2021

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) Write down the Stirling's approximation formula for the factorials of large numbers. Hence calculate the % error involved if 6! is calculated using this formula.

   b) Calculate the molar residual entropy in SI unit for carbon monoxide.

   c) Give the graphical representation for conductometric titration of oxalic acid by NaOH. Also show the differential plot.

   d) Represent Glass electrode.

   e) Define equivalent conductance in SI system.

   f) Write down the assumptions during derivation of Boltzmann distribution law.

   g) What will be the cell reaction of the following electrochemical cell?

   $$H_2(g)(p_1 \text{ atm})\left|H^+\right|\left|OH^-\right|O_2(g)(p_2 \text{ atm}).$$

   h) In a mixture of different electrolytes on which factors activity coefficient of a specific electrolyte depends?

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

   a) Explain the concept of electrokinetic potential with the help of 'Stern' double layer. 5

   b) i) Explain the origin of electrode potential.

      ii) Construct a concentration cell without transport. 3+2

   c) $\wedge_0$ of AB is 227.49 $ohm^{-1}cm^{-2}eqiv^{-1}$ and $t_{A^+} = 0.65$. Calculate ionic conductance and mobility of B^-. $2\frac{1}{2}+2\frac{1}{2}$

   d) i) If internal energy $(U) = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v$, find S. Q=partition function.

ii) State one of the limitations of Nernst heat theorem. 4+1

e) i) Explain why displacement of 'boundary' occurs in the determination of transport number by 'moving boundary method'.

ii) Justify the existence of residual entropy of nitrous oxide at 0 K. 3+2

f) i) Describe the action of a salt bridge taking an example.

ii) Calculate the mean ionic activity coefficient of aq. chromium sulphate of concentration 2×10^{-4}(M) at 25°C. $2\frac{1}{2}+2\frac{1}{2}$

g) i) Explain why saturation of adsorption at higher temperature occurs at higher pressure than that at lower temperature.

ii) At sea level $p_{N_2} : p_{O_2} = 8:2$. Calculate total pressure at 8979 metre height at 27°C. (g=9.80 m/s^2) 2+3

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

a) i) A surface active agent follows the relation with concentration $\gamma = \gamma* - bC^2$;

where γ and $\gamma*$ are the surface tensions of solution and pure solvent respectively (b=constant). Show that for such substance the Gibb's adsorption isotherm corresponds to the two dimentional gas law equation $\Pi\sigma = \frac{1}{2}RT$ (where symbols have their usual meaning).

ii) A film containing 5.14×10^{-5}g of an alcohol (Mol.wt.242) spread on water was compressed into monolayer occupying an area of $15\times17.9\,cm^2$. The density of the alcohol is 0.818g/cc. Calculate the area of cross-section of a molecule and its length.

iii) Determine K_w from EMF measurement. 3+3+4

b) i) How retardation of an ion occurs in a solution by electrophoretic effect?

ii) At 27°C during adsorption of a gas X on charcoal at 2 atm, fraction of surface covered is 0.617. Calculate ΔG^0.

iii) Describe a method to justify that 0 K can never be attained. 3+3+4

c) i) Show according to Boltzmann distribution that the population in three successive energy levels are in geometric progression if the energy-values of those three succssive levels are in arithmetic progression.

ii) What will be the significance of the value of partition function at (a) $T \to 0$ and (b) $T \to \infty$; if the ground energy level has zero energy value and degeneracy of each level is unity?

iii) Write down the Nernst heat theorem and give any one of its implications.

iv) Explain how addition of electrolytes causes coagulation of colloids.

2+2+3+3

d) i) In the expression, $\frac{n_i}{n} = \frac{g_i e^{-\beta t_i}}{\sum g_i e^{-\beta t_i}}$, explain the contribution of 'g_i'.

ii) Draw a graph for titration of KCl by $AgNO_3$ solution conductometrically and explain it.

iii) For the cell $Cd\,|\,CdCl_2(1M)\,|\,AgCl(s);\ Ag$ at 25^oC if $\Delta H = -83925.67$ joule and $\Delta S = -72.34$ joule/deg when one faraday electricity is drawn, find E_{cell} and temperature coefficient of EMF of the cell.

iv) Draw a $\wedge_c$ vs $\sqrt{c}$ plot for 1:1 weak electrolyte and explain its nature.

$2\frac{1}{2}+3+3+1\frac{1}{2}$

GROUP–B

[Marks : 50]

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

a) Calculate the molar extinction coefficient of a complex which transmits 2% incident light from a 6 cm cell filled with 0.02(M) solution of it. Solvent is transparent. 2

b) Write down the expression for Wilson-Sommerfield quantization rule for a system of 3n generalized coordinates. How many phase integrals are there? 1+1

c) Check the Hermitian property of kinetic energy operator. 2

d) Describe the atomic state corresponding to the term symbol $^4P_{5/2}$. 2

e) Write down the expression for Morse function for a real molecule with proper clarification of terms. 2

f) 'For an asymmetric diatomic molecule rotation about the bond axis is rejected'– why? 2

g) After reaching an excited state due to electronic transition in how many ways a molecule may lose the excess energy? State the names. 2

h) A cesium plate is illuminated with UV light of $\lambda = 2000\,\text{Å}$. The stopping potential is found to be 4.21 volts. What is the work function of cesium surface in eV unit?

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

a) i) Draw two potential energy curves of a diatomic molecule showing at least two Franck-Condon transitions. Indicate different states and their transitions.

ii) What is Debye force? Write down the expression for corresponding interaction energy. $2+(1\frac{1}{2}+1\frac{1}{2})$

b) i) Comment on the colour of conjugated compounds on the basis of 1D box model.

ii) If $\hat{A}\psi = e^a\psi$ with the eigen value 'e^a', then show that '$\hat{A}$' has its eigen value equals to 'a' with the same eigen function. 3+2

c) Write down the expressions of wave functions of simple harmonic oscillator at ground and 1st excited state. Show their nature with ψ-x plots. In the lowest quantum state at which x the particle spends maximum time? Is it in agreement with classical theory? $2+1+1\frac{1}{2}+\frac{1}{2}$

d) i) Velocity of an electron ejected from Pt-surface when a radiation of frequency ν falls on it equals to 7.9×10^{-7} m/sec. Calculate ν. Work function for Pt=5 eV.

ii) Write down the statement of Bohr's correspondence principle. 4+1

e) i) What is Lennard-Jones Potential? How does it change with intermolecular distance? Draw a diagram in favour of it.

ii) Comment on the degeneracy of the Ist excited state of a particle in a 2D box. 3+2

f) i) Find out the rotational energy level of diatomic molecule with maximum population.

ii) Explain how photosensitization is used in actinometers. $2\frac{1}{2}+2\frac{1}{2}$

g) i) Show that the azimuthal wave function must be single valued everywhere only when the magnetic quantum no. is zero or a positive or negative integer for H-atm wave function.

ii) Give an example of electroluminescence. 4+1

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

a) i) Write down the wave function (R(r)) for the electron in the ground state of H-atom with proper mentioning of terms. Show that the most probable position of this electron is equal to the radius of the first Bohr orbit.

ii) State Grotthus-Draper's law of photochemistry.

iii) Arrive at the expression for the allowed vibrational-rotational energy changes during a transition from v=0 to v=1 involving a simultaneous change in J value. What is band origin? 4+2+(3+1)

b) i) Show that the quantum mechanical energy levels of a harmonic oscillator are equally spaced with an interval of $h\nu$ by using Wilson-Sommerfeld quantization rule.

ii) What are singlet and triplet states? Discuss on transitions between them after excitation of a molecule by radiation.

iii) Prove that the quantum yield for the photolysis of HI is equal to 2. 3+3+4

c) i) Draw an energy level diagram for the atomic spectra of sodium indicating proper terms and series and transitions.

ii) Find out the term symbols for two non-equivalent electrons with $l_1=l_2=1$ and indicate the corresponding L, S and J values.

iii) What is the probability of locating an electron confined to a molecule of length 2 nm between $0 \leq x \leq 0.3$ nm in its lowest energy state?

iv) Give one example of a $ns^1n^1s^1$ state.

$2\frac{1}{2}+2\frac{1}{2}+4+1$

d) i) Show that the lines in rotational spectrum of a diatomic molecule are equispaced under rigid rotor approximation.

ii) The moment of inertia of N–H radical is 1.68×10^{-40} gcm^2. At what wave number would you expect to defect transition from $J=2 \rightarrow J=3$ level?

iii) Assuming harmonic oscillator model show that the fraction of molecules in v-th vibration level is. 3+4+3

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