QP Code : 75999

(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 **calculator** is **allowed.**

Useful constants:-

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

1. Attempt any **five** of the following:- **20**
   (a) State the third law of thermodynamics and show how it can be used to determine absolute entropies of liquid.
   (b) Obtain an expression for free energy of mixing in terms of mole fraction.
   (c) What is corrosion? Explain the role of different type of inhibitors to prevent corrosion.
   (d) Explain the basic principle of zone refining technique.
   (e) Which of the following are eigen functions of the operator $\frac{\partial^2}{\partial x^2}$? Find the eigen value for the same
      (i) $\sin 3x$ (ii) $3e^{-4x}$
   (f) Show that the probability of finding a free particle in limitless space at all points is the same.
   (g) Explain the following terms:-
      (i) Steric factor
      (ii) Rate determining step

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(h) Predict the effect of ionic strength on the rate constants of the following reactions:-
Justify your answer

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

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

(iii) $Co(NH_3)_5Br^{2+} + OH^- \rightarrow$ Products

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

2. (a) Write the expression for vibrational partition function and explain the terms involved in it. Derive the mathematical expression of partition function from Boltzman's distribution law. 7

OR

(a) What is meant by exact differentials? Give its characteristics. 7

(b) 4 litres of an ideal gas (mol.wt = 16) and 1 litre of another ideal gas (mol. wt. = 40) each at 1 atm and 300K are mixed isothermally in vessel of 3 liters capacity. Find ΔG_{mix}, ΔH_{mix} and ΔS_{mix}. 6

(c) Describe Joule Thomson experiment. Derive an expression for Joule Thomson coefficient and give its one application. 7

OR

(c) What is fugacity? How is it related to activity and activity coefficient? Describe the graphical method of its determination. 7

3. (a) With suitable diagram for three component system, explain the following terms:- 7

(i) Binodal curve
(ii) Plait point and
(iii) Tie line

OR

(a) What is adsorption isotherm? Derive an expression for Gibbs adsorption isotherm. 7

(b) Calculate the mean ionic activity coefficient of cesium chloride in a solution containing 0.01m cesium chloride and 0.01 m aluminium chloride at 298K. [Given A = 0.509 for water at 298K] 6

(c) State Debye-Huckel limiting law. Explain the terms involved. How is it verified experimentally for different electrolytes? 7

OR

(c) Explain different types of phase transitions with suitable example of each type. 7

4. (a) Starting with the equation 7

$$\left(\frac{\partial^2\psi}{\partial x^2}\right)_t = \frac{1}{c^2}\left(\frac{\partial^2\psi}{\partial t^2}\right)_x$$

set up the time independent Schrodinger wave equation. Using the method of seperation of variables, show that it can be expressed as three equations containing one variable each.

OR

(a) Set up and solve the Huckel secular determinant equation for buta-1, 3-diene. Show HMD energy levels. 7

(b) Calculate the spacing between lowest and highest energy level for particle A (mass = 10^{-30} kg) in one dimension box of length 10^{-10}m and particle B of mass 10^{-3}kg in one dimension box of length 10cm. State giving reasons for which particle quantisation is observed. 6

(c) The radial wave function of 2s orbital of a hydrogen atom is given by 7

$$R_{20} = N\left[z - \frac{r}{a_0}\right]e^{-\frac{r}{2a_0}}$$

Where N is constant

(i) Qualitatively sketch the radial distribution curve.

(ii) Determine the distance of node from the nucleus in terms of a_0

OR

(c) Explain the terms 7

(i) Legendre functions

(ii) Odd-Even functions

For a rigid rotor, write the expression for energy level. Calculate the energy for J = 0, 1, 2, 3

5. (a) What are enzyme catalysted reactions? Give an example. On the basis of Michaelis-Menten's mechanism show that the rate of an enzyme catalysed reaction depends on the concentration of the substrate. 7

OR

(a) Why are fast reactions not studied by usual laboratory techniques? Describe flash photolysis technique to study such reactions. 7

(b) The specific reaction rate for the first order decomposition of ethylene oxide into CH_4 and CO follows the equation 6

$$\log_{10} k\left(s^{-1}\right) = 14.34 - 1.25 \times 10^4 K/T$$

Calculate:

(i) Energy of activation

(ii) Frequency factor and

(iii) Specific reaction rate at 600K.

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

OR

(c) What are the factors affecting the rate of the reaction in solution? Derive the following reaction:- 7

$$\ln k = \ln k_0 + 1.018 z_A z_B \sqrt{I}$$

Where the term have the usual meaning.
