

2019

B.Sc.

4th Semester Examination
CHEMISTRY (Honours)

Paper - C8T

Full Marks : 40

Time : 2 Hours

*The figures in the margin indicate full marks.
Candidates are required to give their answers
in their own words as far as practicable.*

Group - A

Answer any *five* questions from the following.

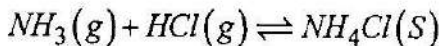
2×5=10

1. (a) When are elevation of freezing point and depression of boiling point observed ? Explain with examples.

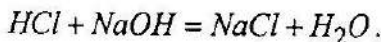
(b) Why is p-dichlorobenzene non-polar but p-dihydroxybenzene is polar ?

[Turn Over]

- (c) Write down the number of components, phases and degrees of freedom of the following equilibrium



- (d) Construct a cell for the following reaction



- (e) I_2 usually sublimes. Why ? How can it be melted ?
- (f) Calculate the ionic strength of a solution obtained by mixing equal volumes of 0.01 (M) $NaCl$ and 0.02 (M) $AlCl_3$.
- (g) Discuss the effect of dielectric constant on activity coefficient.

- (h) Show that $\frac{\partial(E^\circ/T)}{\partial(1/T)} = -\frac{\Delta H^\circ}{nF}$.

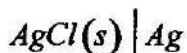
Group - B

Answer any four questions from the following.

2. (a) Derive thermodynamically a relation between the elevation of boiling point and molality of a dilute solution of a non-volatile and non-electrolyte solute.

- (b) How can you form a chemical cell without transference without using a salt bridge ? 4+1
3. (a) Derive Gibb's phase rule.
- (b) Can you use quinhydrone electrodes above pH = 8 ? Explain. 4+1

4. (a) For the following cell with transference,



derive an expression for liquid junction potential.

- (b) Write the expression for thickness of ionic atmosphere and explain the terms involved in this expression. 4+1
5. (a) Derive Duhem-Margules equation.
- (b) Calculate a_{\pm} , c_{\pm} and f_{\pm} of $CaCl_2$ in a 0.01 (M) solution. Given $f_+ = 0.5$ and $f_- = 0.8$.

3+2

[Turn Over]

6. (a) Show that $[\widehat{L}^2, \widehat{L}_z] = 0$.

What does this result signify ?

(b) Using classical mechanics, show that the total energy of a rigid rotator is $E = \frac{1}{2} I \omega^2$ where I is the moment of inertia and ω is the angular velocity.

3+2

7. (a) Considering H_2 as an example, draw, a comparison between Valence Bond and Molecular Orbital model.

(b) Calculate the thickness of ionic atmosphere for a 0.01 (M) $MgCl_2$ solution at 298 K. Given that the thickness of the ionic atmosphere for a 0.1 (M) $NaCl$ solution is 0.96 nm at 298 K.

3+2

Group - C

Answer any *one* question from the following.

8. (a) The normalised radial wave function of hydrogen atom is

$$R_{10}(r) = 2 \left(\frac{1}{a_0^3} \right)^{1/2} \cdot e^{-r/a_0}$$

Where a_0 is a constant. Calculate $\langle r \rangle$.

$$\text{Given, } \int_0^{\infty} r^n \cdot e^{-ar} dr = \frac{n!}{a^{n+1}}, \quad n > 1, \quad a > 0.$$

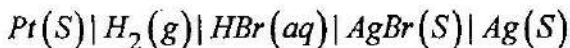
- (b) Draw the phase diagram for water. Apply Gibb's phase rule and Clapeyron equation to explain the diagram.
- (c) Discuss the physico-chemical principle involved in the measurement of pH of an aqueous solution by using a glass electrode. 3+4+3
9. (a) Plot R_{10}^2 and R_{20}^2 as a function of distance (r) of the electron from the nucleus for the hydrogen atom. What discrepancies are observed in these plots ?
- (b) What is radial distribution function ? The radial wave function of 2s orbital of a hydrogen atom is given by

$$R_{20} = N \left(2 - \frac{r}{a_0} \right) \cdot e^{-r/2a_0}$$

[Turn Over]

Where N is a constant. (i) Determine the number and location of node(s) in $2s$ wave function. (ii) Write down the expression of radial distribution function of the $2s$ electron and sketch the radial distribution curve.

(c) The standard e.m.f. of the cell



was measured over a range of temperature, and the data were fitted to the polynomial

$$E^\circ(V) = 0.07131 - 4.99 \times 10^{-4} [T(K) - 298] - 3.45 \times 10^{-6} [T(K) - 298]^2.$$

Determine the standard Gibbs free energy, enthalpy and entropy at 298 K. $2 + (1+3) + 4$
