I.F.S-2009

No 007471

B-JGT-J-DIA

CHEMISTRY

Paper I

Time Allowed : Three Hours | *Maximum Marks : 200*

INSTRUCTIONS

Candidates should attempt questions 1 and 5 which are compulsory, and any THREE of the remaining questions, selecting at least ONE question from each Section.

The number of marks carried by each question is indicated at the end of the question.

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

Answers must be written in ENGLISH.

Unless otherwise indicated, symbols and notations have their usual meanings.

(Planck's constant h = $6{\cdot}62 \times 10^{-34}$ Js

Boltzmann constant k = $1{\cdot}38 \times 10^{-23}$ J K^{-1}

Electron rest mass m = $9{\cdot}1 \times 10^{-28}$ g)

SECTION A

1. Answer any ***four*** of the following :

(a) Show that free energy change $-\Delta G_{P,T}$ is the total amount of non-mechanical work. *10*

(b) Give a short account of "liquid crystals". *10*

(c) Given the following $E^{\circ}_{Ag,\ AgBr} = -0{\cdot}073$ V,

K for the reaction $Ag + \frac{1}{2} Br_2 \rightleftharpoons AgBr$ is

$6{\cdot}46 \times 10^{16}$ at 25° C, calculate $E^{\circ}_{Br_2,\ Br^-}$.

Write the suitable chemical cell. *10*

(d) Explain the Graham's law of effusion. *10*

(e) Calculate the freezing temperature of water when the pressure is increased by two atm.
($\Delta H_f = 79{\cdot}9$ cal g^{-1}; $\rho_{ice} = 0{\cdot}92$ g cc^{-1};
$\rho_{Hg} = 13{\cdot}6$ g cc^{-1}.) *10*

2. (a) Explain the Maxwell's distribution of molecular velocities and show that

$$dn_c / dc = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} c^2 \ e^{-\frac{mc^2}{2kT}}$$

where 'n' is the number of molecules (of mass 'm') per cc, dn_c / dc is the number of molecules per unit range of velocity, 'c' is the velocity and the rest of the symbols have their usual significance. *20*

(b) Define a unimolecular reaction. Explain unimolecular reaction with the help of collision theory. Guess the order of the following reaction

$$A + B \rightarrow 2C + D.$$ *20*

3. Discuss the "Uncertainty principle" in detail. Show that for a macroscopic body this principle is of no importance. What was Einstein's opinion about this principle ? Discuss. *40*

4. (a) Show that. $H_2 + Br_2 \rightarrow 2\,HBr$ does not have an order of reaction and the formation of HBr inhibits the reaction. *30*

(b) A first order decomposition reaction is characterised by a rate constant 4×10^{-2} min^{-1}. Find out the time required to complete one-third of the reaction. *10*

SECTION B

5. Answer any ***four*** of the following :

(a) Draw electronic configuration, atomic and molecular orbitals of F_2. *10*

(b) Draw the structure of (i) dichromate ion (ii) solid HF. *10*

(c) Explain the 'partition function'. Deduce the 'internal energy' and 'entropy' in terms of partition function. *10*

(d) Explain how the filling of 4f energy level affects the rest of the periodic table. *10*

(e) What is 'relaxation time' ? Explain the 'relaxation method' in the study of rate of reaction. *10*

6. (a) Draw the shapes of various 'd' orbitals and explain as to why they are split in two groups e_g and t_{2g} in an octahedral ligand field. *20*

(b) How do cryoscopic and molar conductivity measurements help in establishing the structure of complexes ? Explain with examples. *20*

7. (a) Discuss the laws of photochemistry. What is meant by "One Einstein" ?

On irradiation with light of 300 nm, propionaldehyde yielded CO. If the rate of formation of CO is $2{\cdot}04 \times 10^{-9}$ moles s^{-1} and intensity of light is 10,000 ergs s^{-1}, calculate the quantum yield of CO. *30*

(b) 5% of energy of a 200 W incandescent lamp emits visible light (λ = 600 nm). How many quanta of light is emitted per second ? *10*

8. (a) What is Born – Haber cycle ? Using a modified form of this cycle explain why Li is as strong a reducing agent as Cs. *20*

(b) Discuss limitations and practical uses of liquid ammonia as non-aqueous solvent. What happens when $^{15}NH_4Cl$ is dissolved in unlabelled liquid NH_3 and the solvent evaporated ? *20*