CHEMISTRY
Paper – I

*Time Allowed : **Three** Hours*

*Maximum Marks : **200***

Question Paper Specific Instructions

Please read each of the following instructions carefully before attempting questions :

*There are **EIGHT** questions in all, out of which **FIVE** are to be attempted.*

*Questions no. **1** and **5** are **compulsory**. Out of the remaining **SIX** questions, **THREE** are to be attempted selecting at least **ONE** question from each of the two Sections A and B.*

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

*Answers must be written in **ENGLISH** only.*

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary and indicate the same clearly.

Neat sketches may be drawn, wherever required.

$h = 6{\cdot}626 \times 10^{-34}$ Js

$R = 8{\cdot}314$ JK^{-1} mol^{-1}

$c = 3 \times 10^{8}$ ms^{-1}

$N_A = 6{\cdot}023 \times 10^{23}$ mol^{-1}

$m_e = 9{\cdot}1 \times 10^{-23}$ kg

$k_B = 1{\cdot}38 \times 10^{-23}$ JK^{-1}

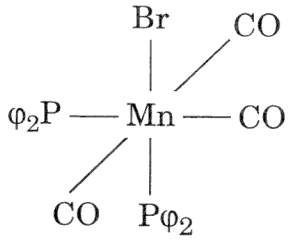
$\pi = 3{\cdot}14$

$F = 96500$ C mol^{-1}

1 atm = 101325 Pa

SECTION A

Q1. (a) (i) Using the internationally accepted naming convention for ligands in an octahedral complex of an element Mn, what name would you give to the following ?



φ is Phenyl group

(ii) Predict the shape of ICl_4^-

Z, Cl = 17

Z, I = 53 *4+4=8*

(b) What oxidant and fuel are generally used in a fuel cell ? Explain the working of Bacon fuel cell. *8*

(c) Explain the effect of temperature on the distribution of molecular velocities. *8*

(d) Deduce Nernst heat theorem and show that this forms the basis of third law of thermodynamics. *8*

(e) Derive Clapeyron equation applicable to sublimation process

$$\log \frac{p_1}{p_2} = -\frac{L}{2{\cdot}303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right],$$

where L is the latent heat per gm-mole. *8*

Q2. (a) Discuss the principle of the following : *4+4+12=20*

(i) Polarography

(ii) Cyclic Voltammetry

(iii) Given a 50·00 mL of an unknown concentration of Zinc solution (taken in a polarographic cell). To this unstirred solution, the following measures of 0·10 M EDTA solution was added. After each increment of EDTA (titrant), the resultant limiting current was measured at – 1·20 V versus SCE.

EDTA (mL) (Titrant)	i_L (mA) (Limiting current)
0·00	0·3
2·0	0·231
4·0	0·167
6·0	0·107
8·0	0·052
10·0	0·0
12·0	0·0
14·0	0·0
16·0	0·0

Z, Zn = 30

Atomic weight 65

(b) (i) A refrigerator working at 50% of ideal efficiency is operating with its interior at 0°C in a room at 25°C. Estimate (I) energy required to freeze 1 kg of water (initially at zero degree Centigrade), and (II) heat discharged into the room during the process (Latent heat of fusion of ice is 334 Jg^{-1}). *4*

(ii) Deduce an expression for the equilibrium constant for an ideal gas reaction. *6*

(c) Describe partial molal quantities. Explain Method of Intercepts for determination of partial molal quantities. *10*

Q3. (a) (i) Define Critical Solution Temperature (CST). Write the degree of freedom (F) for the homogeneous phase of two-component CST system. List three examples of upper consolute temperature system. *12*

(ii) The steam distillation of liquid A (Molar mass, $M_A = 112{\cdot}6$ g . mol^{-1}) is determined to occur at a temperature of 91·3°C when total pressure is 1·0 atm. Calculate the mass of liquid in 100 gm of distillate. The vapour pressure of water at 91·3°C is 539·4 Torr. *8*

(Assume complete miscibility of these liquids and total vapour pressure = 760 Torr.)

(b) (i) Draw hexagonal and cubic close packed systems (assuming that the atoms/ions are spherical in nature). Calculate the packing efficiency and void volume in each case.

(ii) How many kinds of voids are generated in a hexagonal close packed system ? Calculate the maximum size of an atom/ion that can occupy the octahedral and tetrahedral voids in hexagonal close packed system of O^{-2} ions. (Radius of O^{-2} = R)

Explain through diagram. *5+5=10*

(c) (i) Deduce translational partition function. *4*

(ii) Calculate the translational partition function for 1 mol of oxygen at 1 atm pressure at 25°C. Assume the gas to behave ideally (atomic weight of oxygen = 16; $N_A = 6{\cdot}023 \times 10^{23}$ mol^{-1}); $k_B = 1{\cdot}38 \times 10^{-23}$ JK^{-1}; $R = 8{\cdot}314$ JK^{-1} mol^{-1}; and $h = 6{\cdot}626 \times 10^{-34}$ Js). *6*

Q4. (a) (i) Derive the expressions for the critical pressure, critical temperature and critical volume of a Van der Waals gas. *10*

(ii) Deduce an expression for the variation of entropy with temperature at constant volume and pressure. *10*

(b) (i) Which one of the following species would you expect to have the longest bond length ?

A – CN^+

B – CN

C – CN^-

D – NO^+

(ii) How many σ and π bonds are there in tetracyanoethylene molecule ? *5+5=10*

(c) (i) Justify the statement : Instead of being able to describe precise "orbits" of electrons, we can only describe "orbitals". *5*

(ii) Define Hamiltonian Operator. Write the conditions for a physically realistic solution for wave function ψ. *5*

SECTION B

Q5. (a) For multilayer physical adsorption (Type-II), describe Brunauer – Emmett – Teller isotherm. Why is BET isotherm nowadays employed extensively for the determination of surface area ? *8*

(b) Write a brief account on separation of Lanthanides. *8*

(c) The compound with the empirical formula $CsAuCl_3$ is diamagnetic having no metal-to-metal bonds.

(i) Is there gold(II) in the compound ?

(ii) Propose a structure for the compound.

Z, Au = 79 *2+6=8*

(d) Write the photochemical reaction between $H_2 - Cl_2$ and $H_2 - Br_2$ and also write the rate laws. How do you show that the quantum efficiency of $H_2 - Cl_2$ is very low, whereas that of $H_2 - Br_2$ is very high ? *8*

(e) Draw the schematic representation of the mechanism of the function of Cytochrome P– 450 and explain. *8*

Q6. (a) (i) For the reaction of reagent A in solution to give products, the following data were obtained :

t; min	0·0	9·0	12·0	14·0	18·0	20·0	24·0	30·0
log [A]	0·583	0·343	0·257	0·223	0·170	0·133	0·118	0·079

Determine the order of the reaction and calculate the value of the rate constant.

(ii) At 25°C, the second order rate constant for the reaction

$$I^- + ClO^- \longrightarrow IO^- + Cl^-$$

is 0·0606 $M^{-1}s^{-1}$.

If the solution is initially $3{\cdot}50 \times 10^{-3}$ M with respect to each other, what will be the concentration of each species present after 300 s ?

10+10=20

(b) Draw the schematic representation of the mechanism of transport of K^+ by a crown ether type ionophore bearing a carboxylic acid group in the periphery. Explain various stages involved in the process. *10*

(c) What is Lanthanide contraction ? Explain from the atomic radii of + 3 cations, two noticeable differences between the lanthanide and actinide series of ions. *10*

Q7. (a) (i) Define Adsorption isotherm. Using simple model of the solid surface, derive an equation for Langmuir isotherm. What happens to the fraction of adsorption sites occupied by adsorbate (θ) at equilibrium in the low and high pressure limit according to the Langmuir isotherm ? *12*

(ii) The volume of N_2 gas (at STP) needed to cover a sample of silica gel with a monomolecular layer is 122 cc/gm. Calculate the surface area of gel. Each nitrogen molecule occupies $15{\cdot}7\text{Å}^2$. *8*

(b) (i) Give reaction of two compounds containing metal-metal bonds. *5*

(ii) Explain trinuclear clusters and tetranuclear clusters. *5*

(c) How do you interpret the formation of blue colour and bronze coloured phase separation when an alkali is added to liquefied ammonia ? *10*

Q8. (a) (i) State the special properties of HF and show that it is a good non-aqueous solvent. *10*

(ii) Sketch all possible isomers of

$$[Co(NH_3)_2\,(H_2O)_2\,Cl_2]^+.$$ *10*

(b) (i) Explain the difference between trans-influence and trans-effect using appropriate examples.

(ii) Show that all octahedral complexes of nickel(II) must be outer orbital complexes.

Z, Ni = 28 *5+5=10*

(c) Give at least three examples of industrial chemical reactions run in the presence of solid catalysts. Discuss the oxidation of CO on a platinum catalyst.

Why should a good catalyst have moderate values for the enthalpies of adsorption of the reactants ? *10*