[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

$c = 2.998 \times 10^{8}$ m.s^{-1} | $e = 1.602 \times 10^{-19}$ C
$R = 8.314$ J.K^{-1}mol^{-1} | $k = 1.3811$ x 10-23 J.K^{-1}
$= 2.0$ cal.K^{-1} mol^{-1}
$h = 6.626 \times 10^{-34}$ Js | $1J = 6.24 \times 10^{18}$ eV
$m_e = 9.110 \times 10^{-31}$ kg | $1eV = 8.06 \times 10^{3}$ cm^{-1}
$N_A = 6.022 \times 10^{23}$ mol^{-1} | 1 amu = 1.66×10^{-27} kg
Atomic mass of H = 1, C = 12, N = 14, O = 16, S = 32, Cl = 35.5

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

i) Using Maxwell relation prove that **4**

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

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 Cp in JK^{-1}mol^{-1} of a substance is given by following equations **4**
$Cp_{(S)} = 16.74 \times 10^{-5} T^3$ (0<T<50 K)
$Cp_{(S)} = 20.92$ (50<T<150K)
$Cp_{(l)} = 25.10$ (150<T<400K)
At the melting point (150K) $\Delta H_f = 1255.2$ 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 Cp as 36.5 JK^{-1} mol^{-1}. The van der Waal's constant *a* and *b* are 0.139 Nm^{4}mol^{-2} and 3.92×10^{-5} m^{3}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? Find the degree of degeneracy of $\frac{21h^2}{8ma^2}$. **4**

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 $\frac{d}{dx}[CH_4] = k[CH_3CHO]^{3/2}$ **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**

$$R_1 \xrightarrow{k_1} R_2 \xrightarrow{k_2} R_3$$

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 $k_1 = 5 \times 10^{-2}$ min^{-1}.

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

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 $Al_2(SO_4)_3$ (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**

CH_3CH_2OH 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**