Civil Services (Main) Examination, 2001

CHEMISTRY

(Paper I)

Time Allowed : Three Hours **Maximum Marks : 300**

QUESTION PAPER SPECIFIC INSTRUCTIONS

(Please read each of the following instructions carefully before attempting questions)

There are EIGHT questions divided in two Sections.
Candidate has to attempt FIVE questions in all.
Question Nos. 1 and 5 are compulsory and out of the remaining, any THREE are to be attempted choosing at least ONE question from each Section.
The number of marks carried by a question/part is indicated against it.
Wherever any assumptions are made for answering a question, they must be clearly indicated.
Word limit in questions, wherever specified, should be adhered to.

SECTION 'A'

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

(a) Normalize the wave function $\psi = C\sin n\pi x/L$

(b) Calculate the strength of O-O bond from the following data: $H_2O(g)=2H(g)+O(g)$ $\Delta H_{298}=926.98$ kJ/mol $H_2O_2(g)=2H(g)+2O(g)$ $\Delta H_{298}=1070.6$ kJ/mol

(c) Which of the following are more stable? Explain:- (i) F_2 or F_2^+ (ii) He_2 or He_2^+ (iii) N_2 or N_2^+ (iv) H_2^+ or H_2^-

(d) Calculate the wavelength of X-rays if the reflected angle for NaCl with density 2.163 gm per cc. is 5.9°.

2. (a) Calculate the energy spacing between the first two levels if a particle of mass 10^{-27} gm is moving in a box of length 10 cm. **20**

(b) Calculate the mean activity coefficient of an aqueous solution of 0.001 molality of $BaCl_2$ at 25°C. **20**

(c) How is the standard potential E of a half cell determined? **20**

3. (a) Show that the junction potential of a concentration cell is given by the equation

$$E_J=(1-2t_-)RT/F\ln a_2/a_1$$ **20**

(b) Derive Clapeyron equation and show that it can be represented by the equation

$$P=P^* e^{-(\Delta H_{vap}/R)\{(1/T)-(1/T^*)\}}$$

for liquid-vapour boundary assuming ideal gas behaviour and making certain approximations. **30**

4. (a) Show that the total differential of entropy in terms of temperature and volume can be expressed by the equation

$$dS=C_v/T dT+\alpha/\kappa dV$$ **30**

SECTION 'B'

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

(a) The quantum efficiency for the destruction of a substance with 300 nm light is 0.30. How much time irradiation with 100 W source must continue to destroy one mole of the substance?

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(b) Write B.E.T. adsorption isotherm equation. How is the volume v_m (the volume adsorbed when the solid surface is completely covered by monolayers of the adsorbed gas) determined?

(c) Compare the Valence bond and Molecular orbital theory.

(d) Describe the crystal structures of CsCl and CaF_2.

6. (a) Show that the tetrahedral field splitting is 0.444 times the octahedral field splitting. **20**

(b) Identify the less intense band for each of the following pairs of electronic transitions and explain the reason for the difference in intensities: (i) $[Cr(H_2O)_6]^{3+}$; $^4A_{2g} \rightarrow {}^2A_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ (ii) $[Ni(NH_3)_6]^{2+}$; $^3A_{2g} \rightarrow {}^1T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ **20**

(c) Draw the structures of the metal carbonyls given below: $M_3(CO)_{12}$, $M_4(CO)_{12}$, and $M_6(CO)_{12}$. **20**

7. (a) What product will be obtained if $[PtCl_4]^{2-}$ is treated in the following ways? (i) NH_3 and then by NO_2^- (ii) NO_2^- and then NH_3. **20**

(b) The f^1 ion Ce^{III} is colourless in aqueous solution whereas the d^1 ion Ti^{III} is coloured. Explain. **20**

(c) Cyclopentadiene, C_5H_5 molecule bonds as η^1-C_5H_5, η^4-C_5H_5 or η^5–C_5H_5. Show the various modes of bonding of this molecule giving example. **20**

8. (a) Give the mechanism of electron transfer reactions in Ferredoxin Fe_2S_2. **20**

(b) Complete the following reactions in liquid SO_2 solvent: (i) $SbCl_3 + KI \rightarrow$ (ii) $C_6H_6 + SO_3 \rightarrow$ (iii) $KI + SOCl_2 \rightarrow$ (iv) $SbCl_3 + LiI \rightarrow$ **20**

(c) +3 is the normal oxidation state of lanthanides but Eu^{+2} and Yb^{+2} exist as the most stable species. Explain. **20**

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