

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) Chemical potential is a measure of 'escaping tendency' :
Comment. 3+2
2. a) Derive the criteria of spontaneity 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

[Turn over

[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, $b = 3.707 \times 10^{-2} \text{ Lmol}^{-1}$. 3+2
5. a) Derive van't Hoff equation from van't Hoff isotherm.
b) For the reaction $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$, $K_p = 0.0529$ at 26°C . 0.092 mole of NH_4HS is introduced into 2.46 L evacuated flask at 26°C . 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 fraction]
b) Residual entropy of CO is $5.76 \text{ JK}^{-1} \text{ mol}^{-1}$: 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°C . Given latent heat of fusion of ice = 80 cal mol^{-1} . 3+2

[5]

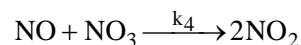
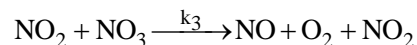
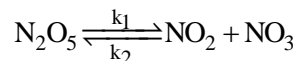
10. a) What is meant by an oscillatory chemical reaction ? Write the various steps of Lotka-Volterra mechanism for such a reaction. Assuming steady state approximation for the intermediates, comment if the mechanism can explain the key feature of the reaction. 3
b) When a chain reaction can have a chain length and hence define it. 2

OR

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

[4]

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



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

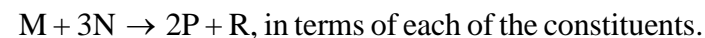
For the consecutive reaction : $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ (each step is first order), derive an expression for the time corresponding to maximum concentration of B.

- 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 $A = 10^{5.61} \text{ L mol}^{-1} \text{ s}^{-1}$ and $E_a = 65.40 \text{ kJ mol}^{-1}$. Calculate $\Delta^\ddagger G^\circ$ and $\Delta^\ddagger S^\circ$ for the reaction. 3

[3]

GROUP - B

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

1 $\frac{1}{2}$

- b) Derive an expression for the rate constant of a second order reaction 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 $k = 1.0 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$. Calculate the concentration of a remaining after 100 s if the initial concentration of each reactant is 0.1 mol L^{-1} .

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