A.R Sir	**Physical Chemistry**	
Full Marks-50	**2017-2018 BATCH**	**Full Syllabus Exam**
Time: 2 hour	**1st Year**	**SET-3**

General Instructions: *Write each unit separately. Complete one unit or leave some vacant space and then move to other units. Write at the top heading for that unit and the question number. Do not attempt extra questions. Read the instructions carefully first. 5 marks will be deducted if these instructions are not followed.*

CHT 13a

Unit-I : **Kinetic Theory of Gases & Real Gas (Answer any 3)**

3 x 5 = 15

1. **(a)** Derive the expression for the most probable speed for a two dimensional gas. Given the two dimensional speed distribution is: $dN_C/N = (m/kT) \cdot c \cdot \exp(-mc^2/2KT) \cdot dc$ [2]

    (b) State the principle of equipartition of energy and apply it to calculate the 'γ' for an ideal gas composed of linear triatomic molecules ($\gamma = C_p/C_v$) [3]

2. **(a)** Justify that a gas obeying the equation of state: $(P + a/V^2)(V) = RT$ does not possess a Boyle's temperature. [3]

    (b) Calculate the mean free path for the oxygen gas molecules at 298K and a pressure of 500 mm. $\left(\sigma = 1.28 \overset{o}{A} \right)$ [2]

3. **(a)** Identify the nature of attractive forces in each of gaseous He and NH_3. How do such forces depend on temperature and size of species? [3]

    (b) Calculate the diameter of oxygen molecule, the Vander Waal's constant b is 3.183×10^{-5} m^3 mol^{-1}. [2]

4. **(a)** Deduce the reduced equation of state for a van der Waal's gas. What is its utility [3]
    (b) Explain the continuity of states. [2]

5. **(a)** Write down the mathematical form and represent graphically the kinetic energy distribution of the molecules of a gas at two different temperatures. How does the shape changes as $T \to 0$. [3]
    (b) How far van der Waal's equation of state is valid for real gases. Explain. [2]

Unit-II : First Law of Thermodynamics (Answer any 2)

$$2 \times 5 = 10$$

6. (a) Prove that $[\partial \Delta H / \partial T]_P = \Delta C_p$.   [3]

   (b) Calculate W in the expression of a real gas in isothermal reversible expansion.   [2]

7. (a) (i) Classify the following as intensive or extensive properties: Pressure, Free energy, Molar enthalpy.
    (ii) Classify the following system as open, closed or isolated: Human body, Thermo flask, Clinical thermometer.   [1.5 + 1.5]
   (b) Given that the bond enthalpies for C – H, Cl – Cl, C – Cl and H – Cl are 415.8, 243.6, 327.6, 432.6 kJ respectively, determine ΔH for the reaction.   [2]

8. (a)   Derive an expression between temperature and volume in an adiabatic reversible expansion of an ideal gas.   [3]

   (b)   Show that $((\partial U / \partial V)_T = 0$ for a gas obeying P (V – nb) = nRT [derivation of Maxwell relation is not required]   [2]

CHT 13b

Unit-I : 2ⁿᵈ Law of Thermodynamics & Thermo-chemistry

(Answer any 3)

9. (a) Prove that all spontaneous process are accompanied by an increase in entropy   [2]

   (b) Obtain an expression for entropy change of a gas when the temperature changes from T_1 and T_2 and volume from V_1 to V_2.   [3]

10. (a) Find the condition of equilibrium and spontaneity of a process in terms of Gibb's free energy using Clausius inequality.   [2]

   (b) Calculate the free energy change accompanying the compression of 1 mole of CO_2 at 57°C from 5 atm to 50 atm, assuming that CO_2 behaves ideally.   [3]

11. (a) Derive the relation: (i) $-(\partial S / \partial P)_V = (\partial V / \partial T)_P$ (ii) $(\partial T / \partial P)_S = (\partial V / \partial S)_P$ [3]

   (b) Establish the relation: $Cp – Cv = \alpha^2 TV / \beta$ where α be the coefficient of expansion and β be the coefficient of compressibility and other terms have their usual significance   [2]

12. (a) Show that Joule-Thomson's coefficient for a real gas obeying Vander Waal's equation of state is $\mu_{JT} = 1/C_p (2a/RT - b)$, where symbols have their usual significance.   [3]

   (b) Why do H_2 and He show heating on adiabatic expansion?   [2]

13. (a) Derive Gibb's – Helmholtz equation.   [2]

   (b) Calculate the minimum work needed to prepare 1 Kg ice from water at 25°C in a refrigerator working between 5°C and 25°C.   [3]

Unit-II :   Chemical Kinetics & Catalysis (Answer any 2)   2 x 5 = 10

14. For the mechanism $A + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} C \xrightarrow{k_3} D$ (i) Derive the rate law using steady state approximation eliminate the concentration of C. (ii) Assuming that $k_3 \ll k_2$, express the pre-exponential factor (A) and the overall activation energy (E) for the formation of D in terms of A_1, A_2 and A_3 & E_1, E_2 and E_3 for three steps. (iii) What is the significance of $(E_1 - E_2)$? [5]

15. (a) For an enzyme catalyzed reaction plot $\frac{1}{r}$ vs. $\frac{1}{[S]}$. Determine the value of k_M using the Michaelis-Menten equation, where notations have their usual significance.   [3]

   (b) Consider the following reversible reaction, first order in both the direction: $A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$; $k_f/k_b = 2$. Plot curve that give the concentration of A and B as a function of time   [2]

16. For the reaction $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ show that when maximum concentration of B is reached the time t can be expressed as follows: $t = (\ln K_1 - \ln K_2) / (k_1 - k_2)$ [5]

"A barking dog is often more useful than a sleeping lion.."