B.Sc. 1st Semester (Honours) Examination, 2021-2022

CHEMISTRY

Course ID: 11412 **Course Code: SH/CHEM/102/C-2**

Course Title: Physical Chemistry-I

Time: 1 Hour 15 Minutes **Full Marks: 25**

Figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five* of the following questions: 1×5 = 5

a) Define activation energy of a reaction.

b) State second law of thermodynamics in terms of entropy.

c) Reaction having first order and second order are common but third order reactions are rare and reaction above third order is impossible. - Explain.

d) The absolute values of enthalpy of neutralization of three acids (A, B and C) towards a common base are 13.7, 9.4 and 11.2 k cal, respectively. Which one is the weakest acid?

e) Can a van der Waals gas with a = 0 be liquified?

f) In a refrigerator heat is flown from a lower temperature to a higher temperature - does it contradict second law of thermodynamics?

g) What would be the units of rate constant if rate = k[A][B]? (Concentration is expressed as mol./L and time in second)

h) The temperature of a gas is doubled at constant P. How many times should the average speed change?

2. Answer *any two* of the following questions: 5×2 = 10

a) i) Show that a gas obeying $P(V - nb) = nRT$ does not have the Boyle temperature.

ii) If the degrees of freedom of a gas are 3, then find the ratio for C_P and C_V for the gas. 3+2 = 5

b) i) Show that the half-life period of a zero order reaction is directly proportional to the initial concentration of the reactant.

ii) Show that for a first order reaction, the concentration of the reactant A after passing n half-life times is given by $[A] = [A]_0[1/2]^n$ 2+3 = 5

c) i) Prove that the work done in an isothermal reversible expansion of n moles of an ideal gas is greater than that of a real gas.

ii) An ideal gas $\gamma = 5/3$, at 27^0C is compressed adiabatically to 8/27 of its original volume. What would be its final temperature? 3+2 = 5

d) i) What are the orders of a gaseous unimolecular reaction at high and low pressure limits according to Lindemann theory?

ii) What is "entropy of activation"? How is it related to the frequency factor? Why is it usually negative? 2+(1+1+1) = 5

3. Answer *any one* of the following questions: 10×1 = 10

a) i) Derive the relations:

(A) $C_p = \alpha VT \left[\partial p / \partial T \right]_S$

(B) $\left[\partial p / \partial V \right]_S = \frac{C_P}{C_V} \left[\partial p / \partial V \right]_T$

ii) The *b* value of a van der Waals gas is 0.032 L/mol. Calculate the radius of the gas molecules.

iii) The exponential term in the Maxwell's distribution law of molecular speed can never be positive. - Explain. (2.5+2.5)+3+2 = 10

b) i) Define Boyle temperature and deduce the expression of Boyle temperature of a gas obeying the van der Waals equation of state.

ii) An elementary reaction cannot be a zero order reaction. - Explain.

iii) A plot of concentration vs. time for a reaction is straight line with negative slope. What is the order of the reaction? Explain.

iv) Two Carnot engines A and B operate in series. The engine A receives heat from the source at T_1 and rejects the heat to the sink at T. The engine B receives the heat at T and rejects the heat to sink at T_2. Find the value T, for which efficiencies of the two engines are equal. 4+2+1+3 = 10