A.R Sir **Physical Chemistry**

Full Marks-50 **2017-2018 BATCH** **Full Syllabus Exam**

Time: 2 hour **1st Year** **SET-4**

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)** The mean free path of an ideal gas at 3°C and 1.01 atm pressure is 10^{-5} cm. Calculate the collision diameter for the gas. [2]

   (b) The compressibility factor (Z) of a real gas is given by $Z = a_1 + a_2P + a_3P^2$, where a_1, a_2 & a_3 are constants and P is the pressure. Find out the sign of a_2 & a_3. [3]

2. **(a)** The equipartition value C_p / C_v for a non-linear molecule AB_y is found to be 1.167, assuming ideal behaviour. Find the value of γ. [2]

   (b) If the compressibility factor (Z) is 1.000054 for a van der Waal's gas at 0° C and 1.0 atm pressure, and the Boyle temperature is 107K, calculate (neglecting the higher terms of P) the values of a, b and the molecular diameter. [3]

3. **(a)** What is Lennard Jones Potential? [3]

   (b) Derive the relationship between (γ) and degree of freedom (f) at ordinary temperature. Show that the lowest value of (γ) tends to be unity. [2]

4. **(a)** Write down Maxwell's distribution function for the speeds of gaseous molecules in 3-dimensions, explaining the terms involved. Draw schematically the speed distribution for two gases (M_1 and M_2) at the same temperature (T). Derive an expression for the most probable speed in terms of M and T. [3]

   (b) The compressibility factor of oxygen gas is 0.927 at 0°C and 100 atm pressures. Calculate the mass of the gas required to fill a 100 litre cylinder under the above conditions. [2]

5. **(a)** If the maximum temperature at which a certain van der Waal's gas can be liquefied is 32.3°C and the minimum pressure to be applied for liquefaction at that temperature is 48.2 atm, then calculate the diameter of the gas molecule. [2]

(b) From the energy distribution of gas molecules (in 3-dimension) derive the expression for the fraction of molecules possessing energy in excess of a critical value E*. $[dn_E / dE = 2\pi N(1/\pi kT)^{\frac{3}{2}} E^{\frac{1}{2}} \exp(-E/KT)$, Symbols have their usual meaning] [3]

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

2 x 5 = 10

6. **(a)** Derive the cyclic rule. [3]
   (b) Classify the following properties as intensive or extensive: mass, density, molar volume, heat capacity. [2]

7. **(a)** Show that there is an increase in internal energy when a van der Waal's gas is allowed to expand isothermally and reversibly. [2]
   (b) The bond dissociation energy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 Kcal/mol respectively. Calculate the enthalpy of formation of HCl gas. [3]

8. **(a)** In a closed system consisting of 0.5 mole of an ideal mono-atomic gas the absorption of 100 calories of heat result in 1 lit-atm of work being done by the system. Estimate the change in internal energy (in joules) and temperature of the system. [3]
   (b) What are the thermodynamic criteria of a gas to be ideal? [2]

CHT 13b

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

(Answer any 3)

9. **(a)** State and explain the Kelvin-Planck statement of the Second Law of Thermodynamics. [2]
   (b) 1.0g each of hydrogen and nitrogen gas kept separately at the same temperature and pressure. They are then allowed to mix uniformly. Calculate the change in entropy of the system. [Assume ideal behaviour for the gases and the gas-mixture, and H = 1, N = 14]. [3]

10. (a) For an irreversible process $\Delta S_{Universe}$ is positive. Justify or criticize [2]

(b) An engine working between 600K and 300K extracts 10^5 KJ of heat. The inventor claims that the engine is a 1 kwatt engine. So how long the engine will work with the supplied heat? [3]

11. Consider two blocks of a metal, each of mass m grams, one at a temperature T_1 and the other at T_2 Kelvin ($T_2 > T_1$). The two blocks are brought in thermal contact with each other, in an adiabatic enclosure, and allowed to attain thermal equilibrium. Show that the change in entropy of the system is given by the expression. Here is the specific heat capacity at constant pressure of the metal, and it is assumed to be constant over the range T_1 to T_2.

$$m.s.\ln\left[\frac{(T_2 - T_1)^2}{4T_1T_2} + 1\right]$$ [5]

12. (a) Using an appropriate thermodynamic equation of state, show that that the inversion Temperature of a van der Waal's gas is given by the expression 2a / Rb. [2]

(b) Calculate the change in Gibbs free energy of 2 moles of an ideal gas when its temperature is raised from 300K to 400K at a constant pressure of 2 atm.

[$S_m = A + B.\ln T$, A =25 and B = 30 in SI units] [3]

13. A Carnot engine whose low temperature reservoir is at 25°C has an efficiency of 40%. If any one decides to increase the efficiency to 50% by how many degree Celsius the temperature of the hot reservoir is to be increased. [5]

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

14. (a) The rate constant of a chemical reaction increase by 2-times and for other reaction by 3 times when temperature changes from TK to (T + 10)K. Find the ratio of their activation energies if they have comparable pre-exponential factor. [3]

(b) Stoichiometry of a reaction indicates order of the function – Justify or criticize. [2]

15. (a) Show mathematically that a catalyst does not affect the position of equilibrium of a reversible reaction. You may assume that the catalyst does not change the collision frequency factors. [3]

(b) Show that the ratio of $t_{0.5}/t_{0.75}$ of any nth order reaction ($n \neq 1$) with identical initial concentration of reactants can be written as a function of n alone. [2]

16. For a consecutive reaction: $A \rightarrow B \rightarrow C$; derive expressions for A, B & C. [5]

"Any man who reads too much and uses his own brain too little falls into lazy habits of thinking."