M.Sc. 1st Semester Examination, 2015

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) State the rules of Convergence/Divergence of an infinite series in comparison test method. Use comparison test to show, wheather the following series Converges or Diverges.

$$1 + 2! + 3! + 4! + 5! + \cdots$$

   (b) Wave function for particle in a 1-dim box of length, a at $n = 1$ state is given by

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

Find the value of 'x' for which $\psi(x)$ is maximum. 5+3

2. Find the Fourier series of the periodic function defined as,

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

Hence deduce that

$$\frac{1}{1^2} + \frac{1}{3^2} + \frac{1}{5^2} + \cdots = \frac{\pi^2}{8} \qquad 5+3$$

GROUP— B

3. (a) Show that time evolution of the expectation value of an operator, D of a system is given by the following expression,

$$\frac{d\langle D \rangle}{dt} = \frac{1}{i\hbar} \langle [D, H] \rangle$$

All the symbols have their usual signifi-cances. Assume operator, D has no explicit time dependence.

(*b*) A particle in the infinite square well has the initial wave function,

$$\psi(x,0) = A\, x(a-x) \quad 0 \le x \le a$$

where '*A*' is the normalization constant. Find $\psi(x, t)$.   4+4

4. Deduce Schwartz inequality relation. Use this principle to obtain Heisenburg uncertainty relation for two non-commutating Hermitian operator.   3+5

GROUP – C

5. (*a*) Derive Sackur-Tetrode equation for entropy.

   (*b*) What is meant by thermodynamic probability ?   6+2

6. (*a*) What is microcanonical ensemble ?

   (*b*) "β can be negative"– Justify.

(c) The rotational constant of gaseous HCl, determined from microwave spectroscopy, is 10.59 cm^{-1}. Calculate the rotational partition function of HCl at 500 K. $2+3+3$

GROUP – D

7. (a) Derive the expression for ion association constant considering Bjerrum's model of ion-pair formation.

(b) What are the disadvantages of Debye-Hückel theory? $6+2$

8. (a) In what type of system, one can measure the practical system of activity coefficient? Describe a suitable method for determination of activity when the dissolved solute is volatile.

(b) Calculate the entropy change accompanying the conversion of 1 mole of ice at 273·1 K and 1 atm. pressure into steam at 373·1 K

(Continued)

and 1 atm. pressure. Given that at 273·1 K, the molar heat of fusion of ice ΔH_{fus} is 6·00 kJ mol^{-1} at 373·1 K, the molar heat of vaporization of water ΔH_{vap} is 40·60 kJ mol^{-1}. Assume that the molar heat capacity, C_p, in the temperature range 373·1-273·1 K remains constant at 75·2 JK^{-1} mol^{-1}. $(1+4)+3$

GROUP– E

9. What is meant by homogeneous and inhomogeneous broadening of spectral lines ? Deduce an expression to show that Doppler broadening of spectral lines are proportional to $\sqrt{T/M}$, where 'T' and 'M' are absolute temperature and molecular mass of molecule. $2+6$

10. (a) Describe the principle involved for the determination of bond lengths of a linear triatomic molecule using its rotational spectral data.

(b) Justify or criticize the following :

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

    (ii) Amplitude of vibration of a linear Harmonic Oscillator increases with the increase of vibrational quantum number.   4 + (2 + 2)

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