

[Time: 2 $\frac{1}{2}$ Hours]

[Marks: 60]

Please check whether you have got the right question paper.

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

Useful constants

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

$$R = 8.314 \text{ J.K}^{-1} \text{ mol}^{-1}$$
$$= 2.0 \text{ cal.mol}^{-1} \text{ .K}^{-1}$$

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

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

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

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

$$k = 1.3811 \times 10^{-23} \text{ JK}^{-1}$$

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

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

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

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

- i) What are the characteristics of entropy? Which molecule of the pair given below has greater molar entropy under same conditions & Why?
 $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{COOH}$ 4

- ii) Starting with van der waal's equation show that $\mu_{J.T} = \frac{1}{C_P} \left(\frac{2a}{RT} - b \right)$
where the terms have usual meaning. 4

- iii) Using Maxwell's relation prove that 4

$$\left(\frac{\delta C_P}{\delta P} \right) = \left(\frac{\delta^2 S}{\delta T \delta P} \right) = -T \left(\frac{\delta^2 V}{\delta T^2} \right)_P$$

- iv) Define and discuss Joule - Thomson coefficient. What happens when various gases are subjected to Joule-Thomson experiment? 4

B) Attempt any one of the following :

- i) Calculate the change in entropy in transforming 24g of ice into water at 0°C . Molar heat of fusion = 6.000 kJmol^{-1} and enthalpy change for transition of one mole of liquid water to steam at 373K is 40.8 kJmol^{-1} . 4

- ii) Calculate the inversion temperature for CO gas using van der waal's constants. 4
 $a = 150.5 \times 10^{-3} \text{ Nm}^4 \text{ mol}^{-2}$ and $b = 3.985 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$

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

- i) Define operator. Prove the commutative property of an operator with a suitable example. 4

- ii) What is meant by normalization of wave function? Normalise the following wave function. 4

$$\psi = A \sin \frac{n\pi x}{L} \text{ in the limit zero to } L$$

- iii) Derive the time independent Schrodinger wave equation from Schrodinger's time dependent wave equation. 4

- iv) What is linear harmonic oscillator? Derive Hermite equation for one dimensional simple harmonic oscillator 4

B) Attempt any one of the following :

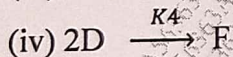
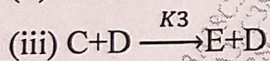
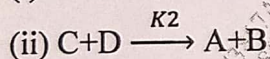
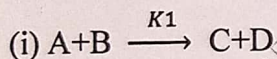
- i) A particle of mass 9×10^{-31} kg is confined in one dimensional box of width 1×10^{-10} m. Calculate the ground state and first excited state energy level in eV. Comment whether the energy levels are quantized. 4
- ii) Which of the following functions are eigen functions for the operator $\frac{d^2}{dx^2}$ a) e^{-4x} b) $3\sin 4x$ 4

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

- i) Show that the rate of polymerization reaction is proportional to square root of its initial concentration of the monomer. 4
- ii) Write the reaction mechanism for the decomposition of acetaldehyde and using steady state principle show that $\frac{d}{dt} [CH_4] = k[CH_3CHO]^{3/2}$ 4
- iii) Discuss Hinshelwood theory of unimolecular reaction. 4
- iv) H_2 reacts with Br_2 to give HBr according to the reactions $H_2 + Br_2 \xrightarrow{205-302^\circ C} 2HBr$. Using the chain reaction mechanism, obtain rate equation for the above thermal reaction. 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 4



- ii) Isopropyl benzene is alkylated by n-butylamine in presence of hydrogen fluoride in a two step consecutive reactions as Isopropyl benzene (A) $\xrightarrow{k_1}$ Isopropyl-sec butylbenzene (B) $\xrightarrow{k_2}$ Isopropyl-di-sec butyl benzene min^{-1} (C). If the initial concentration of isopropyl benzene is 100M and the values of $k_1 = 4.0 \times 10^{-2} \text{ min}^{-1}$ and $k_2 = 4.0 \times 10^{-3} \text{ min}^{-1}$. Find the concentration of each species at the end of 20 minutes. 4

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

- i) State Debye-Huckel-Onsagers equation. Explain the two types of deviations from the equation. 4
- ii) Explain the Debye-Falkenhagen effect for the conductance of strong electrolytes and show that the wavelength for the effect to occur must be about 20 m or less. 4
- iii) Explain the construction and working of the phosphoric acid fuel cell. 4
- iv) Explain the process of adsorption of proteins onto metal surfaces from solution. 4

B) Attempt any one of the following :

- i) Calculate the mean ionic activity coefficient of $ZnCl_2$ in a solution containing 0.05m $ZnCl_2$ and 0.05m $NaCl$ at 298K. (A = 0.509 at 298 K) 4

ii) Calculate the resting membrane potential for the following :

4

Ion Species	Intra Cellular Conc in mM	Extra Cellular Conc in mM
K ⁺	410	10
Na ⁺	49	460

Given that $2.303 RT/F=60$ at 298K

Q.5 Attempt any five of the following :

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a) Derive the Maxwell relation

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_v$$

b) Write a note on third law of thermodynamics

c) Find the degenerate and non-degenerate energy levels for a cubical box from the following

$$E = \frac{6h^2}{8ma^2}, E = \frac{9h^2}{8ma^2}, E = \frac{12h^2}{8ma^2}$$

d) State the main postulates of quantum mechanics.

e) Explain the term consecutive reaction with suitable example.

f) Explain three explosion limits of H₂ and O₂ reaction.

g) Write a short note on the electrochemical enzyme – catalyzed oxidation of Styrene.

h) Explain any three applications of fuel cells.
