B.Sc. Semester-IV Examination, 2022-23

CHEMISTRY [Honours]

Course ID : 41411 Course Code : SH/CHEM/401/C-8

Course Title : Physical Chemistry III (T-8)

Time : 1 Hour 15 Minutes Full Marks : 25

The figures in the right-hand margin indicate marks.

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

1. Give answer to any **five** of the following: 1×5=5

a) Define molal elevation constant.

b) Express overlap integral mathematically.

c) Indicate the number of components and degrees of freedom for the system– 'Solid $CaCO_3$ is heated in a sealed tube'.

d) How liquid junction is eliminated in a cell?

e) What is the unit of $\left[\frac{\partial(G/T)}{\partial T}\right]_P$ in SI unit?

f) Write the Hamiltonian operator for hydrogen atom in spherical coordinates.

g) Why Debye-Huckel limiting law is called 'limiting law'?

h) Write down the Clausius-Mosotti equation.

2. Give answers to any **two** of the following: 5×2=10

a) i) Calculate the e.m.f for the half cell: $Pt(s)|\ H_2(0.01\ atm)|H^+(a=0.1)$ at 25°C.

ii) Acetic acid associates in benzene forming dimers, 0.0016 kg of acetic acid is dissolved in 0.1 kg of benzene raised the boiling point by 0.66 K. Calculate the Vant Hoff 'i' factor and the degree of association. 2+3

b) i) Angular function

$$Y_l^m(\theta, \phi) = N_{lm} P_l^{|m|}(\cos\theta) e^{im\phi},$$

find the eigen value of $L_z Y_l^m(\theta, \phi)$. [N_{lm} is the normalisation constant and $P_l^{|m|}(\cos\theta)$ is the associated Legendre function.]

ii) Following Debye-Huckel limiting law, plot $\log\gamma_\pm$ vs. $\sqrt{I}$ for the electrolytes KCl and $ZnSO_4$ in the same graph. In which case deviation from experimental curve will be higher? 2+3

c) i) Define electrical polarizability (α). Find the unit of $\alpha/4\pi\varepsilon_0$ in SI unit.

ii) Define Triple Point.

iii) Phase rule, $F = C - P + 2$, is valid even if some of the components may not be present in all the phases– Justify / Criticize. 2+1+2

d) i) What do you mean by 1st order phase transition? Give one example.

ii) Show that $\left[L^2, L_z\right] = 0$. 2+3

3. Answer any **one** of the following: 10×1=10

a) i) Consider a trial function that linearly depends on the variational parameters (C_1 and C_2) as $\psi = C_1\phi_1 + C_2\phi_2$. Apply variational method to show that for a homonuclear diatomic molecule the above function leads to the Slater determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0.$$

ii) Write down Vant Hoff equation for osmotic pressure. "Elevation of freezing point may occur in solution"– Comment.

iii) Cite two main differences between electrolytic and galvanic cells. 5+(1+2)+2

b) i) Consider the cell:

$H_1(g, 1\ atm) \mid HCl(a_1)$, $AgCl(s) \mid Ag - Ag \mid AgCl(s)$, $HCl(a_2) \mid H_2(g, 1\ atm)$

Write down anode, cathode and overall reactions. Find the expression for E_{cell} and then comment on the spontaneity condition.

ii) Calculate ionic strength and mean ionic activity coefficient for a 0.02 molal aqueous solution of $ZnCl_2$.

iii) Define radial probability distribution function. 5+3+2

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