INTER B.SC. EXAMINATION, 2018

(3rd Semester)

CHEMISTRY (HONOURS)

PHYSICAL CHEMISTRY

PAPER - V

Time : Two hours Full Marks : 50

(25 marks for each group)

Use a separate answerscript for each group.

GROUP - A

Answer ***any five*** questions .

1. a) Represent Carnot cycle on U vs T diagram for an ideal gas and explain.

   b) Chemcial potential is a measure of 'escaping tendency' : Comment. 3+2

2. a) Derive the criteria of spontaniety and equilibrium when the temperature and volume of the system are kept constant.

   b) Show that $C_v = -T(\delta^2 A / \delta T^2)_v$ 3+2

3. a) For a substance both $(\delta U / \delta V)_T$ and $(\delta H / \delta P)_T$ are zero. Find the equation of state of the substance.

   b) The chemical potential of a substance decreases with increase in temperature at constant pressure and composition : Justify / Criticize. 3+2

4. a) What is fugacity and fugacity coefficient of a gas ?

   b) For NH_3 gas, considering intermolecular attraction to be negligible find effective pressure if the experimental pressure is 10 am at 300 K. Given van der Waals' constant, $b = 3{\cdot}707 \times 10^{-2}$ $Lmol^{-1}$. 3+2

5. a) Derive van't Hoff equation from van't Hoff isotherm.

   b) For the reaction $NH_4HS(s) \rightleftarrows NH_3(g) + H_2S(g)$, $K_P = 0{\cdot}0529$ at 26^0C. 0.092 mole of NH_4HS is introduced into 2·46 L evacuated flask at 26^oC. Calculate the percentage of solid NH_4HS decomposed. 3+2

6. a) Show that the entropy change in a binary mixture of ideal gases under isothermal condition is maximum when $x_1 = x_2 = \frac{1}{2}$. [x represents mole reaction]

   b) Residual entropy of CO is $5{\cdot}76$ JK^{-1} mol^{-1} : Justify.

   3+2

7. a) Show that decrease in Gibbs free energy at constant temperature and pressure represents the net non-mechanical work that can be obtained from the system.

   b) Calculate ΔG per mole for freezing of super-cooled water at -5^oC. Given latent heat of fusion of ice = 80 cal mol^{-1}. 3+2

10. a) What is meant by an oscillatory chemical reaction ? Write the various steps of Lotka-Volterra mechanism for such a reaction. Assuming steady state approximation for the intermediates, comment if the mechanism can explain the key feature of the reaction. 3

    b) When a chain reaction can have a chain length and hence define it. 2

    OR

    Explain the effect of solvation on the rate of a reaction.

GROUP - B

8. a) Define rate of a chemical reaction and hence express it for the reaction :

$M + 3N \rightarrow 2P + R$, in terms of each of the constituents. $1\frac{1}{2}$

b) Derive an expression for the rate constant of a second order reactin when concentrations of both the reactants are different. When will it follow a first order kinetics ? 3

c) Discuss in brief the Ostwald's method to determine the order of a reaction. $2\frac{1}{2}$

OR

Explain the effect of temperature on the rate of a chemical reaction ?

d) Decomposition of gas at an initial pressure of 600 mm of Hg was studied in a closed vessel at a certain temperature. The gas was found to be 50% decomposed in 30 min and 75% decomposed in 90 min. Find the order and rate constant. 3

OR

A certain reaction : $A + B \rightarrow C$; is first order with respect to each reactant with $k = 1{\cdot}0 \times 10^{-2}$ L mol^{-1} s^{-1} . Calculate the concentration of a remaining after 100 s if the initial concentration of each reactant is 0·1 mol L^{-1}.

9. a) The thermal decomposition of N_2O_5 can be explained by the following mechanism : 4

$$N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_3} NO + O_2 + NO_2$$

$$NO + NO_3 \xrightarrow{k_4} 2NO_2$$

Using steady state approximation for NO and NO_3, show that the rate of formation of O_2 follows first order kinetics in N_2O_5.

OR

For the consecutive reaction : $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ (each step is first order), derive an expression for the time corresponding to maximum concentration of B.

b) Why and what will happen to the rate of a reaction between two negatively charged ions as the ionic strength of the solution is increased ? 3

c) A dimerization reaction at about 300 K in the gaseous phase follows the Arrhenius equation $k_2 = Ae^{-E_a/RT}$ where $A = 10^{5.61}$ L mol^{-1} s^{-1} and E_a = 65.40 kJ mol^{-1}. Calculate $\Delta^{\neq}G^{o}$ and $\Delta^{\neq}S^{o}$ for the reaction. 3