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 ?

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

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(S)$$

(d) Construct a cell for the following reaction

$$HCl + NaOH = NaCl + H_2O.$$

(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) Drive Gibb's phase rule.

(b) Can you use quinhydrone electrodes above pH = 8 ? Explain. 4+1

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

$$Ag\left|AgCl(s),\ HCl(a_1)\right|HCl(a_2),$$

$$AgCl(s)\left|Ag\right.$$

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

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

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

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

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

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

(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

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

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

$$Pt(S)\,|\,H_2(g)\,|\,HBr(aq)\,|\,AgBr(S)\,|\,Ag(S)$$

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

$$E°(V) = 0.07131 - 4.99\times10^{-4}\left[T(K) - 298\right]$$
$$-3.45\times10^{-6}\left[T(K) - 298\right]^2.$$

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