



**A.R Sir**

## Physical Chemistry

Full Marks-50

2017-2018 BATCH

Full Syllabus Exam

Time: 2 hour

1<sup>st</sup> 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

1. Draw schematically a set of experimental as well as theoretical P-V isotherms based on van der Waal's equation for real gas. Explain the idea of continuity of state. [5]
2. Give a concise account of various intermolecular forces that leads to van der Waal's forces. What is Lennard - Jones potential? [2+3]
3. (a) How many vibrational degree of freedom does a chlorine molecule possesses ? The  $C_v$  value of  $N_2$  is always less than that of chlorine at ordinary temperature - Why? [3]  
(b) Calculate the diameter of oxygen molecule; the van der Waal's constant b is  $3.183 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ . [2]
4. (a) Derive an expression for the average speed of a two dimensional gas using Maxwell's distribution for the speed of gas molecules. [3]  
(b) Calculate the mean square deviation of oxygen molecules at 300K. [2]
5. Derive the following expression for wall collision frequency:  $Z_w = \frac{1}{4} \langle C \rangle N^*$  (Where the terms have their usual significance) [5]

#### Unit-II :

#### First Law of Thermodynamics (Answer any 2)

2 x 5 = 10

6. One mole of an ideal gas expands from  $T, P_1, V_1$  to  $T, P_2, V_2$  in two stages.

	Opposing pressure	Volume change
1st Stage:	$P_1$ (constant)	$V_1$ to $V'$
2nd Stage:	$P_2$ (constant)	$V'$ to $V_2$

(i) Calculate the amount of work done in the process (expansion) in terms of  $T, P_1, P_2, P'$ .  
(ii) For what value of  $P'$ , work will be maximum? (iii) What is the maximum value? [5]



7. (a) For a reversible adiabatic process derive P-V relation for a monoatomic gas that follows equation of state. [3]  
(b) Joule Thomson expansion is an isoenthalpic process - explain. [2]
8. Justify or criticize - [3+2]  
(i)  $C_v$  is independent of volume at constant temperature for ideal gas.  
(ii) Work done may be state function.

**CHT 13b**

**Unit-I : 2<sup>nd</sup> Law of Thermodynamics & Thermo-chemistry**

**(Answer any 3)**

9. Prove that:  $\left(\frac{\partial H}{\partial V}\right)_T = \frac{C_p - C_v}{\alpha V} - \frac{1}{\beta}$ , where terms have their usual significance. [5]
10. (a) "Spontaneity of a reaction is the resultant of the tendencies to acquire minimum energy and maximum randomness" - Explain [3]  
(b) Show that decrease of G is a measure of available work. [2]
11. (a) 1.0 g each of hydrogen and nitrogen gases are 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 gasses and the gas mixture, and H = 1, N = 14] [3]  
(b) If  $\left(\frac{\partial \Delta H}{\partial T}\right)_p = 0$  for a reaction, then show  $\left(\frac{\partial \Delta S}{\partial T}\right)_p = 0$  for the same reaction. [2]
12. Find out  $\Delta G$  at 1 atm per mole at  $-17^\circ\text{C}$  for the transformation ; given  $C_p(l) = 18 \text{ cal/mol}$ ,  $C_p(s) = 9 \text{ cal/mol}$ . [5]
13. Find the condition of equilibrium and spontaneity in terms of Gibbs free energy (G) using Clausius inequality. Why G rather than S is taken as a better function to ascertain the criteria of equilibrium and spontaneity. [3+2]

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

14. At  $100^\circ\text{C}$  the gaseous reaction  $A \rightarrow 2B + C$  is observed to be 1<sup>st</sup> order. Starting with pure A, it is found that at the end of 10 min the total of pressure 176 mm of Hg. After a long time, it



is found that 270 mm of Hg. From this data find – (i) initial pressure of A (ii) The pressure of A at the end of 10 min. (iii) Rate constant of the reaction. (iv) Half life period of the reaction. [5]

15. (a) Can a reaction rate independent of concentration? If yes, cite an example to explain. Does such a reaction go to completion in finite time? [3]

(b) What is meant by “Order of a reaction”? Cite an example of zero order reaction. [2]

16.  $H_3O^+$  acts as a homogeneous catalyst in reaction of inversion of sucrose. At pH = 3, the reaction in the un-aqueous solution proceeds with a constants half life of 50 min. What value of half life would you expect at pH = 4. [5]

**“Doing your best is more important than being the best”**

