QP Code : 20433

Time : 3 Hours **Total marks: 100**

N.B : 1. **All** questions are **compulsory**.
2. **Figures** to the **right** indicate **full** marks.
3. Use of non-programmable scientific calculator is **allowed**.

Useful constants –

c = $2{\cdot}998 \times 10^{8}$ ms^{-1}

R = $8{\cdot}314$ $JK^{-1}mol^{-1}$

h = $6{\cdot}625 \times 10^{-34}$ Js

m_e = $9{\cdot}11 \times 10^{-31}$ kg

N_A = $6{\cdot}023 \times 10^{23}$ mol^{-1}

e = $1{\cdot}602 \times 10^{-19}$ C

k = $1{\cdot}3811 \times 10^{-23}$ JK^{-1}

1 J = $6{\cdot}24 \times 10^{18}$ eV

1 eV = $8{\cdot}06 \times 10^{3}$ cm^{-1}, 1 a.m.u. = $1{\cdot}66 \times 10^{-27}$ kg

N = 14 O = 16

1. Attempt any **five** of the following :— **20**

(a) Define entropy. How will you determine the absolute entropy of a solid crystalline substance ?

(b) Derive the relation

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

from the definition of enthalpy.

(c) What are Lambda transitions ? Explain with suitable example.

(d) What are fuel cells ? Give advantages of fuel cells over conventional cells.

(e) Transform the cartesian coordinates (x, y, z) into polar coordinates (r, θ, ϕ).

(f) The particle in a one dimensional box of length L has the wave function $\Psi_n = A\sin\frac{n\pi x}{L}$
Normalise the above function and determine the value of A.

(g) Explain the following terms :—

(i) Oscillating reactions

(ii) Explosion reactions

(h) Predict the effect of ionic strength on the rates of following reactions :

(i) $CH_3COOC_2H_5 + OH^- \rightarrow$ Products

(ii) $S_2O_8^{2-} + I^- \rightarrow$ Products

(iii) $Fe^{2+} + Co\,(C_2O_4)^{3-} \rightarrow$ Products

(iv) $H_2O_2 + 2H^+ + 2\,Br^- \rightarrow$ Products.

2. (a) What is partition function ? Derive the following relation for total translational function of a molecule **7**

$$\phi_t = \frac{(2\pi\, mkT)^{3/2} V}{h^3}$$

OR

(a) Explain the term fugacity and activity. How are they related ? How is fugacity determined by van der waal's equation of state ? **7**

(b) Calculate ΔG_{mix}, ΔH_{mix} and ΔS_{mix} at 25ºC and 1 atm when **6**

(i) 10 moles of He are mixed with 10 moles of Ne

(ii) 10 moles of He are mixed with 20 moles of Ne

(iii) 10 moles of Ne are mixed with 20 moles of mixture consisting of Ne and He.

(c) Derive the following relations. **7**

(i) $\mu = \frac{1}{Cp}\left(\frac{2a}{RT} - b\right)$

(ii) $T_i = \frac{2a}{Rb}$

OR

(c) State the third law of thermodynamics. Give its application. Why molecules like CO and N_2O have positive value of entropy at zero Kelvin ? Calculate the value of molar residual entropy for NO molecule at absolute zero. **7**

3. (a) Discuss Gouy and Chapman concept of electrical double layer. How is it modified by Stern ? **7**

OR

(a) State the postulates of B.E.T. theory. Write the B.E.T. equation. How is it used for determination of surface area of adsorbent ? **7**

(b) Calculate the concentration and mean ionic activity coefficient of Aluminium Sulphate solution whose ionic strength is same as that of 0·45M KBr solution. Given: A = 0·509 for water at 298K. **6**

(c) Discuss the Debye-Huckel theory of strong electrolytes. State the Debye-Huckel Onsager equation and explain terms involved in it. **7**

OR

(c) Explain (i) zone refining **7**

(ii) Debye-Falkenhagen effect of electrolytic conductance.

4. (a) Obtain Schrondinger wave equation for energy of a particle in three dimensional box. How can the equation be modified for a cubical box ? **7**

OR

(a) Explain the term 'Hamiltonian operator'. For a particle in one dimensional box of length L, find the probabilities in the states n = 1, 2 and 3 when the particle is in the region $0 \leq x \leq \frac{L}{4}$ **7**

(b) The Hermite Polynomials are derived from the generating function. **6**

$$H_n(y) = (-1)^n \; e^{y^2} \; \frac{d^n\left(e^{-y^2}\right)}{dy^n}$$

where 'n' is vibrational quantum number and also the degree of polynomial. Calculate the polynomial for n = 0, 1, 2.

(c) Set up and solve Huckel determinant equation for butadiene. Show HMO energy levels. **7**

OR

(c) Explain the terms :— **7**

(i) Legendre functions

(ii) Odd-even functions

For a rigid rotor, write the expression for the energy level. Calculate the energy for J = 0, 1 and 2.

5. (a) On the basis of the collision theory, derive an expression for the rate constant of a bimolecular reaction. What are the limitations of the collision theory ? **7**

OR

(a) Explain the flash photolysis technique to study fast reactions which cannot be studied by usual laboratory techniques. **7**

(b) The activation energy of a non-catalysed reaction at 308K was 237·28kJmol^{-1} and the activation energy of the same reaction which was catalysed by an enzyme was 600 kJmol^{-1}. Calculate the ratio of the rate constants of the enzyme catalysed reaction to that of the non-catalysed reaction. State your inference from the value obtained. **6**

(c) What is steady state treatment ? Apply it to obtain the rate law for the decomposition of ozone. **7**

OR

(c) Distinguish between primary and secondary salt effect. Derive an expression to show the influence of ionic strength on the rate of the reaction between the ions. **7**

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