



A.R Sir

Physical Chemistry

Full Marks-50

2017-2018 BATCH

Full Syllabus Exam

Time: 2 hour

1st Year

SET-2

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

- (a) Find the rate of effusion from molecular speed distribution in 3-dimensions. [3]

(b) Calculate the wall-molecule collisions per cm² per second in O₂ at 25°C and 1.0 atm pressure. [2]
- (a) Write down van der Waal's equation in virial form. Hence deduce the expression for Boyle temperature from the second virial coefficient. [3]

(b) Starting from the Maxwell's velocity distribution in one dimension arrive at the speed distribution function in two dimensions. [2]
- (a) State the principle of equipartition of energy. At high temperatures the observed Cp/Cv ratio for non-linear polyatomic ideal gas is 7/6. Determine the atomicity of the gas. [2]

(b) Two van der Waal's gases A and B are at corresponding states. The critical temperatures and pressures of the gases are given below:

	Pc/atm	Tc/atm
A	48	150
B	33	125

Find out the volume of B at this corresponding state if the volume of A is 1.5L. [3]
- (a) Deduce an expression for the total number of collisions in a unit volume and unit time among the molecules or a gas. [The gas is made up of like molecules] [3]

(b) Mention the nature of intermolecular interactions responsible for Keesom, London and Debye forces. How do these forces depend on the temperature and size of the species? [2]
- (a) From the distribution of K.E in 2 dimension derive an expression for the number of molecules possessing energy in excess of a certain amount, ϵ' . [2]

(b) Explain why the contribution of each translational and rotational mode to the average molecular energy is half one vibrational mode. Also explain why the equipartition principle predicts more correct value of heat capacity for He than HCl at 20°C. [3]



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

2 x 5 = 10

6. (a) State the Zeroth Law of Thermodynamics. Define temperature using the above law. [2]
- (b) When one millimole of graphite and diamond are separately burnt in excess of oxygen to produce carbon-dioxide gas, 393.514J and 395.409J of heat are respectively produced at 298.15 temp and 1 atm. pressures. Calculate the molar enthalpy of the following allotropic transition at the same condition of temperature and pressure.
- $$\text{C (graphite)} \rightarrow \text{C (diamond)}. \quad [3]$$
7. State the expression for Joule Thomson Coefficient and explain why both heating and cooling effects are shown by the van der Waal's gas. [5]
8. (a) For every process in an isolated system $\Delta E = 0$ -Justify or criticize the statement. [2]
- (b) One mole of an ideal mono-atomic gas at 300K and 10 atm pressure is expanded adiabatically against constant external pressure of 1 atm, until it reaches equilibrium. Calculate final temperature and W. [3]

CHT 13b

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

(Answer any 3)

9. (a) C_p is independent of pressure for an ideal gas - Justify or criticize [2]
- (b) How much work must be performed to freeze 1 kg of water at 0°C in a refrigerator on a cool day (room temperature is 15°C). What will be the change of entropy of the room? Given, latent heat of fusion of ice = 80cal/gm. [3]
10. (a) What is meant by Clausius inequality? [2]
- (b) Starting from appropriate expression arrive at the condition for a spontaneous process in terms of enthalpy change and change in Gibb's free energy. [3]
11. Define Helmholtz free energy (A). ? Calculate ΔA for vaporization of 0.1 mole of water at 1 atm pressure and 100°C (Given molar volume of $\text{H}_2\text{O}(\text{l})$ at 100°C is 18.8 mL/mole and that of $\text{H}_2\text{O}(\text{g})$ is 30.6 L/mole). [5]
12. (a) Derive the relationship, $C_p - C_v = TV\alpha^2 / \beta$ [2]



- (b) Represent the Carnot's cycle on a TS diagram and indicate what the enclosed area represents. Also show whether higher efficiency is obtained by lowering the temperature of Low Temperature Reservoir (LTR) or by raising the temperature of High Temperature Reservoir (HTR). [3]
13. (a) For a gas following the equation of state $(P + a/V^2)(V) = RT$, obtain an expression for Joule Thomson coefficient and comment on its value. [3]

(b) Prove that $\frac{\partial(\Delta A/T)}{\partial(1/T)} = \Delta E$ [2]

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

14. (a) The activation energy for the decomposition of a gas is 80KJ. What percentage of gas molecules possess sufficient energy to react at 500K? [3]
- (b) Zero order reactions must be multi step reaction explain. Do such reactions go to completion? [2]
15. (a) Show that if A undergoes two simultaneous reactions to produce B and C according to $A \xrightarrow{k_1} B$, $A \xrightarrow{k_2} C$; Where E_a the observed activation energy for the disappearance of A is given by : $E_a = (k_1 E_1 + k_2 E_2) / k_1 + k_2$ [3]
- (b) A substance decomposes according to a second order rate law. If the rate constant is 6.8×10^{-4} lit. mole⁻¹ s⁻¹. Calculate the half life of the substance when the initial concentration is 0.05 mole/lit. [2]
16. (a) At low temperature, change in temperature has greater effect on rate constant as compared to high temperature. Justify/ criticize. [3]
- (b) "Activation energy of some reactions are zero" — justify. [2]

"Luck favours only the prepared mind."