

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	=	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	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 successive lines.
- (iii) Qualitatively sketch the P-branch 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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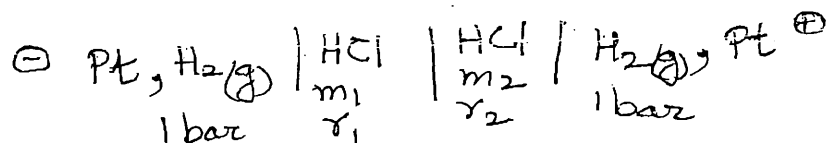
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2. Attempt any **three** of the following :-

(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.

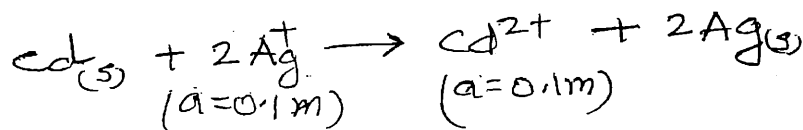
(B) Derive an expression for emf of the following cell at 298K. 5



(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



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

(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. 5
 Calculate the molar mass of the solute. K_f for benzene = 5.12 K kg mol⁻¹,
 density of benzene = 0.800 g/ml

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- (C) Thermodynamically derive Clapeyron equation for the following equilibria. 5
solid \rightleftharpoons 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, Molecular area of nitrogen is 16.2×10^{-20} m². 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 :-

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- (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) $\text{CH}_2 = \text{CH}_2$ (ii) $\text{CH}_3 = \text{CH}_3$ (iii) $\text{CH}_3 - \text{CCl}_3$
- (d) The value of rotational constant B is 192 m^{-1} in $^{12}\text{C } ^{16}\text{O}$, its value for $^{13}\text{C } ^{16}\text{O}$ is
 (i) 194m^{-1} (ii) 190m^{-1} (iii) 192m^{-1}

OR

(A) Say true or false.

- (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.

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(B) Choose the correct answer :-

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- (a) $\text{Pb}_{(s)} | \text{PbSO}_{4(s)}, \text{SO}_4^{2-}$ 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) $E_{\text{cell}} = E_L - E_R$
 (ii) $E_{\text{cell}} = E_R - E_L$
 (iii) $E_{\text{cell}} = E_R + E_L$
- (c) The number of electrons involved in the following cell reaction are _____

$$3\text{Cl}_{2(q)} + 2\text{Al}_{(s)} \rightarrow 6\text{Cl}^- + 2\text{Al}^{3+}$$
 (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) $27m^3r^3$

- (B) State true or false :- 4
- (p) Saturated solution of KNO_3 is used to make salt bridge.
- (q) The ion-specific electrode $\text{Ag(s)}|\text{AgCl(s)}, \text{Cl}^-$ 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 Raoult's 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 ($\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$) in a closed vessel is an example of _____ component system.
- (i) One (ii) Two (iii) Three

OR

- (C) State true or false :- 4
- (p) The saturated solution of NaCl constitutes two phases.
- (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:-

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- (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 :-

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- (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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