

[Time : 2 ½ hrs.]

[Marks : 60]

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

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

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

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

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

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

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

$$\text{Atomic mass of H} = 1, \text{ C} = 12, \text{ N} = 14, \text{ O} = 16, \text{ S} = 32, \text{ Cl} = 35.5$$

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

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

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

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

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

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

- i) Using Maxwell relation prove that

$$\left[\frac{\partial C_V}{\partial V} \right] = 0 \text{ if, } \left[\frac{\partial C_V}{\partial V} \right] = T \left[\frac{\partial^2 P}{\partial T^2} \right]_V$$

4

- ii) Show that Joule Thomson coefficient $\mu_{J,T} = 0$ for an ideal gas. Comment on the liquification of an ideal gas.

4

- iii) Write the expression for entropy change in the following phase transitions.

4

i. Melting

ii. Vapourization

iii. Sublimation

iv. Allotropic transformation

- iv) What is state function? Give the significance of Maxwell's relation.

4

1. B) Attempt **any one** of the following:

- i) The heat capacity C_p in $\text{JK}^{-1}\text{mol}^{-1}$ of a substance is given by following equations

4

$$C_{p(s)} = 16.74 \times 10^{-5} T^3 \quad (0 < T < 50 \text{ K})$$

$$C_{p(s)} = 20.92 \quad (50 < T < 150 \text{ K})$$

$$C_{p(l)} = 25.10 \quad (150 < T < 400 \text{ K})$$

At the melting point (150K) $\Delta H_f = 1255.2 \text{ J mol}^{-1}$. Calculate absolute entropy of the substance in the liquid state at 300K?

- ii) Calculate $\mu_{J,T}$ for a certain gas at 273K and 150 bars taking C_p as $36.5 \text{ JK}^{-1} \text{ mol}^{-1}$. The van der Waal's constant a and b are $0.139 \text{ Nm}^4\text{mol}^{-2}$ and $3.92 \times 10^{-5} \text{ m}^3\text{mol}^{-1}$. Also calculate inversion temperature.

4

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

- i) What do you mean by degeneracy and non degenerate of energy levels?

4

Find the degree of degeneracy of $\frac{21h^2}{8ma^2}$.

- ii) State the basic postulates of quantum mechanics.

4

- iii) Verify that the wave functions of a particle in a one – dimensional box of width a and infinite height are orthogonal.

4

- iv) Explain the concept of particle wave and Schrodinger wave equation.

4

2. B Attempt **any one** of the following:

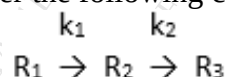
- i) Calculate the energies (in eV) of an electron constrained to move in an infinite one – dimensional box of width 1 Å and exhibit these energies in a suitable energy level diagram. **4**
- ii) If $\hat{A}$ and $\hat{B}$ are two operators such that $[\hat{A}, \hat{B}] = 1$ show that $[\hat{A}, \hat{B}^2] = 2\hat{B}$ **4**

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

- i) Write the reaction mechanism for the decomposition of acetaldehyde and using steady state principle show that $\frac{d}{dx} [\text{CH}_4] = k[\text{CH}_3\text{CHO}]^{3/2}$ **4**
- ii) Explain the kinetics of free radical polymerization. **4**
- iii) Explain in brief the Rice-Ramsperger Kassel Marcus (RRKM) theory. **4**
- iv) Explain the mechanism of decomposition of ozone. **4**

3. B) Attempt **any one** of the following:

- i) Consider the following consecutive reaction **4**



Here k_1 and k_2 are the rate constants for a first order reaction.

If $k_1 : k_2 = 1.0 : 0.25$. After what time from the start of the reaction, the concentration of B will be maximum? Given $k_1 = 5 \times 10^{-2} \text{ min}^{-1}$.

- ii) The rate of formation of C in the reaction, $2\text{A} + \text{B} \rightarrow 2\text{C} + 3\text{D}$ is $5 \text{ mol L}^{-1} \text{ s}^{-1}$. State the rate of reaction and the rates of formation or consumption of A, B and D. **4**

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

- i) Explain the relaxation effect for the conductance of strong electrolytes and write the expression for relaxation force. **4**
- ii) Explain Debye-Falkenhagen effect and Wien effect for the conductance of strong electrolytes. **4**
- iii) Explain the construction and working of the phosphoric acid fuel cell. **4**
- iv) Explain the use of enzymes as electrodes. **4**

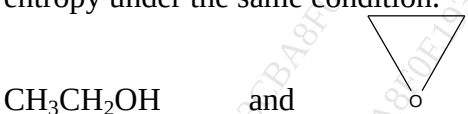
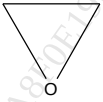
4. B) Attempt **any one** of the following:

- i) Calculate the mean activity coefficient of (i) 0.05m $\text{Al}_2(\text{SO}_4)_3$ (ii) 0.002m K_2SO_4 in aqueous solution at 298K. (Given: A for water at 298K is 0.509) **4**
- ii) Calculate the resting membrane potential for the following: **4**

Ion Species	Intracellular concentration in mM	Extracellular concentration in mM
K^+	0.0001	2.5
Na^+	125	5

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

5. Attempt **any four** of the following

- a) Write a note on the third law of thermodynamics. **3**
- b) Give the reason which molecule of the pair given below has greater molar entropy under the same condition. **3**
- 
- CH₃CH₂OH and 
- c) What is condition required for orthogonality of wave function? Show that two normalized wave function Ψ_1 and Ψ_2 are orthogonal to each other. **3**
- d) Write a note on Hamiltonian operator. **3**
- e) Explain the principle of microscopic reversibility. **3**
- f) Explain in brief about factors affecting explosion limits. **3**
- g) Write any two applications of molten carbonate fuel cell. State one advantage of fuel cell over conventional cell. **3**
- h) State Debye-Huckel-Onsager equation and explain its validity for non-aqueous solutions. **3**