Civil Services (Main) Examination, 2003

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) What are orthonormal wave functions? Normalise the following wave function for a particle in a one-dimensional box $\psi_n(x)=B\sin n\pi x/a$

(b) Define molecular partition function. What is its importance? Calculate the translational contribution to the internal energy of an ideal gas and show that its heat capacity is 3/2 R.

(c) (i) Obtain the expression for the entropy of mixing of two ideal gases with n_1 and n_2 moles respectively at the same temperature and pressure. (ii) What is the entropy of mixing of one mole of oxygen with one mole of nitrogen at 25°C, assuming they are ideal gases?

(d) (i) Write the expression for the activity of 2-1 electrolyte in terms of its molality and mean ionic activity coefficient. (ii) Calculate the activity coefficients γ_+, γ_- and $\gamma_\pm$, and activity for 0.001 molal sodium chloride in water at 25°C. (Take Debye-Huckel constant A=0.509 $kg^{1/2}$ $mol^{-1/2}$)

2. (a) What are concentration cells? Show that the e.m.f. of an anion-reversible cell with transference is: $E=2t_+RT/F\ln a_1/a_2$ **30**

(b) The vapour pressure of water is 23.75 torr at 25°C and 760 torr at 100°C. What will be the heat of vaporisation? **30**

3. (a) (i) What do the indicies of a set of planes passing through the lattice stand for? What is the importance of these planes? Draw two sets of planes viz., 110 and 010, passing through the lattice points of the crystal (ii) What is the perpendicular distance d between 222 planes of a cubic unit cell? **30**

(b) (i) Define "relaxation-time". How is it related to the rate constant of the first-order reaction? (ii) The "relaxation-time" for a reversible first-order reaction is 10 micro second, and the equilibrium constant is 1.0 × 10g [?]. Find K_1 and K_{-1}. **30**

4. (a) Define heterogeneous catalysis. What are the various steps involved in it? Derive the rate equation for the simple surface catalysed reaction involving a single reactant and a single product. **30**

(b) What is residual entropy? Why certain substances like CO and N_2O are associated with residual entropy even at 0K? **30**

SECTION 'B'

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5. Answer any three of the following:

20 × 3 = 60

(a) What do you understand by the term "superacid"? Give two chemical properties to justify this nomenclature.

(b) On doping non-conducting pale-green nickel (II) oxide with a small amount of lithium oxide, not only its colour changes to grey-black but it also becomes a semiconductor. Explain.

(c) A solution of $[Ti(OH)_6]^{3+}$ shows an absorption maximum at 20,300 cm^{-1}. With the help of crystal-field theory, predict the number of absorption bands in the visible spectrum of the above species. Give reason to support your answer.

(d) Write the general expression for filling of electrons in 4f block elements. Justify the statement that 3+ oxidation state dominates the chemistry of lanthanides. Do some members of this series exhibit other oxidation states as well? Explain giving reasons.

6. (a) Discuss the principle of polarographic analysis. What are the advantages of using a dropping mercury electrode over conventional electrodes? Why is it necessary to remove any dissolved oxygen before carrying out voltammetric studies? **20**

(b) What do you understand by an oxidative addition reaction? How does it differ from an insertion reaction? Explain giving two examples of each type supported by chemical equations. **20**

(c) Describe the important structural features of ferrodoxin molecule. What is its role in photo-synthesis? **20**

7. (a) $\mu_{eff.}$ values for the H.S. Fe(II) octahedral complexes are in the range of 5.1-5.7 B.M. while μ_s [?] value is only 4.90 B.M. Why? **20**

(b) Diammine dichloroplatinum (II) exists in two geometrical forms – one of the forms is a well-known anticancer agent. Given that the trans effect of $Cl > NH_3$, outline the steps of preparation of any one of the two isomers. **20**

(c) Draw the MO energy level diagram for CO and discuss the bonding features. **20**

8. (a) Magnetic moment of lanthanides cannot be calculated based only on spin quantum number but by using quantum number J. Explain. **30**

(b) "Ammonium hydroxide is a base in aqueous medium but an acid in liquid ammonia" -Justify this statement using suitable examples. **30**

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