PG/IS/CHEM/CH - 1101/09

2008

CHEMISTRY

PAPER—CH - 1101

Full Marks : 40

Time : 2 hours

Answer any **four** questions
taking at least **two** from each Group

The figures in the right-hand margin indicate marks

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

Illustrate the answers wherever necessary

GROUP—A

(*Physical Chemistry*)

Answer any *two* from the following

1. (*a*) Show that the velocity of a subatomic matter particle is equivalent to the group velocity i.e. wave packet velocity.

(*b*) How does the approximate uncertainty relation appear during space localization ?

(*c*) Find out

$$\left\{\frac{d^2}{dx^2}, x^2\right\}.$$

(*d*) What is meant by precise value and expectation value in quantum mechanics ? 3 + 3 + 2 + 2

2. (*a*) If ψ_1 and ψ_2 are two normalised wave function and $<\psi_1 | \psi_2> = S_{12}$ then construct two ortho-normal wavefunction using these functions.

(*b*) State and prove Turn Over (T . O .) rule.

(*c*) Calculate the wavelength of a ball having mass 10 gm and velocity 10 cm sec^{-1} and comment on the result. 3 + 5 + 2

Or

(*a*) If $\hat{B}$ is an operator which commutes with an operator $\hat{A}$ (both being hermitian), ψ_1 and ψ_2 are the eigenfunctions of $\hat{A}$ and a_1 and a_2 are the corresponding non-degenerate eigenvalues respectively, then the integral $<\psi_1 | \hat{B} | \psi_2>$ vanishes.

(*b*) Describe the stationary state in quantum mechanics. 5 + 5

3. (*a*) How do you obtain the electrical potential as a function of its distance from a central ion in a dilute electrolyte solution?

(*b*) "The ion atmosphere around an ion can be considered to possess certain effective thickness." Explain.

(*c*) Calculate optimum separation distance between Zn^{2+} and SO_4^{2-} in aqueous $ZnSO_4$ solution at 25°C to form Bjerrum's ion pair. (Given, dielectric constant of water = 80, $e = 4{\cdot}8 \times 10^{-10}$ esu, $k = 1{\cdot}34 \times 10^{-16}$ ergs K^{-1} molecule^{-1}.). 5 + 3 + 2

4. (*a*) Why limiting Debye-Huckel expression for ionic activity co-efficient needs modification? Obtain the limiting form from the modified (extended) form of Debye-Huckel equation.

(*b*) Obtain an expression for Bjerrum's critical distance in reference to ion pair formation.

(*c*) If mean ionic activity co-efficient ($f_{\pm}$) of 0·002 molal aqueous NaCl solution at 25°C is 0·952, what will be $f_{\pm}$ of 0·005 molal aqueous $ZnCl_2$ solution at that temperature?

(Assume limiting Debye Huckel expression is valid and there is no ion association.) 4 + 4 + 2

GROUP—B

Answer any *two* from the following

5. (*a*) Wave number of pure, rotational transition of H — ^{79}Br is given by

$$\bar{\nu} = 16{\cdot}62\ (J+1)\ \text{cm}^{-1}$$

(*i*) Calculate the rotational constant for D — ^{79}Br

(*ii*) At which rotational level H — ^{79}Br will have the highest population at 27°C.

(*b*) How do you obtain the bond distance r_{CO} and r_{CS} for a linear triatomic molecule OCS using microwave spectroscopy? (2 + 3) + 5

6. (*a*) Vibrational energy of HCl is given by

$$\bar{E}(v) = 2991(v+1/2) - 52{\cdot}8186\,(v+1/2)^2$$

in cm^{-1}.

Where 'v' in the vibrational quantum number. Calculate the (*i*) force constant and (*ii*) dissociation energy of HCl.

(*b*) State Franck-Condon principle. Predict the relative intensities of vibronic transition when (*i*) the minima of ground and the first excited singlet state are just above each other; and (*ii*) minima of the first excited singlet state in some what shifted to the right compare to the ground state. $(2+2)+(1+2\frac{1}{2}+2\frac{1}{2})$

7. (*a*) Based on activated complex theory derive an expression for the rate constant of a reaction of the type

$$A + B \rightarrow P \text{ in a gas phase.}$$

(*b*) Compare the results of transition state theory with those of Collision theory. 6 + 4

8. (*a*) State third law of thermodynamics. Give one example.

(*b*) What is Gibbs paradox ?

(*c*) Derive the expression for molecular translational partition function and hence obtain the value of internal energy for 1 mole perfect monoatomic gas. 2 + 2 + 6
