

**NAMIBIA UNIVERSITY  
OF SCIENCE AND TECHNOLOGY**

**FACULTY OF HEALTH AND APPLIED SCIENCES**

**DEPARTMENT OF NATURAL AND APPLIED SCIENCES**

<b>QUALIFICATION:</b> VARIOUS	
<b>QUALIFICATION CODE:</b> VARIOUS	<b>LEVEL:</b> 6
<b>COURSE NAME:</b> : PHYSICAL CHEMISTRY	<b>COURSE CODE:</b> PCH602S
<b>SESSION:</b> JANUARY 2020	<b>PAPER:</b> THEORY
<b>DURATION:</b> 3 HOURS	<b>MARKS:</b> 100

<b>SUPPLEMENTARY/SECOND OPPORTUNITY EXAMINATION QUESTION PAPER</b>	
<b>EXAMINER(S)</b>	Prof Habauka M Kwaambwa
<b>MODERATOR:</b>	Prof Rajaram Swaminathan

<b>INSTRUCTIONS</b>
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.

- Which of the following statements is not true about the First Law of Thermodynamics?
  - Although energy may be converted from one form to another, it cannot be created or destroyed.
  - 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.
  - Energy  $U$  is a state function, meaning that its value is completely determined by the thermodynamic state of the system.
  - Energy is not conserved in an isolated system, i.e. energy of an isolated system is not constant.
  - There are 2 distinct ways to transport energy into or out of a closed system that is not isolated, through heat,  $q$ , and work,  $w$
- According to the First Law of Thermodynamics, work done in an adiabatic process between a given pair of end states depends on
  - The end states only, i.e. initial and final state
  - Particular adiabatic process
  - The value of  $\gamma = C_p/C_v$
  - The value of the heat transferred
  - Mass of the system
- Which of the following is a spontaneous process?
  - Freezing water at  $40^\circ\text{C}$
  - Melting of ice at  $-273^\circ\text{C}$
  - Freezing of water at  $-24^\circ\text{C}$
  - Melting of ice at  $-24^\circ\text{C}$
  - Melting of ice at  $100^\circ\text{C}$
- Which of the following processes is most likely to lead to an increase in the entropy of the system?
  - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
  - $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{s})$
  - $\text{SiH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{g})$
  - $\text{NH}_4\text{NO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
  - $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

5. The equilibrium constant for a reaction is 0.48 at 25°C. What is the value of  $\Delta G^\circ$  at this temperature?
- A. 1.8 kJ  
 B. -4.2 kJ  
 C.  $1.5 \times 10^2$  kJ  
 D. 4.2 kJ  
 E. More information is needed
6. Consider the reaction  $A(g) + B(g) \rightarrow 2C(g)$ . For this reaction,  $\Delta H^\circ = -116 \text{ kJ mol}^{-1}$  and the equilibrium constant  $K_p$  is 140 at 600 K. Calculate for this reaction (i)  $\Delta G^\circ$  and (ii)  $\Delta S^\circ$  at 600 K.
- A. (i)  $24.7 \text{ kJ mol}^{-1}$                       and                      (ii)  $-60.4 \text{ kJ K}^{-1} \text{ mol}^{-1}$   
 B. (i)  $-60 \text{ kJ mol}^{-1}$                       and                      (ii)  $-24.7 \text{ kJ K}^{-1} \text{ mol}^{-1}$   
 C. (i)  $-24.7 \text{ kJ mol}^{-1}$                       and                      (ii)  $-154 \text{ J K}^{-1} \text{ mol}^{-1}$   
 D. (i)  $-24.7 \text{ kJ mol}^{-1}$                       and                      (ii)  $-60.4 \text{ kJ K}^{-1} \text{ mol}^{-1}$   
 E. None of the above
7. If  $\lambda_o^+(K^+) = 73.5 \text{ Scm}^2 \text{ mol}^{-1}$ ,  $\lambda_o^+(Al^{3+}) = 189 \text{ Scm}^2 \text{ mol}^{-1}$  and  $\lambda_o^+(SO_4^{2-}) = 160 \text{ Scm}^2 \text{ mol}^{-1}$ , then
- A.  $\Lambda_o(KAl_2(SO_4)_2) = 165 \text{ Scm}^2 \text{ mol}^{-1}$   
 B.  $\Lambda_o(K_2SO_4) = 307 \text{ Scm}^2 \text{ mol}^{-1}$   
 C.  $\Lambda_o(K_2SO_4) = 393.5 \text{ Scm}^2 \text{ mol}^{-1}$   
 D.  $\Lambda_o(Al_2(SO_4)_3) = 887 \text{ Scm}^2 \text{ mol}^{-1}$   
 E. None of the above
8. The conductivity of 0.10 M KCl solution at 20°C is  $0.0212 \text{ Scm}^{-1}$  and the resistance of the cell containing this solution at 20°C is 55  $\Omega$ . The cell constant is:
- A.  $3.173 \text{ cm}^{-1}$   
 B.  $1.166 \text{ cm}^{-1}$   
 C.  $4.616 \text{ cm}^{-1}$   
 D.  $3.324 \text{ cm}^{-1}$   
 E.  $317.3 \text{ cm}^{-1}$
9. When the concentration of the reactants are measured in  $\text{mol dm}^{-3}$  and time in seconds, what are the appropriate units for (i) rate and (ii) rate constant for a second order reaction?
- A. (i)  $\text{mol dm}^{-3} \text{ s}^{-1}$                       (ii)  $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   
 B. (i)  $\text{mol dm}^{-3} \text{ s}^{-1}$                       (ii)  $\text{dm}^2 \text{ mol}^{-1} \text{ s}^{-1}$   
 C. (i)  $\text{mol dm}^{-3}$                       (ii)  $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   
 D. (i)  $\text{mol dm}^{-3} \text{ s}^{-1}$                       (ii)  $\text{dm}^6 \text{ mol}^{-1} \text{ s}^{-1}$   
 E. (i)  $\text{mol dm}^{-3} \text{ s}^{-1}$                       (ii)  $\text{dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$

10. When the concentration of A in a simple reaction  $A \rightarrow B$  was changed from  $0.51 \text{ mol dm}^{-3}$  to  $1.03 \text{ mol dm}^{-3}$ , the half-life dropped from 150 seconds to 75 seconds at  $25^\circ\text{C}$ . What is the (i) order of the reaction and (ii) the value of the rate constant?
- A. (i)  $n = 0$  and (ii)  $k = 1.70 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$   
 B. (i)  $n = 1$  and (ii)  $k = 1.31 \times 10^{-2} \text{ s}^{-1}$   
 C. (i)  $n = 2$  and (ii)  $k = 1.31 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   
 D. (i)  $n = 1$  and (ii)  $k = 4.62 \times 10^{-3} \text{ s}^{-1}$   
 E. None of the above

**SECTION B**

**[80]**

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

**QUESTION 1**

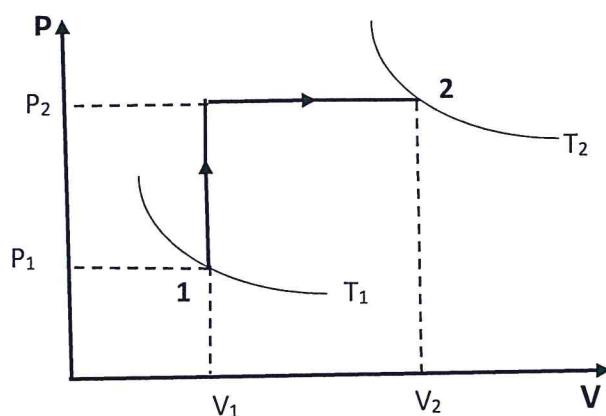
**[16]**

- (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  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta S$  are negative, zero or positive for heating 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)  $C_p = \left( \frac{\partial U}{\partial T} \right)_p$
- (d) For each of the following reactions, show or explain whether the heat evolved at constant pressure ( $\Delta H$ ) is smaller, larger than or the same as the heat evolved at constant volume ( $\Delta U$ ). (2)
- (i)  $C_2H_2(g) + 3H_2(g) \rightarrow 2CH_4(g)$
  - (ii)  $BaCl_2(s) + F_2(g) \rightarrow BaF_2(s) + Cl_2(g)$

**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  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$ . (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<sup>3</sup> and  $P_2 = 200$  kPa,  $V_2 = 10$  dm<sup>3</sup>, 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

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

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 chloromethane is  $-23$  °C) (6)

**QUESTION 3****[20]**

- (a) Give the equations and SI units for the terms **conductivity**,  $\kappa$ , and **molar conductivity**,  $\Lambda$ , as applied to a solution of an electrolyte. (4)
- (b) Show using a schematic diagram how the molar conductivity can be used to distinguish between HCl (strong electrolyte), acetic acid (weak electrolyte) and sodium dodecyl sulphate (surfactant). (4)
- (c) The limiting molar conductivities ( $\Lambda_0$ ) of NaI, CH<sub>3</sub>COONa and Mg(COOCH<sub>3</sub>)<sub>2</sub>, in mS $\text{m}^2\text{mol}^{-1}$ , are 12.69, 9.10 and 18.78, respectively (all at 25°C). What is the limiting molar conductivity of MgI<sub>2</sub> at this temperature? (3)
- (d) The molar conductivity at infinite dilution,  $\Lambda_0$ , of acetic acid is 390.7 S $\text{cm}^2\text{mol}^{-1}$ . What is the acid dissociation constant,  $K_a$ , if the molar conductivity,  $\Lambda$ , of 0.0100 mol $\text{dm}^{-3}$  acetic acid is 16.5 S $\text{cm}^2\text{mol}^{-1}$ ? (3)
- (e) Suppose that you construct a Galvanic cell which combines the Ce<sup>4+</sup>(aq), Ce<sup>3+</sup>(aq)/Pt cell having a standard reduction potential ( $E^\circ$ ) of 1.61 V with a Cu<sup>2+</sup>(aq)/Cu(s) cell having a standard reduction potential of 0.158 V at 298 K.
- (i) Write balanced chemical equations for the reactions at the anode and cathode, indicating which reaction occurs at a particular electrode, and the resulting spontaneous overall reaction. (3)
- (ii) Devise the cell notation and calculate standard emf ( $E^\circ$ ) of the cell. (3)

**QUESTION 4****[20]**

- (a) The reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$  is first order with respect to [H<sub>2</sub>] and [I<sub>2</sub>]. When [H<sub>2</sub>] = 1 mol $\text{L}^{-1}$  and [I<sub>2</sub>] = 2 mol $\text{L}^{-1}$ , the following kinetic data are observed.
- $$\frac{d[\text{HI}]}{dt} = 1.78 \times 10^{-4} \text{ molL}^{-1}\text{s}^{-1} \text{ at } 556 \text{ K and } \frac{d[\text{HI}]}{dt} = 0.2572 \text{ molL}^{-1}\text{s}^{-1} \text{ at } 700 \text{ K.}$$
- 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)
- (b) The reverse reaction, i.e.  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ , has an activation energy of 183 kJ $\text{mol}^{-1}$ . Does this make the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$  exothermic or endothermic? Explain your answer with a diagram of the energy profile of the reaction. (6)
- (c) Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, decomposes in water by a first order kinetics process. A 0.156 mol $\text{dm}^{-3}$  solution of H<sub>2</sub>O<sub>2</sub> in water has an initial rate of 1.14  $\times 10^{-5}$  mol $\text{dm}^{-3}\text{s}^{-1}$ . Calculate the rate constant,  $k$ , for the decomposition reaction and the half-life of the decomposition. (4)

**END OF EXAM QUESTIONS**

## LIST OF USEFUL EQUATION AND CONSTANTS

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

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

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