वियोज्य *DETACHABLE*

I.F.S. EXAM-2015

0000071

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.

Question 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 answer book 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}
$N_A = 6{\cdot}023 \times 10^{23}$

$k_B = 1{\cdot}38 \times 10^{-23}$ JK^{-1}
$\pi = 3{\cdot}14$
$F = 96500$ C
1 atm. = 101325 Pa

c-geq-o-dina

SECTION 'A'

1.(a) Explain the number of metal-metal bonds in the following molecules which obey 16/18 e rule. Draw their structures

(i) $Fe_3(CO)_{12}$ (crystal)

(ii) $[(\eta^5 - Cp)Fe(CO)(\mu - CO)]_2$

(iii) $[Rh(COD)Cl]_2$ 12

1.(b) Sketch all isomers of $[Co(NH_3)_2(H_2O)_2Cl_2]$ 12

1.(c) Write the name of macrocyclic ligand present in haemoglobin. Explain the coordination of Fe, and its coordinating atoms. Give the importance of the coordination number of Fe and geometry of Fe. 6

1.(d) Write Born-Lande equation for lattice energy of NaCl and explain parameters on which it depends. 10

2.(a) $Co(CO)_4$ and $Mn(CO)_5$ dimerize but $V(CO)_6$ does not. Explain. 10

2.(b) A molecule $Ni(PEtPh_2)_2Br_2$ crystallizes as brown and green crystals. One of them is diamagnetic and other paramagnetic. Explain with the help of crystal field theory. 10

2.(c) For Rubredoxin explain the following :
(1) Metal atom present (2) Its coordination number and geometry (3) Donor atoms surrounding metal (4) Aminoacids to which these donor atoms belong. 12

2.(d) Explain the following :

(i) $[Mn(H_2O)_6]^{2+}$ has a very feeble colour

(ii) CrO_4^{2-} has very intense colour 8

3.(a) For CdI_2 theoretically calculated lattice energy differs significantly from the value of Born-Haber lattice energy. Explain. 8

3.(b) In Zeise salt explain coordination of Pt and bonding of ethylene with Pt. 12

3.(c) In $[Fe(NO)(CN)_5]^{2-}$, $[Co(NO)(en)_2Cl]^{+}$ and $[Ru(NO)(OH)(NO_2)_4]^{2-}$ explain angle (∠)M–N–O if they all follow 18 e rule. 12

3.(d) Complete the following equations :

(i) $[Mn(CO)_5]^- + H_3PO_4 \longrightarrow$

(ii) $Mn_2(CO)_{10} + I_2$

(iii) $RCOMn(CO)_5 \xrightarrow{\Delta}$

(iv) $FeCl_2 + C_5H_5Na \longrightarrow$ 8

4.(a) What is graphene ? Explain bonding in it. 10

4.(b) Define liquid crystals. Give any 3 types of liquid crystal states. 8

4.(c) Write wave function for 1*s* orbital of hydrogen atom. What is the probability of finding electron at a point in a small volume δV ? 8

4.(d) Using crystal field splitting of octahedral complex derive splitting for linear complex having Z axis as molecular axis. 8

4.(e) Write three complexes of Cobalt which follow 18 e rule, using at least two of cyclopentadienyl CO and ethylene as ligands. 6

SECTION 'B'

5.(a) Calculate the root mean square velocity of O_2 at 300 K. 5

5.(b) One mole of an ideal gas undergoes expansion from an initial volume of 2·5 *l* to final volume of 25 *l* against a constant external pressure of 1 atm. at 300 K. Calculate the work done and the change in internal energy. 5

5.(c) Calculate the entropy of mixing when one mole of toluene is mixed with 0·5 mole of benzene at 300 K. Assume the solution to be ideal. 5

5.(d) Calculate the ionic strength of the following solutions :

(i) 0·01 molal $LaCl_3$

(ii) 0·01 molal $CuSO_4$ 5

5.(e) A hydrogen electrode and a standard calomel electrode are combined to give a cell with a potential of 0·340 V at 25°C. Calculate the pH of the solution. What is H^+ activity ? Standard electrode potential of calomel is 0·28 V. 5

5.(f) The following data are obtained for the decomposition of an organic compound. Find the order of the reaction and also the rate constant.

Initial conc. (a_0) M	0·5	1·0	2·0
Half life period(s)	4000	2000	1000

5

5.(g) The photochemical reaction between H_2 and Cl_2 has a quantum yield of 10^5 at a wavelength of 600 nm. Calculate the number of moles of HCl produced per Joule of radiant energy. 5

5.(h) Spontaneous adsorption is always exothermic. Justify the statement. 5

6.(a) Define mean free path. Calculate the mean free path of O_2 at 300 K and 1 atm. pressure. The collision diameter is 3·61 A°. 10

6.(b) What is meant by most probable velocity ? Derive an equation for most probable velocity from Maxwell's distribution of molecular velocities of gases. 10

6.(c) From the following data find the enthalpy of formation of benzene.

$C_6H_{5(l)} + \frac{15}{2} O_{2(g)} \rightarrow 6CO_2 + 3H_2O_{(l)}$ $\Delta H = -3267$ kJ

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393{\cdot}5$ kJ

$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H = -285{\cdot}9$ kJ 10

6.(d) Write equation for translational partition function. Use the equation to find translational contribution towards internal energy. 10

7.(a) (i) Distinguish between molar volume and partial molar volume.

(ii) Define chemical potential in terms of U, H, A & G. 10

7.(b) Two components *A* (melting point 85°C) and *B* (melting point 60°C) form a compound *X* with congruent melting at 100°C having 40 mole% of *B*. There are two eutectic points at 50°C, 25% B and 40°C, 60% B. Construct the phase diagram. Indicate the components and phases at various regions. What is the formula of the compound *X*. (All compositions are reported as mole%). 10

7.(c) Ionic mobilities of K^+ and Cl^- are $7{\cdot}62 \times 10^{-8}$ and $7{\cdot}91 \times 10^{-8}$ $m^2\ V^{-1}\ S^{-1}$. Calculate the specific conductance of 0·01 molar KCl. 10

7.(d) A dilute solution of $CuSO_4$ in water is electrolysed between two Pt electrodes. What are the products of electrolysis ? Write corresponding equations. If a current of 0·800 A is passed for 20 minutes calculate the amount of the products liberated at cathode and anode. 10

8.(a) For two parallel first order reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, derive equations for the concentration of *A*, *B* and *C* as function of time. Represent [*A*], [*B*] and [*C*] graphically. 10

8.(b) Write equation for rate constant of a bimolecular reaction according to Transition State Theory. What is the thermodynamic formulation of this equation ? Compare it with Arrhenius equation of reaction rate and derive equation for enthalpy and entropy of activation. 10

8.(c) Mechanism for a photochemical reaction is given below. Assuming state concentration for A^*, derive the rate law. What is the quantum yield ?

$A \xrightarrow[I]{h\nu} A^*$ (I = intensity of light)

$A^* + A \xrightarrow{k_2} A_2$

$A^* \xrightarrow{k_3} A + h\nu'$ 10

8.(d) (i) Unimolecular surface catalysed gas phase reactions follow first order kinetics at low pressures and zero order kinetics at high pressures. Account for the observation.

(ii) The limiting rate for an enzyme catalysed reaction obeying Michaelis Menton mechanism was 0·02 MS^{-1}. Km (Michaelis Menton constant) was 0·025. The enzyme concentration was 2×10^{-5} M. Find the turn over number. 6+4=10
