

[Time: 2hr]

[Marks:50]

Please check whether you have got the right question paper.

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

**Useful constants**

$$c = 2.998 \times 10^8 \text{ m.s}^{-1}$$

$$R = 8.314 \text{ J.K}^{-1}\text{mol}^{-1}$$

$$= 2.0 \text{ cal.K}^{-1} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$m_e = 9.110 \times 10^{-31} \text{ kg}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

Atomic mass of H = 1, C = 12, N = 14, O = 16, S = 32, Cl = 35.5

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$k = 1.3811 \times 10^{-23} \text{ J.K}^{-1}$$

$$1\text{J} = 6.24 \times 10^{18} \text{ eV}$$

$$1\text{eV} = 8.06 \times 10^3 \text{ cm}^{-1}$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

1. Attempt **any two** of the following:

- Derive the following Maxwell equation.  $(\partial T / \partial V)_S = -(\partial P / \partial S)_V$  05
- Calculate  $\mu_{JT}$  for certain gas at 373 K and  $1.01235 \times 10^5 \text{ pa}$  taking  $C_P$  as  $55.5 \text{ J.K}^{-1}\text{mol}^{-1}$ . The Van der Waals constant  $a$  and  $b$  are  $0.0125 \text{ Nm}^4\text{mol}^{-2}$  and  $3.15 \times 10^{-5} \text{ m}^3\text{mol}^{-1}$ . Given  $R = 0.0821 \text{ Cal}$ . 05
- Define entropy. Write the expression for entropy change in the following phase transition. 05  
 1) Vaporization 2) Melting 3) Sublimation 4) Allotropic transformation.
- State the third law of thermodynamics. How will you determine the absolute entropy of a liquid using third law of thermodynamics. 05

2. Attempt **any two** of the following:

- Set up a Schrodinger wave equation for a particle in one dimensional box and obtain a normalised wave function for it.
- State the postulates of Quantum Mechanics.
- Determine the degeneracy of the levels.  
 a)  $E = \frac{9h^2}{8ma^2}$  b)  $E = \frac{26h^2}{8ma^2}$
- Derive the Hermite differential from the relation.

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

3. Attempt **any two** of the following:

- Explain the kinetics of free radical polymerization. 05
- Explain the Rice-Ramsperger-Kassel-Marcus theory. 05
- Write the reaction mechanism for the decomposition of acetaldehyde and using steady state principle show that  $d/dt[\text{CH}_4] = k[\text{CH}_3\text{CHO}]^{3/2}$ . 05
- The rate of formation of C in the reaction,  $2\text{A} + \text{B} \rightarrow 2\text{C} + 3\text{D}$  is  $4\text{molL}^{-1}\text{s}^{-1}$ . 05  
 State the rate of reaction and the rates of formation or consumption of A, B and D.

4. Attempt **any two** of the following:

- i) a) Explain Wein effect for the conductance of strong electrolytes. 02
- b) Calculate mean ionic activity coefficient of 0.05m  $\text{Al}_2(\text{SO}_4)_3$  in aqueous solution at 298K. (Given:  $\Lambda = 0.509$  at 298 K). 03
- ii) With the help of diagram explain construction and working of Alkaline fuel cell. Also write one advantage of fuel cell over conventional cell. 05
- iii) a) Write a note on the electrochemical enzyme – catalysed oxidation of Styrene. 03
- b) Calculate the resting membrane potential for the following: 02

Ion Species	Intracellular concentration in mM	Extracellular concentration in mM
$\text{Cl}^-$	12	0.003

(Given that  $\frac{2.303RT}{F}$  at 298K = 61 )

- iv) a) What is ion atmosphere? Explain the relaxation effect for the conductance of strong electrolytes. 03
- b) Draw well labelled diagram and write one application of Molten carbonate fuel cell. 02

5. Attempt **any five** of the following:

- i) Explain the term residual entropy. 02
  - ii) Explain exact differential equation. 02
  - iii) If  $\hat{A} = \frac{d^2}{dx^2}$ , and  $f(x) = \cos(2x)$  then show that  $f(x) = \cos(2x)$  is an eigen function of operator  $\frac{d^2}{dx^2}$ . Find its eigen value 02
  - iv) Define a) Commutative Operator b) Hamiltonian Operator 02
  - v) In the following reaction scheme, write the rate equation for the removal of species C and D in differential form. 02
- 1)  $\text{A} + \text{B} \xrightarrow{k_1} \text{C} + \text{D}$
  - 2)  $\text{C} + \text{D} \xrightarrow{k_2} \text{A} + \text{B}$
  - 3)  $\text{C} + \text{B} \xrightarrow{k_3} \text{E} + \text{D}$
  - 4)  $2\text{D} \xrightarrow{k_4} \text{F}$
- vi) Explain any two explosion limits of non – stationary chain reaction. 02
  - vii) Write Debye-Huckel-Onsager equation and briefly explain its validity for non-aqueous solutions. 02
  - viii) Write two functions of cell membrane. 02

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