[Time: 2 ½ Hours] **[Marks:60]**

Please check whether you have got the right question paper.

N.B: १. All questions are compulsory.
२. Figures to the right indicate full marks.
३. Use of non-programmable calculator is allowed.

Useful constants:

$c = 2.998 \times 10^{8}\ ms^{-1}$	$N_A = 6.022 \times 10^{23}\ mol^{-1}$
$h = 6.626 \times 10^{-34}\ Js$	$k = 1.381 \times 10^{-23}\ JK^{-1}$
$e = 1.602 \times 10^{-19}\ C$	$1\ eV = 8.06 \times 10^{3}\ cm^{-1}$
$R = 8.314\ JK^{-1}\ mol^{-1}$	$1\ atmosphere = 1.01325 \times 10^{5}\ Nm^{-2}$
$m_e = 9.11 \times 10^{-31}\ kg$	

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

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

i) State the third law of thermodynamics. How will you determine the absolute entropy of a liquid using third law? **(04)**

ii) Derive an expression for Joule-Thomson coefficient in terms of Van der Waal's constants. **(04)**

iii) What are the characteristics of exact differential? **(04)**

iv) What is standard molar entropy? How does it depends on the molar mass and molecular structure of a substance? **(04)**

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

i) Find the increase in entropy when 1g of ice at – 10˚C is converted to steam at 100˚C. **(04)**
Given : specific heat of ice = 0.5
Latent heat of steam = 540cals/g
Latent heat of fusion = 80cal/g

ii) Calculate the Joule-Thomson coefficient for ammoniac gas at 298K and at 100 atmospheric pressure if the Van der Waal's constant 'a' and 'b' for ammonia are $0.138 Nm^4\ mol^{-2}$ and $3.94 \times 10^{-5} m^3 mol^{-1}$ respectively. Cp for ammonia is $25.99 JK^{-1}\ mol^{-1}$ **(04)**

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

i) State the main postulates of quantum mechanics. **(04)**

ii) Derive an expression for energy of a particle in two dimensional box from Schrodinger wave equation. **(04)**

iii) What do you mean by degeneracy of energy levels? Determine the degree of degeneracy of the energy level $\frac{17h^2}{8ma^2}$ for a particle in a cubical box. **(04)**

iv) For Hermites differential equation, **(04)**

$$\frac{d^2F}{dy^2} - 2y\frac{df}{dy} + \left(\frac{\propto}{\beta} - 1\right) = 0$$

obtain the recursion formula.

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

i) Consider an electron moving in one dimensional box of 2A˚ width. **(04)**
Calculate the transition in energy when an electron jumps from second orbit to first orbit. Also calculate the wavelength of the emitted radiation

ii) If f(x) = $5.e^{-3x}$ and operator $\widehat{A} = \frac{d^2}{dx^2}$, then show that f(x) is an eigen function. Find the eigen value. **(04)**

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

i) Using steady state approximation for the thermal decomposition of acetaldehyde. **(04)**
Show that d/dt $[CH_4] = K [CH_3CHO]^{3/2}$

ii) H_2 reacts with Br_2 to give HBr according to reaction $H_2 + Br_2 \xrightarrow{h\nu} 2HBr$. **(04)**
Using the chain reaction mechanism, obtain the rate equation for the above thermal reaction.

iii) Discuss the various factors affecting the rate of a non-stationary chain reaction and occurrence of three explosion limits using suitable example. **(04)**

iv) Give a brief account of Rice-Ramsperger-Kassel theory. **(04)**

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

i) The rate of formation of C in the reaction, 2A+B→ 2C + 3D is 2 mol $L^{-1}s^{-1}$. State the reaction rate and the rates of formation or consumption of A,B and D **(04)**

ii) Consider the following consecutive reaction **(04)**

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

where k_1 and k_2 are the rate constants for a first order reaction. If the initial concentration of R_l is 1 M and $k_l : k_2 = 1.0 : 0.15$, calculate the concentration of each species after 10 seconds. Given: $k_l = 6 \times 10^{-2}$ min^{-1}

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

i) Write Debye-Huckel and Onsager equation and show that at infinite dilution, Λ_m approaches to Λ°_m. **(04)**

ii) State Debye-Huckel theory for strong electrolytes and explain the term asymmetry effect. **(04)**

iii) Derive an equation of mean ionic activity coefficient and ionic strength for strong electrolytes. **(04)**

iv) Illustrate the construction and working of phosphoric acid fuel cell. **(04)**

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

i) Calculate the activity coefficient of Cu^{2+} and NO_3^- ions in 2.5 x 10^{-3}M aqueous solution of $Cu(NO_3)_2$. Using these values, calculate the mean ionic activity coefficient and the mean ionic concentrations. (Given, A = 0.509 at 298K) **(04)**

ii) Calculate the Nernst equilibrium potential for each of the following ions at 293 k **(04)**

	Ionic concentrations inside cell	Ionic concentrations outside cell
1) Calcium	0.009mm	10mm
2) Chloride	56mm	550mm.

(Given; R = 8.315 joules K^{-1} mol^{-1}, F = 96485 Joules $volt^{-1}$ mol^{-1})

Q. 5 Attempt **any four** of the following: **(12)**

a) For one mole of an ideal gas, PV = RT. Show that dP is an exact differential.
b) Explain the concept of residual entropy with a suitable example.
c) Give the limitations of quantum mechanics.
d) Show that eigen values of a Hermitian operator are real.
e) Explain the principle of microscopic reversibility.
f) Explain consecutive reactions with suitable examples.
g) Write a note on theory of membrane potentials and interfacial electron transfer in biological system.
h) With suitable examples, explain the uses of enzyme as an electrode.

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