[Time : 2.30 Hours] **[Marks: 60]**

Please check whether you have got the right question paper.

NB:

1. All questions are compulsory.
2. Figures to the right indicate full marks.
3. Use of non-programmable calculator is allowed.

Useful constants:

$c=2.998 \times 10^{8} ms^{-1}$	$e = 1.602 \times 10^{-19} C$
$R = 8.314\ JK^{-1}mol^{-1}$	$J = 6.24 \times 10^{18} eV$
$h = 6.626 \times 10^{-34} Js$	$1atm = 1.013 \times 10^{5}\ Nm^{-2}$
$N_A = 6.022 \times 10^{23}\ mol^{-1}$	$1eV = 8.06 \times 10^{3}\ cm^{-1}$
	$1\ amu = 1.66\ X10^{-26} kg$

Atomic mass of H = 1, C = 12, N = 14, O =16

Q.1(a) Attempt any two of the following :

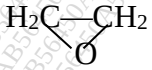
(i) Starting with van der waal's equation, show that 4

$$\mu_{JT} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)$$

where the terms have usual meaning.

(ii) What is Joule-Thomson effect? Explain the consequences of this effect on real and ideal gases. 4

(iii) State the characteristics of entropy. Giving reason, say which molecule of the pair given below has greater molar entropy under the same conditions. 4

CH_3CH_2OH and 

(iv) What are the deviations of third law of thermodynamics? 4

(b) Attempt **any one** of the following:

(i) Calculate the Joule Thomson coefficient (μ_{JT}) for N_2 gas at 298K and 100 atmospheric pressure if the van der waal's constants a and b for N_2 are $1.41 Nm^4 mol^{-2}$ and $3.92 \times 10^{-5}\ m^3\ mol^{-1}$ respectively.(Cp for N_2 = $29.04 JK^{-1}mol^{-1}$ 4

(ii) Calculate the residual entropy of a crystal in which molecules can adopt six orientations of equal energy at absolute zero. 4

Q.2(a) Attempt **any two** of the following **:**

(i) Set up a Schrodinger wave equation for a particle in two dimensional box and obtained a normalised wave function for it. 4

(ii) What is the condition for orthogonality of wave function? Show that the two dimensional wave functions ψ_1 and ψ_2 are orthogonal to each other. 4

(iii) Explain the term 'expectational value' of a dynamic quantity. 4

(iv) Derive the Hermite's differential from the relation 4

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

(b) Attempt **any one** of the following: 4

(i) Calculate the spacing between lowest and highest energy level for particle 'A' of mass 10^{-30}kg confined in a one dimensional box of length 10^{-10}m and particle B of mass 10^{-3} kg in one dimensional box of length 10 cm. State giving reasons for which particle quantisation is observed?

(ii) Determine the degree of degeneracy of the energy level: 4
a) E = $11h^2/8ma^2$ b) $17h^2/8ma^2$

Q.3(a) Attempt any two of the following :

(i) Explain the mechanism of decomposition of ozone 4

(ii) Obtain rate law expression for the thermal reaction 4

$H_2 + Br_2 \rightarrow 2HBr$

(iii) Show that the rate of polymerization reaction is proportional to the square root of initial concentration of the monomer. 4

(iv) Explain the Rice-Ramsperger-Kassel-Marcus theory. 4

(b) Attempt **any one** of the following:

(i) In the following reaction scheme, write the rate equation for the removal of species A, B, C and D in differential form

$A + B \xrightarrow{k_1} C + D$
$C + D \xrightarrow{k_2} A + B$
$C + B \xrightarrow{k_3} E + D$
$2D \xrightarrow{k_4} F$ 4

(ii) The following process follows first order kinetics 4

$x \xrightarrow{22.5d} y \xrightarrow{33.0d} z$

where the times are half lives in days. At what stage of time will the concentration of y become maximum?

Q.4(a) Attempt any two of the following:

(i) State the Deby-Huckel theory of strong electrolytes and explain the terms Asymmetry effect and electrophoretic effect. 4

(ii) Explain the conductance behaviour of a solution of a strong electrolyte by applying alternative current of different frequencies and discuss the Wien effect. 4

(iii) With the help of diagram explain the working of molten carbonate fuel cell. 4

(iv) Write a note on catalysed oxidation of styrene. 4

(b) Attempt **any one** of the following:

(i) Calculate the ionic strength of a solution which is 0.1 molal in KCl and 0.2 molal in K_2SO_4. 4

(ii) Calculate the resting membrane potential for a living cell for the following concentrations of Na^+ and K^+ 4

Intra cellular concentration of K^+ = 390mM and Na^+= 48mM

Extra cellular concentration of K^+ = 12mM and Na^+= 412mM

(given that 2.303RT/ F = 59.4 at 300K)

Q.5 Attempt any four of the following :

a Derive the Maxwell relation 3

$(\partial T/\partial V)s = -(\partial P/\partial s)v$

b What are exact and inexact differentials? Draw the Maxwell thermodynamic square. 3

c If operator A =Cos 5x and operator B = $\int$, then state whether operate A and operator B commute with each other or not. 3

d State the postulates of quantum mechanics. 3

e Explain consecutive reactions with examples. 3

f Explain three explosion limits of non-stationary chain reaction. 3

g Write any three applications of phosphoric acid fuel cell. 3

h Explain the theory of membrane potential in biological cell. 3
