[This question paper contains 6 printed pages.]

1263 *Your Roll No.* .....

**B.Sc. (Hons.) / III** **A**

CHEMISTRY – Paper XVII

(Physical Chemistry – III)

*Time : 3 Hours* *Maximum Marks : 38*

*(Write your Roll No. on the top immediately on receipt of this question paper.)*

*Attempt* **six** *questions in all, including Question No.* **1** *which is compulsory.*
*Attempt at least* **one** *question from each Section.*
*Use of scientific calculator is permitted.*

1. Explain any **four** of the following :–

   (a) Difference between stationary and non-stationary chain reactions.

   (b) The rate of reaction decreases with increase of temperature for the reaction

   $$2NO + O_2 \longrightarrow 2NO_2$$

   (c) Photosynthesis is a photosensitised reaction.

   (d) When a gas is adsorbed on the surface of a catalyst, the rate of decomposition of HI on Pt is proportional to concentration of HI but is independent of the concentration of HI on Gold.

P.T.O.

(e) Why is KCl salt bridge used to eliminate liquid junction potential ? (2×4)

## SECTION – A

2. (a) Give the mechanism for enzyme catalysed reactions and derive Michaelis Menter Equation. Show that the rate of reaction changes from first order to zero order as the concentration of the substrate is increased. Also obtain an expression for the Lineweaver–Burk Equation. Show how it can be used to determine $r_{max}$ and $K_m$.

($K_m$ – Michaelis constant, $r_{max}$ – maximum rate).

(b) At a certain temperature the half–life periods for the decomposition of ammonia ($NH_3$) in contact with tungsten were as follows :–

| Pressure (mms of Hg) | 50 | 100 | 200 |
|---|---|---|---|
| Half-Life period | 3.52 | 1.82 | 0.93 |

Find the order of the reaction. (4,2)

3. (a) Describe the collision theory of bi-molecular gaseous reactions. Find out the rate expression. Also explain the significance of the term $\rho$, called the steric factor in the rate expression. (6)

**OR**

The conversion of compound A into compound B was followed by adding KI solution and titrating the iodine liberated with standard $Na_2S_2O_3$ solution. The KI reacts with A only. The following data was obtained.

| Time (hrs) | 0 | 1 | 2 | 3 | 4 | 6 | 8 |
|---|---|---|---|---|---|---|---|
| V(0.1 $MS_2O_3^{-2}$)/cms$^3$ | 49.3 | 35.6 | 25.7 | 18.5 | 14.0 | 7.3 | 4.6 |

Determine the order of the reaction and its rate constant.

(b) The following mechanism was proposed for the reaction between $Cl_2$ & $O_3$ at 323 K

$$Cl_2 + O_3 \xrightarrow{K_1} ClO + ClO_2$$

$$ClO_2 + O_3 \xrightarrow{K_2} ClO + 2O_2$$

$$ClO + O_3 \xrightarrow{K_3} ClO_2 + O_2$$

$$2ClO \xrightarrow{K_4} Cl_2 + O_2$$

Apply Steady State Approximation to ClO & $ClO_2$. Show that :-

$$\frac{d}{dt}[O_3] = 2[O_3]\{K_1[Cl_2] + K_3\left(\frac{K_1}{K_4}[Cl_2][O_3]\right)^{1/2}$$

(3,3)

P.T.O.

## SECTION – B

4. (a) Fluorescence is a fast process whereas phosphorescence is a slow process. Explain with the help of a diagram.

   (b) A radiation of 254 nm was passed through a 10 $cms^3$ solution of 0.0495 mol. $dm^{-3}$ oxalic acid and 0.01 mol. $dm^{-3}$ uranyl sulfate. After the end of the experiment oxalic acid was found to be 0.0383 mol. $dm^{-3}$. Calculate the amount of energy absorbed if quantum yield $\phi = 0.6$. (3,3)

5. (a) Define quantum yield. How is it determined experimentally using a uranyl oxalate actinometer ? Give at least two reasons each for high and low quantum yield.

   (b) Formaldehyde can be synthesised by irradiating a mixture of CO and $H_2$ containing a trace of Hg with light of wavelength 253.7 nm. Show that the reaction mechanism

$$Hg \xrightarrow{I_{abs}} Hg^*$$

$$Hg^* + H_2 \xrightarrow{K_2} 2H + Hg$$

$$H + CO \xrightarrow{K_3} HCO$$

$$HCO + H_2 \xrightarrow{K_4} HCHO + H$$

$$2HCO \xrightarrow{K_5} HCHO + CO$$

$$2HCO \xrightarrow{K_6} \begin{matrix} CHO \\ | \\ CHO \end{matrix}$$

confirms the following rate law

$$\frac{d}{dt}[HCHO] = \frac{K_5 I_{abs}}{K_5 + K_6} + K_4[H_2]\left(\frac{I_{abs}}{K_5 + K_6}\right)^{1/2} \quad (3,3)$$

## SECTION – C

6. (a) Derive an equation to determine the pH of a solution using a quinhydrone electrode. What are the limitations of this electrode and in what pH range is it useful ?

(b) The Emf. of the following cell

$$Cd / CdCl_2 \cdot \frac{5}{2} H_2O(satd.) // AgCl(S)/Ag$$

is 0.6753 volts at 25°C and 0.6915 volts at 0°C. Calculate the free energy charge ($\Delta G$), enthalpy charge ($\Delta H$) and entropy charge ($\Delta S$) of the cell reaction at 25°C. (3,3)

7. (a) For the following electrochemical cell

$$Fe / Fe^{+2}(0.1M) / Cd^{2+}(0.01M) / Cd$$

Write down the cell reaction and determine the Emf of the cell. Also indicate the direction of the spontaneous cell reaction.

P.T.O.

(b) At 0°C and 1 atmospheric pressure, volume of $N_2$ gas required to cover a sample of silica gel assuming Langmuir monolayer adsorption is found to be 130 $cms^3g^{-1}$ of the gel. Calculate the surface area per gm of silica gel. Given that the area occupied by a $N_2$ molecule is 0.162 $nm^2$. (3,3)

8. (a) (i) Give the postulates on which Langmuir's adsorption isotherm is based and develop an expression for the same. What form does the equation take under conditions of low pressure and high pressure ?

(ii) Show that when a diatonic gas is adsorbed as atoms on the surface of a solid, Langmuir's adsorption isotherm takes the form

$$\theta = \frac{(K_P)^{1/2}}{1+(K_P)^{1/2}}$$

(b) At 360 nm a blue filter transmits 37.0% and a yellow filter 19.0% of a radiation. What is the transmittance at the same wavelength of the two filters in combination ? (2,2,2)

9. Write short notes on any **three** of the following :–

(a) Potentiometric Titrations

(b) Physical adsorption and chemical adsorption

(c) Gibbs adsorption Equation

(d) Einstein's Law of Photochemical Equivalence

(e) Vantt Hoff's Differential Method (2×3)