PG/IS/CEM-101/14

M.Sc. 1st Semester Examination, 2014

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*) Find the constrained maxima of the function, $f(x) = e^{-x^2-y^2}$ subject to the condition, $x + y = 1$. 3

   (*b*) Write the appropriate functional dependence of 'H' and 'S' and complete the following equation : $2\frac{1}{2} \times 2$

   (*i*) $\left(\dfrac{\partial H}{\partial T}\right)_{p,\,n} = \left(\dfrac{\partial H}{\partial T}\right)_{v,\,n} + \ ?$

(**2**)

$(ii)\ \left(\dfrac{\partial S}{\partial T}\right)_{u,\,n} = \left(\dfrac{\partial S}{\partial T}\right)_{u,\,v} + \ ?$

2. (a) How do you determine the convergence or divergence of an infinite series using ratio test ? Use ratio test to justify whether the following series converges or diverges :

$$\dfrac{1}{2} + \dfrac{2^2}{2^2} + \dfrac{3^2}{2^3} + \dfrac{4^2}{2^4} + \dfrac{5^2}{2^5} + \cdots \qquad 2+2$$

(b) Expand the function e^x in the power of $x + 2$. ⠀⠀⠀⠀2

(c) Write down the Fourier series for the function $f(x)$ [odd function] in the interval $-l$ to $+l$. ⠀⠀⠀⠀2

GROUP – B

3. (a) What is meant by Hermitian operator ? ⠀⠀2

(b) State and prove Turn over rule. ⠀⠀6

4. Derive $\hat{L} \times \hat{L}$ and comment on the result. ⠀⠀6 + 2

GROUP – C

5. (a) What is the utility of partial molar quantity in thermodynamics ? 1

(b) What do you mean by fugacity of a gas ? Discuss how this is measured by measuring the compressibility factor of the gas. 1 + 3

(c) "In a binary system, the greatest decrease in Gibb's free energy on mixing occurs having equal number of moles of two components." — Justify the statement. 3

6. Starting from Maxwell expression for number of molecules having the velocity component lying between u and $(u + du)$, v and $(v + dv)$, w and $(w + dw)$ deduce the number of molecules having velocities lying between c and $(c + dc)$. 8

GROUP – D

7. (a) The linearised Poisson-Boltzmann equation, considering Debye-Hückel ionic atmosphere theory for very dilute solution is,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = \left(\frac{4\pi}{\in KT}\sum n_i^0 z_i^2 e_0^2\right)\psi_r$$

where symbols have their usual significances. Find the expression of ψ_r. 5

(b) Why

$$\left(\frac{4\pi}{\in KT}\sum n_i^0 z_i^2 e_0^2\right)^{-1/2}$$

is called the effective thickness of ionic atmosphere in Debye Hückel theory ? 3

8. (a) Derive an expression of Gibbs energy of ionic solvation using Born model. 5

(b) Estimate the transfer Gibbs energy of Cl^- (radius : 181 pm) from water ($\in = 78\cdot54$) to ethanol ($\in = 24\cdot30$) at 298 K by Born model. Given electronic charge, $e_0 = 4\cdot802 \times 10^{-10}$ esu. 3

GROUP – E

9. (a) How do you classify the molecules according to their moment of inertia along the three perpendicular directions ? Justify the class of benzene according to your classification. 2 + 2

(b) Justify or criticize the following statements :

2×2

(i) Rotational lines of a non-rigid rotator are equispaced.

(ii) It is possible to obtain the vibrational frequency from the rotational spectral data of a non-rigid rotator.

10. (a) Deduce the expression of dissociation energy of an Anharmonic Oscillator. State the consequence of anharmonicity to a diatomic oscillator. $3 + 2$

(b) Write down the energy expression of a diatomic vibrator. Show that the P and R branch lines are equispaced. (Assume there is no coupling between the rotational and vibrational motion of the molecule). 3

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