CSM – 16/19

Chemistry

Paper – I

Time : 3 hours

Full Marks : 300

The figures in the right-hand margin indicate marks.

*Candidates should attempt Q. No. 1 from Section – A and Q. No. 5 from Section – B which are compulsory and any **three** of the remaining questions, selecting at least **one** from each Section.*

SECTION – A

1. Answer any **three** of the following : 20×3 = 60

   (a) Write the electronic configuration of NO and CN. Draw their energy level diagrams and predict magnetic character and bond order.

   (b) What are Walsh diagrams ? Explain with the help of a Walsh diagram that the BeH_2 molecule would have a linear geometry and H_2O molecule would have an angular geometry.

(c) Using the Boltzmann equation for entropy, viz., $S = k \ln W$, where W is the number of microstates corresponding to a given macrostate, calculate the residual entropy of crystalline carbon monoxide.

(d) Calculate the translational partition function for argon atom in a cubical box of side 1 cm_3 at 25°C.

2. Answer the following : 20×3 = 60

(a) According to the Born interpretation, the probability of finding an electron in a volume element $d\tau$ is proportional to $\psi^2 d\tau$:

(i) What is the most probable location of an electron in an H atom in its ground state ?

(ii) What is its most probable distance from the nucleus and why is this different ?

(b) Distinguish between kinetic and thermodynamic control of a reaction ? Is it possible for the activation energy of a

reaction to be negative ? Explain. How can we study the fast reactions by relaxation methods ?

(c) Which oxidizing agent reacts more readily in dilute aqueous solution, perchloric acid or periodic acid ? Give a mechanistic explanation for the difference.

3. Answer the following : $20 \times 3 = 60$

(a) Derive the expression of Schrodinger wave equation for a particle in 3D box of length 'x'. Calculate the number of degeneracy of energy $14h^2/8mx^2$.

(b) Distinguish between kinetic and thermodynamic control of a reaction. How can we study the fast reactions by relaxation methods ?

(c) Give an example with chemical equation for each of the following reactions in liquid ammonia :

(i) Precipitation reaction

(ii) Acid-base reaction

(iii) Redox reaction

(iv) Complex formation reaction

4. Answer the following : $20 \times 3 = 60$

(a) Depending on temperature, RbCl can exist in either the rock-salt or caesium-chloride structure.

(i) What is the coordination number of the cation and anion in each of these structures ?

(ii) In which of these structures will Rb have the larger apparent radius ?

(b) Derive thermodynamically the Gibbs adsorption isotherm for the adsorption of a solute on the surface of a liquid. Derive the Freundlich adsorption isotherm from the Gibbs adsorption isotherm as applied to a gas.

(c) Discuss the nature and consequences of hydrogen bonding. Discuss the importance of hydrogen bonding in sustaining life. Why do H_2O and HF have abnormally high boiling points ?

SECTION – B

5. Answer any **three** of the following : 20×3 = 60

(a) Discuss the Debye-Huckel theory of mean ionic activity coefficients. Derive the Debye-Huckel limiting law equation. How can this equation be verified ?

(b) Discuss the structures of $Cr(CO)_6$, $Re_2(CO)_{10}$ and $Fe_2(CO)_9$. Show that the metal atoms in these carbonyls obey the inert gas rule. Differentiate between terminal CO and bridging CO.

(c) What is lanthanoid contraction ? What are the problems in the separation of lanthanoids from one another ?

(d) Discuss the ion exchange and solvent extraction methods for the separation of lanthanoids.

6. Answer the following : $20 \times 3 = 60$

(a) State and explain the term 'quantum yield'. How do you account for the fact that the quantum yield of the photochemical reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ is low (= 0.01) while that of the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ is very large ($=10^5$) ?

(b) The Racah parameter B is 460 cm^{-1} in $[Co(CN)6]^{3-}$ and 615 cm^{-1} in $[Co(NH_3)6]^{3-}$. Consider the nature of bonding with the two ligands and explain the difference in nephelauxetic effect.

(c) What is hybridization ? What are the important characteristics of hybridization ? What shapes would you expect for the species (a) ClF_3, (b) ICl_4^- and (c) ClO_4^- ?

7. Answer the following : 20×3 = 60

(a) The reaction of sodium carbonate, boron oxide and silicon dioxide gives a borosilicate glass. Explain why the powder diffraction pattern of this product shows no diffraction maxima.

(b) Explain the terms consolute temperature, upper consolute temperature, lower consolute temperature and conjugate solutions and tie line as applied to solubilities of partially miscible liquids. Discuss the variation of mutual miscibility of (i) Aniline-Hexane (ii) Nicotine-Water with variation of temperature.

(c) Write a role on biological fixation of nitrogen.

8. Answer the following : 20×3 = 60

(a) Draw and discuss the phase diagram for ferric chloride-water system. What changes are observed if a solution of ferric chloride is subjected to isothermal evaporation at 50°C ?

(b) Explain the Poisson effect of Hg^{2+} in dissolve water.

(c) Disucss the principle of the following :

(i) Polarography

(ii) Cyclic voltammetry