Time: $2^{1/2}$hrs   **[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

$c = 2.998 \times 10^8$ m.s^{-1} $e = 1.602 \times 10^{-19}$ C

$R = 8.314$ J.K^{-1} mol^{-1}= 2.0 cal..K^{-1}mol^{-1} $k = 1.3811 \times 10^{-23}$ JK^{-1}

$h = 6.626 \times 10^{-34}$Js $1J = 6.24 \times 10^{18}$eV

$m_e = 9.110 \times 10^{-31}$ kg $leV = 8.06 \times 10^3$ cm-1

$N_A = 6.022 \times 10^{23}$ mol^{-1} $1amu = 1.66 \times 10^{-27}$ kg

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

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

i) Separate the following Schrodinger equation into two equations each with a single variable in it.   **04**

$$\frac{\partial^2 \psi}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta}\frac{\partial \psi}{\partial \theta} + \frac{1}{\sin^2 \theta}\frac{\partial^2 \psi}{\partial \theta^2} + \frac{8\pi^2 m r^2}{h^2} E\psi = 0 \text{ where } \psi \text{ is } \psi(\theta, \phi).$$

ii) Explain why hydrogen like atoms represent a two particle problem. Write the Hamiltonian operator for it. What are "coordinates of center of mass" and "relative coordinates"? Why are they necessary?   **04**

iii) What are spherical harmonics? Write its expression in terms of Θ and ψ.Give the significance of spherical harmonics.   **04**

iv) Write the secular determinant for Buta-1,3-diene molecule. Indicate HOMO, LUMO and the energy levels.   **04**

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

i) The approximate energy of a system is given by E= K^2 + 2K -5 where K is a variational parameter. What value of K leads to the lowest energy and what is the value of minimum energy?   **04**

ii) Considering NO molecule as a rigid rotator rotating freely in three dimensional space, calculate the rotational energy for first two energy levels.   **04**
.

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

i) What is partial molal volume? How is evaluated by intercept method. **04**

ii) Derive thermodynamically the Kelvin equation of vapour pressure of droplets. **04**

iii) What is ATP? How is it synthesize from ADP? **04**

iv) How will you determine fugacity from equation of states? **04**

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

i) Calculate ΔG_{mix} and ΔH_{mix} at 25^0C and 1 atmospheric pressure when 10 moles of helium gas is mixed with 10 moles of neon gas. **04**

ii) The partial molal volume of methanol-water solution containing 0.61 mole fraction of water is 17.2 cm^3 mol^{-1}.The density of the solution is 0.92 gcm^{-3}. Calculate the partial molal volume of methanol in solution. **04**

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

(i) Derive the parabolic rate law equation for the reaction of a gas on the surface of solid particles. **04**

(ii) Obtain Lineweaver-Burk equation for the reaction catalysed by enzymes. **04**

(iii) Explain the kinetics of enzyme inhibition action by competitive inhibition method. **04**

(iv) Derive a mathematical relation between rate constant and dielectric constant of a medium for elementary reaction in a solution. **04**

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

(i) The following data have been obtained for the enzyme catalysed reaction:

[S] mol dm^{-3}	Rate, R mol $dm^{-3}s^{-1}$
3.5×10^{-4}	3.7×10^{-4}
7.0×10^{-3}	1.23×10^{-3}

Using Michaelis-Menten's equation, calculate the Michaelis constant K_m and the limiting rate V. **04**

(ii) Predict the effect of ionic strength on the rate constant for each of the following reactions: **04**

1) $[Co(NH_3)_5 Br]^{2+} + Hg^{2+} \longrightarrow$ Product
2) $Fe^{2+} + [Co (C_2O_4)_3]^{3-} \longrightarrow$ Product
3) $S_2O_8^{2-} + I^- \longrightarrow$ Product
4) $CH_3COOC_2H_5 + OH^- \longrightarrow$ Product

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

(i) Derive an equation for vacancy defects in elemental solids **04**

(ii) Draw and discuss the phase diagram of solid-gas system involving **04** formation of amino compounds.

(iii) What is incongruent melting point? Explain the phase diagram of suitable **04** system consisting of incongruent melting point?

(iv) Draw and discuss the phase diagram of a three component system **04** consisting of two pairs of partially miscible liquids.

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

(i) Determine the number of phases, the number of components and degree of freedom of the following systems. **04**

a) $CaCO_{3(S)} \rightleftarrows CaO_{(S)} + CO_{2(g)}$
b) I_2 dissolved in CCl_4

(ii) Calculate the ratio of vacancies in the metal at 627°C and 177°C, if the average energy required to create a vacancy in a metal is 1eV.(Given $K_B = 8.625 \times 10^{-5}$ eV/K.) **04**

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

a) Write only the expression for theta equation, phi equation and R equation.

b) State and explain variation principle.

c) Write the BET equation and explain the terms involved in it

d) What do you understand by thermodynamic excess functions? Write an expression for i) Excess entropy (S^E)   ii) Excess enthalpy(H^E)

e) Write a note on enzyme activation by metal ions.

f) State the comparison between regulatory enzymes and non-regulatory enzymes.

g) Explain the terms   (i) Plait point   (ii) Binodal curve

h) What are point defects? Explain Schottky defects.

---------------------- X --------------------------