(**2 ¹/₂ Hours**)   Marks : **75**

NB : (1) **All** questions are **compulsory.**
       (2) **Figures** to the **right** indicate full **marks**.
       (3) Use of log tables/ non-programmable calculator is allowed

1.   Physical constants

N_A = 6.022×10^{23} mol^{-1} 1 amu   = 1.66×10^{-27} kg

F   =   96500 C $\dfrac{2.303 \ RT}{F}$ =   0.0592 at 298 K

R   =   8.314 JK^{-1} mol^{-1}

C   = 3×10^8 m s^{-1} π =   3.142

k   = 1.38×10^{-23} K^{-1} h   = 6.626×10^{-34} Js

H   =   1 amu   Br   =   80 amu

C   =   10 amu   0   =   10 amu

1.   Attempt **any three** of the following :

(A)   Define dipole moment. Explain with the help of suitable examples, how it is   **5**
       used to differentiate (i)   cis and trans isomers (ii)   O, m and P isomers

(B)   Justify the statement - " The vibration of CO_2 which are Raman active are IR   **5**
       inactive and vice-versa".

(C)   Derive an expression for wave number of R-branch lines in vibrational rota-   **5**
       tional spectra. Mention the transitions that give rise to R_0, R_1, R_2 and R_3 lines in
       the spectrum, also qualitatively sketch them.

(D)   Explain (i) Raman Shift   (ii)   Stoke's lines   (iii)   Antistokes lines   **5**
        (iv)   Rayleigh scattering.

(E)   In the IR spectrum of HBr, the absorption maxima was observed at 37.6 nm.   **5**
       Calculate the force constant of the bond between HBr.

(F)   The frequency difference between successive lines in the rotational spectra is   **5**
       2.12×10^2 m^{-1} for a diatomic molecule as a perfect rotor. Calculate rotational
       constant, moment of inertia and frequency of first and second absorption in
       m^{-1} for the molecule.

[TURN OVER

2. Attempt **any three** of the following :

(A) Answer the following with respect to given ion specific electrodes. **5**

     (a) $Ag_{-(s)} AgCl_{(s)} | Cl^-_{(aq)}$ (b) $Pt | Fe^{2+}, Fe^{3+}_{aq}$
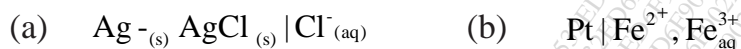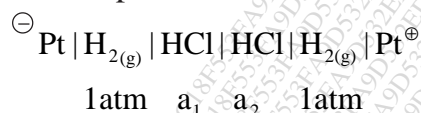
    (i) Classify the electrode   (ii) Write the electrode reaction
    (iii) Say , which ion it is reversible to ?
    (iv) Write the expression for the single electrode potential.

(B) Device and derive an expression for emf of electrolyte concentration cell with- **5** out transference reversible to anion.

(C) Derive an expression for emf of following cell **5**

$$^{\ominus}Pt | H_{2(g)} | HCl | HCl | H_{2(g)} | Pt^{\oplus}$$
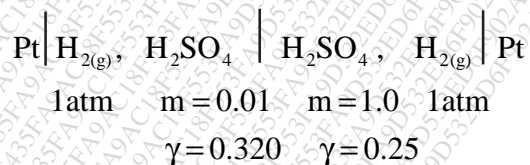
         1atm a_1 a_2 1atm

(D) Answer the following :
    (i) Distinguish between chemical and concentration cells. **3**
    (ii) Derive expression for activity of $Al_2(SO_4)_3$ **2**

(E) Calculate the mean activity coefficient of 0.01m NaCl in 0.001m Na_2SO_4 **5** (A = 0.509 at 298K for water)

(F) The emf of the cell **5**

$$Pt \Big| H_{2(g)}, \; H_2SO_4 \; \Big| \; H_2SO_4, \; H_{2(g)} \Big| Pt$$

    1atm   m = 0.01   m = 1.0   1atm
         $\gamma = 0.320$ $\gamma = 0.25$

0.060 V at 298 K. Calculate the transport numbers of both the ions under transfer of 1 Faraday.

3. Attempt **any three** of the following :

(A) Derive the integrated form of Clapeyron-Clausius equation. **5**

(B) A solutions containing 0.512 g of solute 'A' (mol.wt =128) in 50g of carbon **5** terta chloride shows boiling point elevation of 0.402K. Another solution of 0.622 g of solute 'B' in the same weight of solvent gives a boiling point elevation of 0.647 K. Find the molecular weight of of the solute B.

[TURN OVER

(C) Derive thermodynamically the relationship between the boiling point **5** elevation of a solution and the mole fraction of the dissolved solute.

(D) Explain the phase diagram of lead-silver system. **5**

(E) Answer the following with respect to sulphur system.
   (i) Draw the phase diagram and identify the curves, area and triple points. **3**
   (ii) Apply the phase rule to the area and triple points. **2**

(F) Draw and explain the phase diagram for a mixture of three liquids, one pair of **5** which is partially miscible.

4. Attempt **any three** of the following :
   (A) Give the postutates of BET equation. State the equation and identify the terms **5** involved in it.

   (B) Differentiate between physical adsorption and chemical adsorption. **5**

   (C) The adsorption coefficient of a gas according to Langmuir adsorption isotherm **5** is 0.85 kPa^{-1}. Calculate the pressure (kPa) required for 15% coverage.

   (D) For a general acid catalysed reaction show that rate of reaction is directly pro- **5** portional to the concentration of the acid catalyst.

   (E) What is meant by electro-osmosis ? Explain how the phenomenon of electro- **5** osmosis can be observed experimentally.

   (F) Prove "The distribution of diffusible ions across a semipermeable membrane **5** is affected by presence of non-diffusible ion"

5. Answer the following :
   (A) State whether the following statement is True or False. **4**
      (a) Rotational spectra is not observed for homopolar molecules.
      (b) Greater the value of force constant greater is the bond length
      (c) The O-D bond absorbs at a lower frequency as compared to O-H bond.
      (d) Water is used as solvent to obtain IR spectra because it does not show absorption in IR region.

OR

[TURN OVER

(A) Match the following columns.   **4**

A	B
Molecules	Vibrational Degree of freedom
NH_3	7
HCl	6
C_2H_2	3
H_2S	1

(B) State whether the following statement is True or False.   **4**
   (a) The net electrical work done by a cell is characterised by increase in free energy.
   (b) The single electrode potential depends on temperature of the system.
   (c) In galvanic cells oxidation takes place at cathode.
   (d) Activities of pure solids, insoluble solids and pure gas under unit atmosphere pressure are taken as unity.

OR

(B) Choose the correct answer :   **4**
   (p) The electrode $Pb_{(s)}$-$PbSO_{4(s)}$ | $SO^{2-}_{4\,aq}$
       (i) Reversible to cation (ii) Reversible to anion
       (iii) Reversible to cation as well as anion.

   (q) $Pt, H_2(g)|HCl|AgCl_{(s)} - Ag_{(s)}$

       The above cell is
           (i)   Chemical cell without transference
           (ii) Concentration cell
           (iii) Chemical cell with transference.

   (r) The reduction potential for $Zn|Zn^{2+}$ a = 0.001 m
       $E^0_{zn|zn2+}$ = -0.76 v is
       (i) 0.671 V   (ii) -0.671 V   (iii) -0.848 V

   (s) Salt bridge is used to
           (i)   Eliminate junction potential
           (ii) Connect two half cells electrolytically
           (iii) Both i and ii are true

[TURN OVER

(C) Choose the correct answer : **4**
  (a) If the boiling point of 2.5m glucose solution (mol.wt 180) in water is 101.3^{0}C, the molal elevation constant of water is
    (i) 3.25 (ii) 0.52 (iii) 5.2

  (b) The relative lowering of vapour pressure is
    (i) dependent on nature of solvent
    (ii) dependent on temperature of solvent
    (iii) depends on mole fraction of solute.

  (c) osmotic pressure is
    (i) directly proportiomnal to the volume of the solutions
    (ii) inversely proportional to the temperature
    (iii) directly proportional to the concentration of the solution

  (d) Decomposition of CaCO$_3$ in a closed vessel is
    (i) two component system
    (ii) one component system
    (iii) three component system

OR

(C) State whether the following statement is True or False. **4**
  (p) Mixture of oxygen, nitrogen and hydrogen will form three phases.
  (q) Saturated solution of salt is two phase system.
  (r) Two phases are formed in the system

$$CuSO_4.5H_2O \rightleftharpoons CuSO_4 \; 3H_{2(s)}O + H_2O$$

  (s) Heating NH$_4$Cl in closed vessel is one component system.

(D) Choose the correct answer : **3**
  (a) At CMC ,the surfactant molecules ---------
    (i) decompose (ii) dissociate (iii) associate
  (b) In adsorption of SO$_2$ gas on activated charcoal, the charcoal serves as -----------
    (i) adsorbate (ii) adsorbent (iii) catalyst
  (c) Freundlich adsorption isothern is given by----------

    (i)   (ii) $\dfrac{x}{m} = \log K + \dfrac{1}{n} \log P$

    (iii) $\log \dfrac{x}{m} = \log K + n \log P$

OR   **[TURN OVER**

(D) State whether the following statement is True or False.   **3**

  (p) Fog is a colloidal system of liquid in gas

  (q) Catalyst can initiate a reaction.

  (r) k_m is Michealis constant in enzyme catalysis.