[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:

$c=2.998 \times 10^8 ms^{-1}$	$e = 1.602 \times 10^{-19} C$
$R = 8.314\ JK^{-1}mol^{-1}$	$J = 6.24 \times 10^{18} eV$
$h = 6.626 \times 10^{-34} Js$	$1atm = 1.013 \times 10^5\ Nm^{-2}$
$N_A = 6.022 \times 10^{23}\ mol^{-1}$	$1eV = 8.06 \times 10^3\ cm^{-1}$
	$1\ amu = 1.66 \times 10^{-27} kg$

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

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

(i) Show that the pressure is a state function for an ideal gas obeying the equation of state 4

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

(ii) State the third law of thermodynamics. Give its application. Why molecules like CO and N_2O have positive value of entropy at zero Kelvin.? 4

(iii) Define Joule-Thomson coefficient. Give its significance. 'Ideal gases do not show Joule-Thomson effect.' Explain. 4

(iv) Write the expression for entropy changes in the following phase transitions 4
i) Melting ii) Vapourisation
iii) Sublimation iv) Allotrpoic transformation

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

(i) A function ϕ is defined as $\phi(x,y) = x^2y^3 + x$ .Write its partial derivatives and total differential. Test whether $d\phi$ is an exact differential or not. 4

(ii) A piece of alloy weighing 2 kg and at a temperature of 500^0C is placed in 4 kg of water at 300K.If the heat capacity of water is $4.184 JK^{-1}g^{-1}$ and that of alloy is $22 JK^{-1}g^{-1}$ Calculate the entropy change. 4

Q.2 a Attempt any two of the following :

(i) What are the characteristics of a wave function to be acceptable? Show that the normalised wave function of a particle in a one dimensional box is given by, 4

$$\varphi_{(n)} = \left(\frac{2}{a}\right)^{1/2} sin\ \left(\frac{n\pi x}{a}\right)$$

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

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

(iii) Obtain an expression for energy of a particle in one dimensional box of length '**a**'. 4

(iv) State the postulates of quantum mechanics. 4

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

(i) The Hermite polynomials are derived from the generating function 4

$$H_{n(y)} = (-1)^n e^{y^2} \frac{d^n}{dy^n}\left(e^{-y^2}\right)$$

Calculate the polynomial for n=1 and n=3

(ii) Calculate the lowest kinetic energy of an electron in a three dimensional box of dimensions 0.001pm, 0.0015pm amd 0.002pm. 4

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

(i) Write the reactions for thermal decomposition of acetaldehyde. Using steady state approximation show that the rate of formation of methane is given by 4

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

(ii) H_2 reacts with Br_2 to give HBr according to the reaction 4

$H_2 + Br_2 \xrightarrow{h\upsilon} 2HBr$. Using the chain reaction mechanism, obtain the rate equation for the above thermal reaction.

(iii) Describe the effect of pressure and temperature on the rate of an explosion reaction with the help of a suitable example. 4

(iv) Give a brief account of the Lindeman-Hinshelwood theory of unimolecular reactions in gas phase. 4

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

(i) The rate of formation of C in the reaction, 4

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

(ii) Consider the following consecutive reaction 4

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

Where k_1 and k_2 are the rate constants for a first order reaction. If the initial concentration of R_1 is 1 M and k_1:k_2 1.0:0.15. Calculate the concentration of each species after 10 seconds. Given $k_1 = 4 \times 10^{-2}$ min^{-1}.

Q.4a Attempt any two of the following :

(i) Derive an equation for the Debye -Huckel limiting law. 4

(ii) State Debye-Huckel-Onsager equation and discuss its validity for aqueous solutions. 4

(iii) With the help of diagram explain the working of solid oxide fuel cell. 4

(iv) Explain Deby-Falkenhagen and wien effect. 4

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

(i) Calculate the mean activity coefficient of (i) NaCl at a molality of 0.01 (ii) Na_2SO_4 at a molality of 0.001 in aqueous solution at 25°C. (Given :A for water at 25° C is 0.509) 4

(ii) Calculate the resting membrane potential for a living cell for the following concentrations of Na^+ and K^+at 298K. 4

Intra cellular concentration of K^+= 410mM Na^+= 40mM

Extra cellular concentration of K^+= 16mM Na^+= 380mM
(given : 2.303RT/ F = 60 at 298K)

Q.5 Attempt any four of the following :

a Explain the determination of absolute entropy with the help of heat capacity concept. 3

b Derive the relation: 3

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

c State Heisenberg's uncertainty principle. An electron moves in the first orbit with a speed of 2 X 10^6 ms^{-1}.If its momentum is measured with a accuracy of 1 %, what is uncertainty of position? 3

d Give an expression for allowed energy levels of linear harmonic oscillator. Comment on spacing of energy levels. What is zero point energy? 3

e Explain consecutive reactions with examples. 3

f Give a brief account of Rice-Ramsperger-Kassel-Marcus theory. 3

g Write a note on enzyme-catalysed oxidation of styrene. 3

h State any three applications of Alkaline fuel cell. 3
