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2016

## M.Sc. Part-I Examination

# CHEMISTRY -

#### PAPER-I

The figures in the margin indicate full marks.

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

Illustrate the answers wherever necessary.

## (Physical Chemistry)

For Old Syllabus

Full Marks: 75

Time: 3 Hours

Answer questions for Group-A and Group-B.

Answer five questions taking at least two from each group.

### Group-A

1. (a) Constructing a wave packet from two sine waves prove that for a particle (which is represented by the wave packet)  $\Delta x \Delta p_x \ge h$ . Where  $\Delta x \& \Delta p_x$  are position and momentum uncertainty respectively.

- (b) The work function of metallic cesium is 2.14 ev.Calculate the kinetic energy of the electron ejected by light of wave length 300 nm.
- (c) What do you mean by linear and hermition operator?

  Prove that two non-degenerate eigerfunctions of a hermition operator must be orthogonal to each other.

  2+2+3
- 2. (a) Write down he schrödinger equation for simple hermoric oscillator and express its Hamiltonian in term of ladder operators.
  - (b) With the help of ladder operator find out the normalised ground state wave function of simple hermonic oscillator.
  - (c) Show that according to Hygenburg uncertinity principle the ground state energy of simple hermonic oscillator can not be zero and also prove that its minimum possible value is  $\frac{1}{2}h\nu$ .
- 3. Explain what is meant by fugacity. How is this quantity determined experimentally?

  5+10
- 4. Obtain the expression for the thermodynamic probability of distribution of particles describable by symmetric wave function. Derive the appropriate destribution law.

7+8

(Continued)

- Busingso alay aman anoning Group-B and hatso at the W. (5)
- 5. (a) Derive an expression for 1st order reaction of integrated rate equation by flow method.
  - (b) What is 'contact time'?
  - (c) Calculate the relaxation time of the reaction —

$$A + B \stackrel{K_p}{\searrow} C$$

(d) For parallel reaction prove that

$$\frac{C_{B}}{C_{C}} = \frac{K_{1}}{K_{2}}$$

for the reaction A 
$$K_2 C$$

(e) For a certain reaction time (t) varises arithmatically while ccn<sup>c</sup> varises geometrically —

time 0 t 2t 3t  $\cos^c$  a aa  $a^2a$   $a^3a$  Show that the reaction is of 1st order.

- 6. (a) State limitations of Collision theory.
  - (b) Using transition state theory prove that

$$K_2 = \left[\frac{RT}{N_0h} \cdot e^{\frac{AS^{0+}}{R}} \cdot e^{\left(1 - An^{0+}\right)}\right] \times e^{-Ea/RT}$$

(c) What is catalysis? For homogeneous catalysis explain the terms — 'Arrhenius Complex' and 'Van't Hoff Complex'.

1+2×2

(d) Give the mechanism of the following reaction —

$$\left[ \text{Co}^{3+} (\text{NH}_3)_5 \text{Cl} \right]^{2+} + \left[ \text{Cr}^{2+} (\text{H}_2 \text{O})_6 \right]^{2+} + 5 \text{H}_2 \overset{+}{\text{O}} \rightarrow$$

$$\left[ \text{Co}^{2+} (\text{H}_2 \text{O})_6 \right]^{2+} + \left[ \text{Cr}^{3+} (\text{H}_2 \text{O})_5 \text{Cl} \right] + 5 \text{NH}_4^+$$

7. (a) Show that —

$$P_{\text{(moist)}} = P_{\text{(bulk)}} \cdot e^{\frac{2v}{R} \cdot \frac{Ve}{RT}}$$

where the terms indicate the usual meaning.

- (b) Established B.ET Adsorption equation.
- (c) A certain solid sample adsorls 0.52 mg of hydrogen when the pressure of the gas is 34 KPa at the temperature 35°C and 0.21 mg when the pressure is 5 KPa at the same temperature. The Langmuir isotherm describe the above process. Calculate the fraction of surface covered.
- 8. (a) What do you mean by (i) first overtone (ii) second overtone and (iii) hot bands?

- (b) For the vibration of a diatomic molecule, assuming anhermonic oscillator model calculate bond dissociation energy.

  4
- (c) Calculate the no. of vibrational modes of the following molecule and predict which is IR active and which one is Raman active

$$SO_2$$
,  $N_2O$  and  $C_2H_2$  5

(d) Calculate the force constant for a bond in HCl from the fact that, the fundamental vibrational frequency is  $8.667 \times 10^{13} \text{ sec}^{-1}$  atomic mass of H = 1 gm., Cl = 35.5 gm.

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