B.Sc. Part-III (Honours) Examination, 2020

Subject: Chemistry

Paper: XI

(New Syllabus)

Time: 2 Hours **Full Marks: 50**

The figures in the right hand margin indicate full marks.

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

Group – A

1. Answer *any three* questions from the following: **5 × 3 = 15**

(a) Starting from the van't Hoff reaction isotherm, arrive at the Nernst equation for an electrochemical cell and hence derive the relation, $\Delta H^0 = -nF\frac{\partial(E^0/T)}{\partial(1/T)}$

(b) (i) Briefly discuss the effect of temperature and pressure on the process of adsorption.

(ii) The process of adsorption is exothermic – justify the statement.

(c) (i) Predict the nature of variation of molar polarization with the inverse of temperature for the following molecules: CH_3Br, HCl, CCl_4

(ii) What do you mean by the terms 'symmetry element' and 'symmetry operation'?

(d) (i) Calculate the potential of the half cell: Pt $\vert$ H_2 (1.5 atm) $\vert$ HCl (0.01 M)

(ii) The specific conductance of a solution of NaCl in water decreases with dilution while the equivalent conductance increases with dilution – explain.

(e) (i) Distinguish between Schottky defects and Frenkel defects. Give one example of a crystal lattice in which both types of defects are observed.

(ii) Define micelle and reverse micelle with one specific example of each type.

2. Answer *any one* question from the following: **10 × 1 = 10**

(a) (i) The equivalent conductance of a 0.014 N solution of chloroacetic acid is 1.09×10^{-2} Ω^{-1} m^2. The ion conductances of chloroacetate and hydrogen ions are 4.02×10^{-3} Ω^{-1} m^2 and

$3.49 \times 10^{-2}\ \Omega^{-1}\ m^2$ respectively. Calculate the degree of dissociation and the dissociation constant of the given acid.

(ii) Why KCl is often used in preparing salt bridge to connect the half cells of a cell during electrochemical experiments?

(iii) From the given value of molar conductivities at infinite dilution, calculate λ_m^{∞} for NH_4OH. Given: λ_m^{∞} for $Ba(OH)_2$ = 457.6 $ohm^{-1}\,cm^2\,mol^{-1}$, λ_m^{∞} for $BaCl_2$ = 240.6 $ohm^{-1}\,cm^2\,mol^{-1}$ and λ_m^{∞} for NH_4Cl = 129.8 $ohm^{-1}\,cm^2\,mol^{-1}$.

(b) (i) Calculate the Miller indices of a crystal plane which cut the crystallographic axes as follows: $\frac{3}{2}a, 2b, c$; $4a, 2b, \infty$; $-2a, -3b, 4c$

(ii) The edge length of a body centered cubic unit cell of iron metal (At. mass of Fe = 55.85) is 288 pm. Find the density of iron.

(iii) Show that Gibbs adsorption isotherm leads to a two dimensional ideal gas equation for small concentration of surface active substance.

Group - B

3. Answer *any three* questions from the following: **5 × 3 = 15**

(a) (i) Show that the function $\psi = e^{-iax}$ is an eigenfunction of the operator $\frac{d}{dx}$ and write down the corresponding eigenvalue.

(ii) Test which one of the following operators maintain eigenfunction relationship with $e^{-\alpha x^2}$ (where α is a constant): $\frac{d^2}{dx^2}$, $\frac{1}{x}\frac{d}{dx}$

(b) (i) Define partition function. Also explain why the partition function is a dimensionless quantity.

(ii) Calculate the entropy for a system consisting of 10 particles distributed over four energy levels with occupancies of (5, 3, 2, 0).

(c) (i) Which of the following molecules will show pure rotational spectra and why?

CH_4, CH_3Cl, H_2, NH_3

(ii) How many normal modes of vibration in H_2O molecule can exist? Also predict the number of Raman active vibrational modes of this molecule.

(d) (i) Explain the physical significance of molar absorption coefficient using Beer's law.

(ii) The quantum yield of a fluorescent dye molecule can never be equal to 1.0 – explain.

(e) (i) What do you mean by residual entropy? Nitric oxide exhibits appreciable amount of residual entropy – explain.

(ii) The work function for Cs metal is 3.43×10^{-19} Joule. Find the kinetic energy of an electron emitted by an incident radiation of 550 nm.

4. Answer *any one* question from the following: **10 × 1 = 10**

(a) (i) Assuming the expression of rotational energy of a rigid diatomic molecule, show that the spectral lines are equispaced.

(ii) Draw a labeled Jablonski diagram with brief explanation of the processes shown over there.

(iii) Estimate the force constant for the molecule $H^{35}Cl$ from the fact that the fundamental vibrational frequency is 58.667×10^{13} s^{-1} and the reduced mass is 1.627×10^{-27} kg.

(b) (i) Normalize the function $\psi = x^2$ over the interval $0 \leq x \leq k$ (where k is a constant).

(ii) Show that the following two functions are orthogonal over the interval $0 \leq x \leq 2\pi$:

$$\left(\frac{1}{\pi}\right)^{\frac{1}{2}} \cos nx \text{ and } \left(\frac{1}{\pi}\right)^{\frac{1}{2}} \sin nx$$

(iii) Phosphorescence occurs at a much slower rate than fluorescence – explain.

(iv) Show that the heat capacity remains unchanged in any transformation in the vicinity of absolute zero.

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