(2½ Hours)   **Marks: 75**

N.B.   1) All questions are compulsory.
2) Figures to the right indicate full marks.
3) Use of logarithmic table / non programmable calculator is allowed.

Physical constants:

$N = 6.023 \times 10^{23}$ $\pi = 3.142$
$F = 96500$ C 1 amu $= 931$ MeV $= 1.66 \times 10^{-27}$ kg
$R = 8.314$ JK^{-1} mol^{-1} $\dfrac{2.303RT}{F} = 0.05916$ at 298K

$h = 6.626 \times 10^{-34}$Js $H = 1$ amu
$c = 3 \times 10^{8}$ ms^{-1} $Br = 79.9$ amu

1.   **Attempt any three of the following.**
A)   Show that for an anharmonic oscillator the frequency of fundamental, first and   **5**
second overtone bands are in the ratio of 1:2:3.
B)   Explain zero point energy.   **5**
The vibrational frequency of a molecule is 2.5×10^{5} m^{-1}. Calculate the zero point
energy of the molecule.
C)   Explain the rule of mutual exclusion with the help of CO_2 molecule.   **5**
D)   The frequency separation of successive lines in the rotational spectrum of HBr is 1.72   **5**
$\times 10^{3}$ m^{-1}. Calculate the equilibrium inter-nuclear distance in the molecule.
E)   Answer the following:
  a) Define force constant and explain its significance.   **3**
  b) Explain the structure of H_2O molecule on the basis of dipole moment.   **2**
F)   Explain the Raman effect on the basis of quantum theory.   **5**

2.   **Attempt any three of the following.**
A)   Derive Nernst equation for single electrode potential.   **5**
B)   Define electrode concentration cell and derive an expression for emf of electrode   **5**
concentration cell reversible to anion.
C)   Explain the term, ionic strength.   **5**
Calculate the ionic strength of 0.01 m Aluminium sulphate solution.
D)   Derive an expression for emf of electrolyte concentration cell with transference   **5**
reversible to cation
E)   Calculate the mean activity coefficient of 0.02 m K_2SO_4 solution.   **5**
(A = 0.509 for water at 298 K)
F)   What is liquid junction potential? Explain its origin. How is it eliminated?   **5**

3.   **Attempt any three of the following.**
A)   Derive Clapeyron equation.   **5**
B)   An aqueous solution of a non-volatile solute boils at 373.09 K. Calculate the freezing   **5**
point of the same solution.
(Kb = 0.512 K kg mol^{-1} and Kf = 1.86 K kg mol^{-1})
C)   State the phase rule.   **5**
Explain the meaning of number of phases and number of degree of freedom with
suitable example.
D)   Explain the application of phase rule to water system.   **5**

68525   Page **1** of **3**

E) What is meant by reverse osmosis? State the applications of reverse osmosis. **5**

F) Explain molal elevation constant. **5**

A solution containing 1.5 g of non-volatile solute in 100 g of CCl_4 gave boiling point elevation of 0.75 K. if molal elevation constant is 5.02 K kg mol^{-1}. Calculate the molecular weight of solute.

4. **Attempt any three of the following.**

A) Give the postulates on which Langmuir adsorption isotherm is based. **5**

B) Describe any two methods by which colloids acquire electric charge. **5**

C) Derive Michaelis-Menten equation for enzyme catalysis. **5**

D) Answer the following:

  a) Distinguish between physical adsorption and chemical adsorption **3**

  b) Explain the term inhibitors. **2**

E) Write a note on electro-osmosis. **5**

F) Explain the term surfactant. Explain the use of surfactants in food industry. **5**

5. A) **State whether the following statements are true or false.** **4**

  a) In bending vibrations the bond angle changes.

  b) The minimum value of rotational energy is zero.

  c) For diatomic molecule rotational constant is directly proportional to the moment of inertia.

  d) The vibrational energy levels are equally spaced.

OR

A) **Choose the correct answer.** **4**

  p) ………… are in-plane bending vibrations.

    i) Rocking and twisting

    ii) Rocking and scissoring

    iii) Twisting and wagging

  q) For stokes lines Raman shift is --------.

    i) positive   ii) negative   iii) zero

  r) ---------- is the unit of moment of inertia.

    i) kg m^2 ii) kg m^{-2} iii) kg m

  s) The non-linear molecule like ethane shows …….. fundamental modes of vibrations.

    i) 18   ii) 17   iii) 19

B) **State whether the following statements are true or false.** **4**

  a) In galvanic cell, reduction takes place at left hand electrode.

  b) For an ideal solution activity coefficient is unity.

  c) Metal – metal insoluble salt electrode is reversible to anion.

  d) For 1:1 type electrolyte, molality is equal to its ionic strength.

OR

B) **Match the following:**   **4**

p	$AlCl_3$	i)	$4m^3\gamma^3$
q	Na_2SO_4	ii)	$27\ m^4\gamma^4$
r	$Ca_3(PO_4)_2$	iii)	$6\ m^4\gamma^4$
s	$AgNO_3$	iv)	$108\ m^5\gamma^5$
		v)	$m^2\gamma^2$

C **State whether the following statements are true or false.**   **4**
   a) Osmotic pressure is inversely proportional to volume of solution.
   b) In sulphur system curves are bi-variant.
   c) Phase rule is applicable to homogeneous system.
   d) Lowering of vapour pressure is a colligative property.

<div align="center">OR</div>

C **Choose the correct answer.**   **4**
   p) The number of component for the system, $NH_4Cl_{(s)} \rightarrow NH_4Cl_{(g)}$, is ……..
      i) 2   ii) 1   iii) 3
   q) Sulphur system has …………. triple points.
      i) 3   ii) 2   iii) 4
   r) The relative lowering of vapour pressure is equal to ----------.
      i) mole fraction of solute
      ii) mole fraction of solvent
      iii) both (i) and (ii)

   s) The freezing point of solvent ---------, on addition of non-volatile solute.
      i) increases
      ii) decreases
      iii) remain constant

D **State whether the following statements are true or false.**   **3**
   a) A catalyst lowers the energy of activation of reaction.
   b) In Helmholtz model the adsorbed layer of ions is fixed whereas the oppositely
      charged layer in the dispersion medium is mobile.
   c) The catalyst poisons reduce the catalytic activity of the catalyst.

<div align="center">OR</div>

D **Choose the correct answer.**   **3**
   p) Lyophilic sols are ---------.
      i) solvent loving   ii) solvent hating   iii) none
   q) ---------- increase the catalytic activity of the catalyst.
      i) Promoters   ii) Inhibitors   iii) Catalyst poisons

   r) Adsorption is an ---------- process.
      i) exothermic   ii) endothermic   iii) adiabatic

<div align="center">----------------------------</div>