QP Code : 75460

(3 Hours) [Total Marks : 75

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

Useful constants

$c=2.998\times10^{8}$ ms^{-1}
$h=6.626\times10^{-34}$ J.s
$R=8.314$ JK^{-1} mol^{-1}
$m_e=9.110\times10^{-31}$ kg
$N_A=6.022\times10^{23}$mol^{-1}
$e=1.602\times10^{-19}$C
$k=1.3811\times10^{-23}$JK^{-1}
$1J=6.24\times10^{18}$eV
$1eV=8.06\times10^{3}$cm^{-1}

1. Attempt **any five** of the following 15
   (a) Prove that the Joule - Thomson effect is isoenthalpic.
   (b) What is partition function? Give its physical significance.
   (c) State BET adsorption isotherm equation. Explain the terms involved in it.
   (d) Explain Wein effect in the case of conductivity measurements of strong electrolytes.
   (e) What are the characteristics of well behaved function? Indicate which of the following wave functions are acceptable
      (i) $\psi = e^{-x}$ (ii) $\psi = \tan x$
   (f) If $\psi = e^{-x}$ and $\varphi = \sin x$ then show that the operator $\frac{d^2}{dx^2}$ is Hermitian
   (g) Explain :
      (i) oscillating reactions
      (ii) explosion reactions
   (h) Predict the effect of ionic strength on the rates of the following reactions:- Justify your answer
      (i) $S_2O_8^{2-}+2I^- \rightarrow$ Products
      (ii) $[Cr(urea)_6]^{3+} + H_2O \rightarrow$ Products
      (iii) $Fe^{2+} + Co(C_2O_4)^{3-} \rightarrow$ Products

2. (a) Explain the concept of residual entropy with suitable examples. How can you determine absolute entropies of solids at different temperatures? 6

OR

(a) Derive mathematical relationship between partition function and internal energy. 6

(b) Calculate the entropy of ideal mixing when 2 moles of N_2 , 3 moles of H_2 and 2 moles of NH_3 are mixed at constant temperature, assuming no chemical reaction is occurring 5
[Atomic mass of N=14, H=1]

(c) State the fundamental equation for Boltzman distribution and explain the terms involved in it. 4

OR

(c) Starting with the concept of fugacity, obtain the relation between activity and activity coefficient in terms of chemical potential. 4

3. (a) What is polarised electrode? Explain Lippman's experiment related to electrocapillary phenomenon. 6

OR

(a) Derive an expression for the Debye-Huckel limiting law. How is it extended to be applicable to higher concentrations? 6

(b) Calculate the mean ionic activity coefficient of aluminium sulphate solution whose ionic strength is same as that of 0.03 m sodium chloride solution. at 298K. 5
(Given A = 0.509 for water at 298 K)

(c) Distinguish between first order and second order phase transitions. Give one example of each transition. 4

OR

(c) Explain the phase diagram of three component system exhibiting formation of one pair of partially miscible liquids. 4

4 (a) Obtain the Hermite's differential equation for linear Harmonic oscillator from the following equation. 6

$$\frac{d^2\psi}{dy^2}+\left(\frac{\alpha}{\beta}-y^2\right)\psi=0$$

OR

(a) Set up and solve Huckel determinants equation for ethylene. Show the Huckel molecular orbital energy levels. Indicate HOMO and LUMO in ethylene. 6

(b) For a particle of mass 'm' moving in a cubical box of side 'a', calculate the degeneracy of the level corresponding to the energy. 5

(i) $E=\frac{18h^2}{8ma^2}$ (ii) $E=\frac{21h^2}{8ma^2}$

(c) State and prove any one theorem of Hermitian operator. 4

OR

(c) The internuclear distance in HI molecule is 163 pm. Calculate the energy of the first rotational level. 4
[Atomic mass of H=1, I= 127]

5 (a) Derive an expression for the rate constant of a bimolecular reaction on the basis of the collision theory of reaction rate. 6

OR

(a) Explain the shock tube and flash photolysis techniques used to study fast reaction. 6

(b) The rate constants for a second order reaction are 3.45×10^{-5} dm^3 mol^{-1} s^{-1} at 25°C and 1.35×10^{-6} dm^3 mol^{-1} s^{-1} at 35°C. Calculate the activation energy and the pre-exponential factor. 5

(c) Derive an expression to show the influence of ionic strength on the rates of reaction between ions. 4

OR

(c) State the expression for the rate law on the basis of Michaelis-Menten's mechanism. What is Michaelis constant? Discuss the effect of concentration of the substrate on the rate of enzyme catalysed reaction. 4
