

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 $\langle \psi_1 | \psi_2 \rangle = S_{12}$ 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 $\langle \psi_1 | \hat{B} | \psi_2 \rangle$ 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, $e = 4.8 \times 10^{-10}$ esu, $k = 1.34 \times 10^{-16}$ ergs $\text{K}^{-1} \text{molecule}^{-1}$). 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 ZnCl₂ 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 — ⁷⁹Br is given by

$$\bar{\nu} = 16.62 (J + 1) \text{ cm}^{-1}$$

- (i) Calculate the rotational constant for D — ⁷⁹Br
- (ii) At which rotational level H — ⁷⁹Br 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

$$\bar{E}(v) = 2991(v + 1/2) - 52.8186(v + 1/2)^2$$

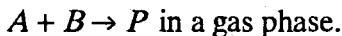
in cm^{-1} .

Where 'v' is 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 is somewhat shifted to the right compared 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



(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
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