Q.P. Code : 77098

(2½ Hours) **[Total Marks : 75**

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

Physical constants :–

N	=	6.023×10^{23}	Mass of electron	=	9.109×10^{-31} kg
F	=	96500 C	π	=	3.142
R	=	8.314 J K^{-1} mol^{-1}	H	=	1 amu
h	=	6.626×10^{-34} Js	Cl	=	35.5 amu
c	=	3×10^{8} ms^{-1}	I	=	127 amu
$\frac{2.303\ RT}{F}$	at 298K	= 0.05916	1 amu	=	1.66×10^{-27} kg

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

(A) What is the origin of dipole moment ? Explain the structure of BF_3 and NH_3 on the basis of dipole moment. **5**

(B) Considering diatomic molecule as a rigid rotor, show its moment of inertia is related to the reduced mass μ of the system rotating at a distance 'r' from the axis of rotation. **5**

(C) With respect to P-branch lines in vibrational rotational spectra, answer the following : **5**
(i) Derive the expression for its wave number.
(ii) State the expression for the spacing between two each successive lines.
(iii) Qualitatively sketch the P-brach lines for first four transitions and name them.

(D) State the 'Rule of Mutual exclusion'. Giving reason predict, which mode/s are IR active and which one/s are Raman active in CO_2 molecule. **5**

(E) Define zero point energy. The force constant of the bond in HCl molecule is 482.0 Nm^{-1}. Calculate the zero point energy. **5**

(F) The equilibrium internuclear distance in the molecule of HI is 160 pm. Calculate the spacing between two successive lines in pure rotational spectrum. **5**

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

(A) Name the different types of ion-specific electrodes. Discuss any three of them with reference to. 5

(a) Formation of the electrode.
(b) Electrode reaction.
(c) Nernst expression for its electrode potential.

(B) Derive an expression for emf of the following cell at 298K. 5

$$\ominus\ Pt, H_2(g)\ (1\ bar)\ |\ HCl\ (m_1, \gamma_1)\ |\ HCl\ (m_2, \gamma_2)\ |\ H_2(g)\ (1\ bar), Pt\ \oplus$$

(C) What is meant by electrode concentration cells ? Derive an expression for emf of electrode concentration cell reversible to anion. 5

(D) (i) Distinguish between chemical cells and concentration cells. 5
(ii) Derive an expression for emf of electrolyte concentration cell without transference reversible to cation.

(E) Answer the following with respect to the given cell reaction. 5

$$Cd_{(s)} + 2Ag^{+}_{(a=0.1\,m)} \longrightarrow Cd^{2+}_{(a=0.1m)} + 2Ag_{(s)}$$

(a) Represent the cell.
(b) Write the electrode reactions.
(c) Calculate the emf of the cell at 310K. $E^{o}_{cell} = 1.202V$

(F) Calculate the mean activity coefficient of 0.01m HCl in 0.001 m $CaCl_2$ 5
(A = 0.509 at 298 K for water)

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

(A) Explain the term 'Reverse Osmosis'. Mention any four applications of it. 5

(B) A solute weighing 0.650g was added to 50mL of benzene. The freezing point of benzene was lowered from 6.51°C to 5.03°C on addition of the solute. Calculate the molar mass of the solute. K_f for benzene = 5.12 K kg mol^{-1}, density of benzene = 0.800 g/ml 5

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(C) Thermodynamically derive Clapeyron equation for the following equilibria. 5
solid ⇌ liquid

(D) Draw a well labelled phase diagram of water system. Describe the phase diagram by applying phase rule. 5

(E) What is 'Eutectic Point' ? Construct a detailed phase diagram of lead-silver system and explain it. 5

(F) State the phase rule and explain the meaning of the terms in it with suitable example. 5

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

(A) (i) What is meant by :- 2
(a) Heat of Adsorption
(b) Adsorption isotherm

(ii) To what form is the langmuir adsorption isotherm reduces at 3
(a) low pressure
(b) high pressure
(c) moderate pressure

(B) Explain the origin of charge on colloidal particles. 5

(C) (i) State the BET equation. 2

(ii) Adsorption of nitrogen on a silica gel was studied at 90.2K. Amount of nitrogen gas adsorbed per gram of the adsorbent to completely cover the surface by a monolayer is 3.3×10^{-4} mol. Assuming the gas molecules adsorbed in the first layer are closely packed, calculate the surface area of the adsorbent, Moleculare area of nitrogen is 16.2×10^{-20} m^2. 3

(D) What is meant by enzyme catalysis ? Derive Michaelis - Menten equation. 5

(E) What is electro-osmosis ? How is it demonstrated with the help of experiment. 5

(F) Name and explain the different types of surfactants. 5

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5. (A) Choose the correct answer :- 4

(a) Which of the following molecule will undergo rotational transition when microwave radiations are incident on it.

(i) CH_4 (ii) H_2O (iii) C_6H_6

(b) The number vibrational degrees of freedom for benzene is

(i) 12 (ii) 30 (iii) 31

(c) In which of the molecule C=C stretching is IR active.

(i) $CH_2 = CH_2$ (ii) $CH_3 = CH_3$ (iii) $CH_3 - CCl_3$

(d) The value of rotational constant B is 192 m^{-1} in $^{12}C\ ^{16}O$, its value for $^{13}C\ ^{16}O$ is

(i) $194m^{-1}$ (ii) $190m^{-1}$ (iii) $192m^{-1}$

OR

(A) Say true or false. 4

(p) The molecules of CO_2 and SO_2 possess same number of vibrational degree of freedom.

(q) When Raman shift is positive, Stoke's line is observed.

(r) Total degree of freedom in CO_2 molecule is 9.

(s) Greater the value of force constant, greater is the bond length.

(B) Choose the correct answer :- 4

(a) $Pb_{(s)} | PbSO_{4(s)}$, SO_4^{2-} is _____ type of ion-specific electrode.

(i) Metal-Metal insoluble salt electrode

(ii) Redox electrode

(iii) Metal metal ion electrode

(b) As per IUPAC convention, the e.m.f of the cell can be expressed in terms of reduction potential of the anode (E_L) and cathode (E_R) as _____.

(i) $E_{cell} = E_L - E_R$

(ii) $E_{cell} = E_R - E_L$

(iii) $E_{cell} = E_R + E_L$

(c) The number of electrons involved in the following cell reaction are _____.

$3Cl_{2(g)} + 2Al_{(s)} \rightarrow 6Cl^- + 2Al^{3+}$

(i) 2 (ii) 3 (iii) 6

(d) The activity of the electrolyte Na_3PO_4 is given by _____

(i) $4m^3r^3$ (ii) $27m^4r^4$ (iii) $27m^3r^3$

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(B) State true or false :- 4

(p) Saturated solution of KNO_3 is used to make salt bridge.

(q) The ion-specific electrode Ag(s)| AgCl (s), Cl^- is reversible to cation.

(r) For uni-univalent electrolyte, molality is equal to ionic strength.

(s) Anode constitutes the positive terminal in galvanic cells.

(C) Choose the correct answer :- 4

(a) According to Raoults law, the relative lowering of vapour pressure of a solution on adding of solute is _____ .

(i) proportional to vapour pressure of solute.

(ii) proportional to the mole fraction of solvent

(iii) equal to the mole fraction of the solute.

(b) Osmotic pressure of the solution can be decreased by _____ .

(i) decreasing the temperature of the solution.

(ii) increasing concentration of the solution.

(iii) increasing the volume of the vessel.

(c) The number of phases in a closed vessel, partially filled with CCl_4 and H_2O are _____ .

(i) 2 (ii) 1 (iii) 3

(d) The decomposition of $CaCO_3$($CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$) in a closed vessel is an example of _____ component system.

(i) One (ii) Two (iii) Three

OR

(C) State true or false :-

(p) The saturated solution of NaCl constitutes two phases. 4

(q) An eutectic mixture has definite composition and sharp melting point and is regarded as a compound.

(r) Molal depression constant is defined as 'depression of freezing point when one mole of non-volatile solute is dissolved per 1000 mL of the solvent'.

(s) Boiling point of pure water decreases on addition of non-volatile solute.

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(D) Choose the correct answer:- 3

(a) Which of the following system is not a colloidal dispersion.
(i) gas in liquid (ii) Solid in gas (iii) gas in gas

(b) At the critical micelle concentration, the surfactant molecules _____
(i) associate (ii) dissociate (iii) become completely soluble

(c) Presence of a catalyst in a reaction _____ the energy of activation.
(i) lowers (ii) increases (iii) does not affect

OR

(D) State true or false :- 3

(p) The adsorption of gas by a solid is exothermic in nature.
(q) Chemisorption is characterised by formation of multimolecular layers.
(r) Lyophilic sols are more stable than lyophobic sols.

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