[This question paper contains 4 printed pages.]

Sr. No. of Question Paper : 5826 **D** **Your Roll No.....**

Unique Paper Code : 217153 / 217181

Name of the Course : **B.Sc. (H) Physics / Mathematics / Mathematical Science**

Name of the Paper : CHEMISTRY CHCT – 101

Semester : I

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **3** questions from **Section A** and **3** questions from **Section B.**
3. Please indicate the section you are attempting by putting a heading and do not intermix the sections.
4. The questions should be numbered in accordance to the number in the question paper.
5. Calculators and log tables may be used.

SECTION A

Attempt **three** *questions in all.*

1. (a) Explain the following :

   (i) Boiling point of $H_2O > NH_3$ while $CH_4 < SiH_4$.

   (ii) PF_5 exists but PH_5 does not.

   (iii) The bond angles in the fluoride of Nitrogen are less than that of its hydride whereas reverse is true for Phosphorous :

   $NF_3 = 102.1°$ $PF_3 = 98°$

   $NH_3 = 107.3°$ $PH_3 = 94°$

   (iv) The order of energy of different d-orbitals in square planar complex is :

   $d_{yz} = d_{zx} < d_{z2} < d_{xy} < d_{x2-y2}$.

P.T.O.

(v) $[Fe(CN)_6]^{3-}$ is a low spin complex whereas $[FeF_6]^{3-}$ is high spin.

(b) In Born-Lande equation what does 'A' (Madelung constant) signify ?

(c) Predict the shapes of ICl_2^-, PCl_4^+, OF_2. (7½,2,3)

2. (a) Calculate the cation to anion ratio for the coordination number 6 in an arrangement in which the cation is in contact with anions but does not push them apart.

(b) Can hypothetical ($NaCl_2$) exist ? Justify your answer.

(c) State Bent's rule. Predict whether H – C – H bond angle in CH_2F_2 is higher or lower than tetrahedral angle.

(d) Draw molecular orbital energy level diagram for O_2. Write its electronic configuration. Comment on its magnetic properties. (2,2,3½,5)

3. (a) Calculate enthalpy of formation, ΔH_f, of MgF_2 from its elements using the following data :

Sublimation energy of magnesium (S) = 146.4 kJ mol^{-1}

Dissociation energy of fluorine (D) = 158.9 kJ mol^{-1}

Ionization enthalpy of Mg (g) to Mg^{2+} (g) (I) = 2184.0 kJ mol^{-1}

Electron gain enthalpy of F (g) to F^- (g) = –334.7 kJ mol^{-1}

Lattice energy of MgF_2 (U_0) = –2922.5 kJ mol^{-1}

(b) Discuss inter- and intra- molecular hydrogen bonding with suitable examples.

(c) How does π bonding affect Δ_0 ?

(d) Differentiate between inert and labile complexes.

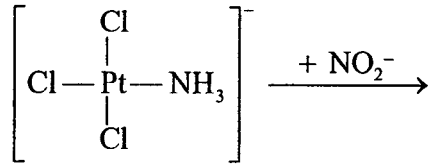
(e) Draw crystal field splitting diagram for octahedral complexes $[CoF_6]^{4-}$ and $[Co(CN)_6]^{3-}$. (2,2,2,2,4½)

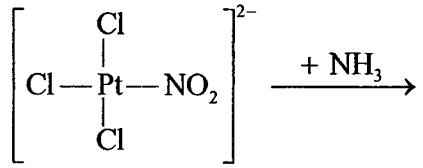
4. (a) What is Jahn-Teller effect ? Describe the conditions which lead to –

(i) A perfectly octahedral complex.

(ii) Strong distortions in octahedral complexes.

(b) On the basis of trans- effect, predict the final product formed in the following reactions :

(i) 

(ii) 

(c) What mechanism will you suggest for the reduction of $[Co(NH_3)_5Cl]^{2+}$ by $[Cr(H_2O)_6]^{2+}$? Can you apply the same mechanism for the reduction of $[Co(NH_3)_6]^{3+}$? Justify your answer.

(d) Differentiate between, thermodynamic stability and kinetic stability giving suitable examples. (4,2,3½,3)

SECTION B

Attempt **three** *questions in all.*

5. Explain why ?

(a) Ethyne is more acidic than ethene.

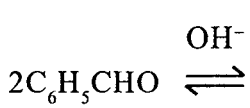
(b) N-methyl aniline is more basic than aniline.

(c) Chair conformation of cyclohexane is more stable than boat conformation.

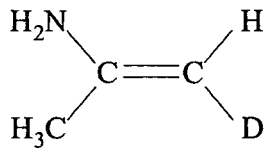
(d) Benzyl carbanion is more stable than t- butyl carbanion.

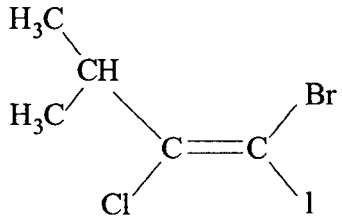
(e) Rate of alkylation of phenol is more than nitrobenzene. (2½×5)

6. (a) Give product/s with mechanism :



(b) Assign E/Z to the following geometrical isomers :

(i) 

(ii) 

(c) Arrange in decreasing order of acidic strength and give reason :
CH_3CH_2OH, CH_3COOH, HCOOH, C_6H_5OH

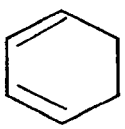
(d) Write all the possible stereoisomers of 2,3-dihydroxybutane and give their relationship with respect to each other. (3,2,3½,4)

7. (a) Write short notes on :
   (i) Natural and synthetic rubber
   (ii) Addition and condensation polymerization

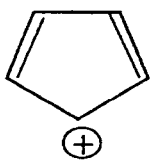
(b) Draw all the possible conformations of n- butane; give their relative stability order with respect to each other.

(c) Arrange the following carbocations in the increasing order of stability, give reason: Methyl carbocation, isopropyl carbocation, t-butyl carbocation.

(d) Which of the following possesses aromaticity and why ?



(i)



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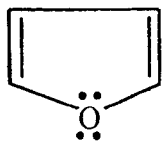
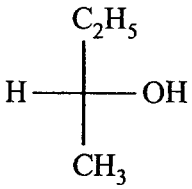


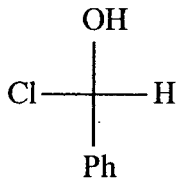
(iii)

(4,3,2½,3)

8. (a) Assign R and S configuration to the following :



(i)



(ii)

(b) Explain :
   (i) Claisen ester condensation.
   (ii) pK_a of benzoic acid is higher than that of m- nitro benzoic acid.

(c) What happens when methyl magnesium bromide is treated with CO_2 followed by hydrolysis ? (4,6,2½)

(1800)