[This question paper contains 04 printed pages]

Himachal Pradesh Administrative Service Combined Competitive (Main / Written) Examination, 2020

CHEMISTRY (PAPER-I)

Time allowed: 3 Hours Maximum Marks: 100

QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions.

1. There are EIGHT questions printed in English.
2. Candidate has to attempt FIVE questions in all.
3. Question No.1 is compulsory. Out of the remaining SEVEN questions, FOUR are to be attempted.
4. All questions carry equal marks. The number of marks carried by a question / part is indicated against it.
5. Write answers in legible handwriting. Each part of the question must be answered in sequence and in the same continuation.
6. Unless otherwise mentioned, symbols and notations carry their usual standard meanings.
7. Assume suitable data, if considered necessary, and indicate the same clearly.
8. 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 answer book must be clearly struck off.
9. Re-evaluation / Re-checking of answer book of the candidate is not allowed.

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1. (a) Define chemical shift. Which compound is most commonly used as a reference for its measurement and why? (5)

   (b) Draw the neat and clean Jablonski diagram indicating all the processes. (5)

   (c) Lanthanum exhibits only +3 oxidation state whereas certain other f-block elements also show +2 and +4 oxidation states. Explain. (5)

   (d) What is crystal field theory? On its basis, account for the magnetic properties of $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ complexes. (5)

2. (a) Write down the Planck's expression for energy density of black body radiation based on quantum theory of radiation. Also state and explain Einstein's photoelectric equation. (5)

(b) Draw the ESR spectra of: (5)

(i) 1, 4-benzosemiquinone radical anion and

(ii) $(SO_3)_2NO^-$ anion giving the hyperfine structures.

(c) Derive an expression for Maxwell's distribution of molecular velocities for a gaseous molecule of mass **m** having a velocity component **u**. Also illustrate the effect of temperature on distribution of molecular velocities. (5)

(d) The work differential *dw* is not an exact differential for an ideal gas. Prove it. (5)

3. (a) Draw and discuss the phase diagram for carbon dioxide system. How does this system differ from the water system? (5)

(b) The freezing point depression of a 1/200 molal solution of Na_2SO_4 in H_2O was found to be 0.0265^oC. Calculate the degree of dissociation of the salt at this concentration. (K_f for H_2O is 1.86 K kg mol^{-1}) (5)

(c) Explain in brief flash photolysis and pulse radiolysis. (5)

(d) Define and explain: (5)

(i) Phosphorescence and Fluorescence

(ii) Energy pooling

4. (a) What is Tyndall effect? Give its use in devising the ultra-microscope. (5)

(b) Discuss the Schrodinger wave equation for a particle in 3-dimensional cubical box with edges of length **a** and volume equal to $\mathbf{a^3}$ having the potential zero within the box and infinite outside the box and its boundaries. Also explain the degeneracy of energy levels. (6)

(c) Give the normal modes of vibrations of carbon dioxide and acetylene molecules. Show them pictorially indicating as IR- active and IR-inactive. (4)

(d) At 27^oC, one mole of an ideal mono-atomic gas expands from a volume of 10 dm^3 to a volume of 20 dm^3 reversibly and adiabatically. Assuming C_v = 3/2 R, calculate the values of ΔU and ΔH. (5)

5. (a) Show that for an ideal gas, (5)

(i) $(\partial V/\partial S)_P = nRT/(PC_P)$ and

(ii) $(\partial U/\partial V)_T = 0$

(b) State the Fick's laws of diffusion. Using these laws derive the Ilkovic equation for diffusion current in polarography. (5)

(c) Define the terms K_m and V_{max}. Explain, how are the Lineweaver-Burk plot and Eadie-Hofstee plot used for their determination. (5)

(d) Discuss the absolute reaction rate theory of bimolecular reactions. How can it help in evaluating the standard entropy of activation? Explain. (5)

6. (a) Give the structure of heme group present in myoglobin and haemoglobin. Discuss their role in biological oxygenation. (5)

(b) Write the IUPAC names of the following complexes: (6)

(i) $[Fe(NCCH_3)_6]Br_2$

(ii) $[PtCl(NO_2)(NH_3)_4]SO_4$

(iii) $[Co(NH_3)_5(ONO)]SO_4$

(iv) dextrorotatory $K_3[Ir(C_2O_4)_3$

(v) $[(NH_3)_5Co\text{-}NH_2\text{-}Co(NH_3)_4(H_2O)]Cl_5$

(vi) $[Cr(PPh_3)(CO)_5]$

(c) What is the concept of double quartet? Explain its application in determining the magnetic behaviour of O_2 molecule. (4)

(d) Complete the following reactions by giving the product(s): (5)

$$C_{12}H_{22}O_{11} \xrightarrow{\text{Anh. } H_2SO_4} ?$$

$$6KI + 3SbCl_5 \xrightarrow{\text{liq. } SO_2} ?$$

$$SOCl_2 + Cs_2SO_3 \xrightarrow{\text{liq. } SO_2} ?$$

$$HgI_2 + 2KI \xrightarrow{\text{liq. } SO_2} ?$$

$$Al_2(SO_3)_3 + 3[N(CH_3)_4]_2SO_3 \xrightarrow{\text{liq. } SO_2} ?$$

7. (a) What are the sodium pump and calcium pump in biological systems? Discuss in brief. (4)

(b) Arrange the following species: (6)

(i) $Ni(CO)_4$, $[Fe(CO)_4]^{2-}$ and $[Co(CO)_4]^-$ in terms of decreasing M-C bond order

(ii) $Ni(CO)_4$, $[Fe(CO)_4]^{2-}$ and $[Co(CO)_4]^-$ in terms of increasing C-O bond order

(iii) $[V(CO)_6]^-$, $[Mn(CO)_6]^+$ and $[Cr(CO)_6]$ in terms of increasing $\nu_{CO}(cm^{-1})$

(iv) $[Fe(NO)(CN)_5]^{2-}$, $[V(NO)(CN)_5]^{3-}$, and $[Mn(NO)(CN)_5]^{3-}$ in terms of decreasing $\nu_{NO}{}^{+}(cm^{-1})$

(c) Explain why: (6)

(i) Strong oxidizing agents do not exist in liq. Ammonia
(ii) Solution of alkali metals are coloured in liquid ammonia
(iii) Nitric acid behaves as base in hydrogen fluoride
(iv) Benzene gives conducting solution in liquid hydrogen fluoride

(d) Of the following species, which would have the maximum bond strength? (4)

(i) O_2, O_2^+, O_2^- and O_2^{2-}

(ii) NO, NO^+, NO^{2+} and NO^-

8. (a) Comment upon the structures of the following complexes: (6)

(i) $K^+[PtCl_3(C_2H_4)]^-$

(ii) $CH_3C_6H_4NH_2PtCl_2C_2(t\text{-Bu})2$

(iii) $[C_2Ph_2Pt(PPh_3)_2]$

(iv) $[C_2Ph_2Co_2(CO)_6]$

(b) Draw the molecular orbital energy diagrams of CO_2 and NH_3 molecules. (5)

(c) Discuss the structures of tetracyanonickelate(II) ion and tetrachloronickelate(II) ion on the basis of valence bond theory. (4)

(d) Discuss the use of ion-exchange chromatography for separation of lanthanides. (5)

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