PG/IS/CEM-101/13

M.Sc. 1st Semester Examination, 2013

CHEMISTRY

PAPER—CEM-101

Full Marks : 40

Time : 2 hours

Answer **five** questions taking **one** question from each Group

The figures in the right-hand margin indicate marks

GROUP – A

1. (*a*) Illustrate the principle of constrained maxima/minima using Lagrange's method of undetermined multiplier. 5

(*b*) Use the above principle to find the dimension of a rectangular area for which the area is maximum and the circumference is a minimum. 3

2. (*a*) State the Fourier series of a function, $f(x)$ in the interval $[-\pi, \pi]$. Write down the Fourier series of $f(x)$ in the interval $[-\pi, \pi]$ when $f(x)$ is an odd function. 1 + 2

(*b*) Find the Fourier series of the periodic function defined as,

$$f(x) = \begin{cases} -\pi\,; -\pi < x < 0 \\ x\,; \quad 0 < x < \pi \end{cases}$$

Hence deduce that $\frac{1}{1^2} + \frac{1}{3^2} + \frac{1}{5^2} + \cdots = \frac{\pi^2}{8}$. 5

GROUP – B

3. (*a*) State and proof the criterion that a ladder operator must satisfy. 4

(*b*) Verify that L_+ and L_- act as ladder operator. 4

4. Explain clearly the stationary states in quantum mechanics. 8

Or

Define angular momentum L of a sing be particle as a vector product, write it in the farm of a determinant and hence define the components of angular momentum L. Show that the square of the angular momentum operator $\hat{L}^2$. Commutes with $\hat{L}_z$ and explain the significance of the result : $1 + 1 + 1 + 4 + 1$

GROUP – C

5. (*a*) Derive the expression for kinetic energy distribution from Maxwell's velocity distribution law. 5

(*b*) Calculate the entropy change when 1 kg water at 27 °C is converted to superheated steam at 200 °C under constant atmospheric pressure.

(sp. heat of liquid water = 4180 J/kg sp. heat of steam = (1670 + 0·49 T) J/kg at TK and latent heat of vaporization = 23×10^5 J/kg. 3

6. (*a*) Explain what is meant by fugacity co-efficient and derive it's expression for a real gas. 4

(*b*) Define partial molar volume and find out it's value graphically for a binary system. 2 + 2

GROUP – D

7. (*a*) Prove that the charge content of ion atmosphere around an ion is exactly equal and opposite to the charge of the ion. Given that the electrostatic potential at a distance 'r' $\psi = -(z_i e/\varepsilon r)ex^{-\kappa r}$, where $z_i e$ is the charge on the ion and ε and κ are the dielectric constant of the medium and inverse of the effective thickness of ion atmosphere respectively. 4

(*b*) Derive an expression for Gibbs energy change of ionic salvation using Born model. 4

8. (*a*) Deduce the expression for "Bjerrum critical distance" and thereby obtain the condition for ion-pair formation. 3 + 1

(*b*) What do you mean by mean ionic activity co-efficient ? Calculate the mean ionic activity co-efficient of 0·02 M $Zn_3(PO_4)_2$ solution at 298 K assuming complete dissociation of the electrolyte and using Debye-Hückel limiting equation [Given A = 0·51 $M^{-1/2}$] 1 + 3

GROUP – E

9. (*a*) Write down the expression of (*i*) Harmonic, (*ii*) Anharmonic (Morse) potential for one dimensional quantum oscillator. How does Harmonic potential differ from Anharmonic potential ? 2 + 3

(*b*) There must be some fluctuation in dipole moment during vibration for a molecule to show IR activity. 3

10. (*a*) Find the change in rotational constant of H_2 when

(*i*) one H-atom is replaced by 'D'

(*ii*) both H-atoms are replaced by 'D' 4

(*b*) Justify or criticize the following statements :

(*i*) Frequency of rotation of a rigid diatomic molecule will decrease with the increase of rotational quantum number.

(*ii*) A quantum Harmonic Oscillator can not be in rest even in its ground vibrational level. 2 + 2
