2020

CHEMISTRY

[HONOURS]

Paper : XI

Full Marks : 100 Time : 4 Hours

The figures in the right-hand margin indicate marks.

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

Terms have their usual significance.

GROUP–A

[Marks : 50]

1. Answer any **five** questions: 2×5=10

   a) Draw a graph showing conductometric titration of Acetic acid by NaOH. Explain the nature in short.

   b) How much amount of stearic acid (M=284) when placed on water forms a close packed monolayer of area 226 sq cm? Cross sectional area of each stearic acid molecule=20.42 sq Å.

   c) State one application of calomel electrode.

   d) Write down the expression for Boltzmann distribution law involving degeneracies.

   e) Construct an electrochemical cell with reaction

$$Hg_2Br_2 + H_2 \rightleftharpoons 2Hg + 2H^+ + 2Br^-$$

   f) Why equivalent conductance at infinite dilution is maximum for an electrolyte?

   g) Using the concept of Nernst heat theorem, prove that all processes should occur without alteration in entropy-values in the vicinity of absolute zero.

   h) How peptising agents stabilize colloids?

2. Answer any **four** questions: 5×4=20

   a) If $S=k_B \ln w$ and $E=TS-Nk_BTX$,

      i) Find X. 4

      ii) Write down Debye-Hückel-Onsagar equation for an electrolyte. 1

   b) i) How can you determine standard electrode potential of silver electrode? 3

ii) Draw a diagram showing zeta potential. 2

c) Justify: "Absolute zero cannot be attained." 5

d) i) Show that the Gibbs adsorption isotherm leads to a two dimensional perfect gas equation for small concentration of surface active substances.

ii) What is the liquid junction potential? How is it eliminated? 3+2

e) i) State Walden rule. 1

ii) Prove that Barometric distribution formula is a simple corollary of Boltzmann distribution law. 4

f) i) How can you determine pH of a solution using Quinhydrone electrode? 4

ii) State Schulze-Hardy rule. 1

g) i) How $\wedge^{o}$ depends on temperature? Why? 2+2

ii) Give an example of precipitation titration. 1

3. Answer any **two** questions: 10×2=20

a) i) A cell is set up with an aqueous solution containing Ce^{+4} and Ce^{+3} in the proportion of 80% and 20% coupled with an aqueous solution containing Fe^{+3} and Fe^{+2} in the proportion of 10% and 90%. The observed EMF at 25°C is 0.93 V. Find the equilibrium constant for the reaction $Ce^{+4}+Fe^{+2} \rightleftharpoons Ce^{+3}+Fe^{+3}$ at 25°C. Can this reaction be used for quantitative analysis estimation? 4+1

ii) Show how transference number can be determined from concentration cell. 5

b) i) Arrive at the relation $\left(\frac{\partial \pi}{\partial S}\right)_V = -\left(\frac{\partial \gamma}{\partial V}\right)_S$ using four steps of a thermodynamical cycle. 4

ii) Why 'Liquid Junction Potential' arises in concentration cells? 3

iii) Show that $\Delta S = R \ln \frac{V_f}{V_i}$ justifies $S=k_B \ln w$. 3

c) i) What is Debye Falkenhagen effect? $2\frac{1}{2}$

ii) Calculate the number of ways of arranging 7 distinguishable particles among four energy levels such that one energy level has 1 particle and rest levels have 2 particles. $2\frac{1}{2}$

iii) At $18^{o}C$, the mobility at infinite dilution of NH_4^+ and ClO_3^- ions are 6.6×10^{-4} $V^{-1}cm^2\,sec^{-1}$ and 5.7×10^{-4} $V^{-1}cm^2sec^{-1}$ respectively. Calculate the transport numbers of two ions. 3

iv) What is coagulation of colloids? 2

d) i) How can you determine K_a of a weak acid from conductance measurements? 3

ii) Solubility of $MgCO_3$ at a particular temperature is 10^{-3} moles/litre. Calculate its solubility in 0.1(M) KNO_3 solution. 4

iii) "The entropy of a substance at any temperature be greater than its entropy at absolute zero."– Comment. 3

GROUP–B

[Marks : 50]

4. Answer any **five** questions: 2×5=10

a) Write down Bohr's correspondence principle. 2

b) What will be the expressions for Ψ_{12} and Ψ_{21} for a particle in a 2D box system? 2

c) Show that the successive energy levels of a linear harmonic oscillator are equally spaced. 2

d) 'p orbital has yz nodal plane.'– Comment. 2

e) Draw a diagram showing occurence of 'predissociation' during transition. 2

f) The rotational spectrum of HCl has lines $21.1\,cm^{-1}$ apart. Calculate the moment of inertia of HCl. 2

g) What is London force? 2

h) Check the function $\left(\Psi = e^{-x}\right)$ in the interval $(0, \infty)$ whether it is acceptable in QM or not. 2

5. Answer any **four** questions: 5×4=20

a) i) Describe the energy level with term symbol $2p_{3/2}$. 2

ii) A particle has the ware function

$$\psi(r) = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{x}{a_0}}$$, where a_0 is constant.

Find <r>. 3

b) i) Show that during photochemical decomposition of HI, two moles of HI decompose per einestein of radiation absorbed. 4

ii) What is uncertainty product inequality? 1

c) The Threshold wavelength for photo-electric emission in Tungsten is 2300Å. What wavelength of light should be used to eject electrons with a maximum energy of 1.5 eV? 5

d) i) Draw a diagram in favour of transitions responsible for Sodium D-lines. Explain in short. 4

ii) Give an example of $np^1n^1p^1$ system. 1

e) i) What is Born-Oppenheimer approximation? 2

ii) Calculate $\bar{\nu}_{absorption}$ for the lowest energy band of the molecule Butadiene. C–C distance=139 pm. 3

f) i) How do HCl and DCl differ in respect of vibrational and rotational spectra? Explain the each case separately. 3

ii) Find out the normalizing factor of the wave function,

$$\psi = N.\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}$$

for a particle in a two dimensional box where $0 \le x \le a$ and $0 \le y \le b$. 2

6. Answer any **two** questions: 10×2=20

a) i) Evaluate $\left[\hat{x}^n, \hat{p}_x\right]$. 2

ii) A 0.003(M) solution of a coloured substance transmits 75% of the incident light of 500 nm when placed in a cell of length 1 cm. Calculate t. 3

iii) Write down the radial distribution function for 2s orbital of H-atom. Comment on the maximum probability of finding the electron. 2+2

iv) What is the expression for wave function for v=1 state of a simple harmonic oscillator? 1

b) i) Explain in the light of Heisenberg uncertainty principle energy of a particle in a 1D box cannot be zero. 2

ii) Find out most probable perition for particle in a 1D box for n=3 state. 3

iii) How can you apply Wilson-Sommerfeld quantization rule to Bohr atom? 3

iv) Give an example of a chemical actinometer and write the chemical changes occurring within it. 2

c) i) Explain the mechanism of fluorescence. 3

ii) Absorption maximum in the IR spectra $H^{1}Br^{80}$ was observed as 37.8 nm. Calculate the force constant of H–Br bond. 3

iii) Give an example of degeneracy for a particle in a 3D-box system. 3

iv) State one application of electroluminescence. 1

d) i) Arrive at the eigen value equation of the operator $\left(\frac{dr}{dx^2} - x^2\right)$ for the wave function $\psi = e^{-\frac{x^2}{2}}$. 2

ii) How can you determine ground state term symbol for a transition element? Take an example. 3

iii) Explain the shape of Morse potential energy curve. 3

iv) For N_2 molecule, fundamental first overtone and second overtone bands are given as 2345.15, 4661.40 and 6983.73 cm^{-1}. Calculate x_e of the molecule. 2

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