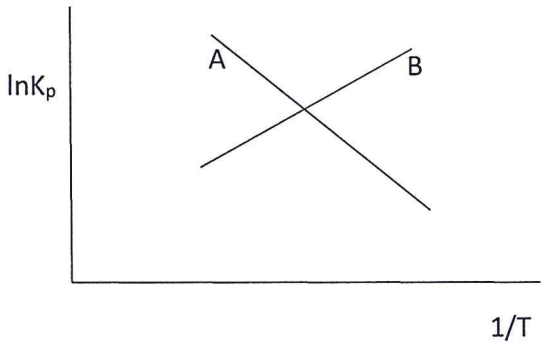
$COCl_2(g) \rightleftharpoons CO)g) + Cl_2(g)$

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 **[20]**

(a) Explain briefly why **conductivity, κ,** is not the most convenient quantity to use for the study of electrolytic conduction. (2)

(b) The molar conductivities at infinite dilution (in $\Omega^{-1}cm^2mol^{-1}$) of NaCl, HCOONa and HCl are 126.4, 104.6 and 426.1, respectively, at 25°C. The molar conductivity of the carboxylic acid, HCOOH, at a concentration of 0.100 M is 50.5 $\Omega^{-1}cm^2mol^{-1}$. Calculate the following:

(i) molar conductivity at infinite dilution, Λ_o, of HCOOH. (2)

(ii) dissociation constant K_a and the pH of the acid solution. (6)

(c) State the two functions of a salt bridge in an electrochemical cell. (2)

(d) Given the following electrochemical cell notation

$$Pt\left|Ti^{3+}(0.1m), Ti^{4+}(0.1m)\right\|Cu^{+}(0.1m)\left|Cu(s)\right.$$

(i) Deduce the overall chemical reaction of the electrochemical cell. (2)

(ii) If the emf of the cell, E_{cell}, is 0.442 V at 25°C, calculate ΔG, ΔH and ΔS for the reaction if the temperature coefficient of the emf is -1.25×10^{-4} VK^{-1} at this temperature. (6)

QUESTION 5 **[20]**

(a) What is the overall order of the reaction described by each of the rate expressions below? State the units of the rate coefficient of 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) The rate of a reaction A → Product(s) is given by

$$-\frac{d[A]}{dt} = k[A]^2$$

(i) Derive the integrated rate law equation and state assumptions involved. (7)

(ii) Deduce the expression for the half-life of A showing your working. (3)

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