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, whether the following series Converges or Diverges.

\[ 1 + 2! + 3! + 4! + 5! + \ldots \]

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

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

(Turn Over)
Find the value of \( x \) for which \( \psi(x) \) is maximum.

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

\[
\frac{1}{1^2} + \frac{1}{3^2} + \frac{1}{5^2} + \cdots = \frac{\pi^2}{8}
\]

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 significances. Assume operator, \( D \) has no explicit time dependence.
(3)

(b) A particle in the infinite square well has the initial wave function,
\[ \psi(x,0) = A x(a-x) \quad 0 \leq x \leq a \]
where 'A' is the normalization constant.
Find \( \psi(x,t) \).

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) "\( \beta \) 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.  

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?

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 $\Delta H_{\text{fus}}$ is 6.00 kJ mol$^{-1}$ at 373.1 K, the molar heat of vaporization of water $\Delta H_{\text{vap}}$ 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 $\sqrt{\frac{T}{M}}$, 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.  \[ 4 + (2 + 2) \]