SHP

2010

CHEMISTRY - I (Optional)

100043

Standard : Degree **Total Marks : 200**

Nature : Conventional **Duration : 3 Hours**

Note :

*(i) Answers must be written in **English** only.*

*(ii) Question **No. 1** is **Compulsory.** Of the remaining questions, attempt **any four** selecting one question from **each section.***

*(iii) Figures to the **RIGHT** indicate marks of the respective question.*

(iv) Use of log table, Non-Programmable calculator is permitted, but any other Table / Code / Reference book are not permitted.

(v) Make suitable assumptions, wherever be necessary and state the same.

(vi) Number of optional questions upto the prescribed number in the order in which they have been solved will only be assessed. Excess answers will not be assessed.

(vii) Credit will be given for orderly, concise and effective writing.

(viii) Candidate should not write roll number, any name (including their own), signature, address or any indication of their identity anywhere inside the answer book otherwise he/she will be penalised.

(ix) For each slab of 10 and 15 marks, the examinee is expected to write answers in 125 and 200 words respectively.

Answer ***any Four*** of the following :

(a) What do you understand by structural and stereoisomerism. Explain the ionisation, linkage, ligend and geometrical isomerism with suitable examples. **10**

(b) Draw the structures of the following metal carbonyls and count the number of electrons in them. State whether they follow eighteen electron rule or not. **10**

$Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Co_2(CO)_8$, $Os_3(CO)_{12}$

Atomic Numbers : Mn = 25, Fe = 26, Co = 27, Os = 76

(c) What is a protective colloid? How does a hydrophilic colloid stabilise a hydrophobic one? Give an account of gold-number in this context. Write the difference between gels and emulsions. **10**

P.T.O.

Marks

(d) State the phase rule. Explain the terms involved in it. Discuss the derivation of phase rule from thermodynamic consideration. Explain the phase diagram for water system. 10

(e) How are air pollutants classified? Describe the sources and effects of air pollutants. Discuss the various methods used for waste water treatment. 10

SECTION A

2. Answer the following sub-questions.

(a) (i) Set up and solve the Schrodinger's wave equation for particle in one dimensional box. 5

(ii) What do you mean by Diagonal relationship? Explain the diagonal relationship between lithium and magnesium. 5

(b) Define hybridisation. Discuss the structure of sulphur-hexafluoride molecule considering d^2sp^3 hybridisation. Explain the shape and bonding in ClF_3 with the help of VSEPR theory (Atomic Numbers S=16, Cl=17) 10

(c) Give the methods of preparation, properties and structures of diborane (B_2H_6) and tetrasulphur tetranitride (S_4N_4). 10

(d) Write the elements of first transition series. Discuss the general trends in the properties of first transition series with respect to ionic radii, oxidation states, magnetic behaviour and stereochemistry. 10

3. Answer the following sub-questions

(a) (i) State and explain the Pauli's exclusion principle and Hund's rule of maximum multiplicity with suitable examples. 5

(ii) Discuss the salient features of hydrides, solvation and complexation tendencies of alkaline earth metals. 5

(b) Explain how paramagnetism of oxygen molecule can be accounted by molecular orbital theory whereas valency bond theory predicts it to be dimagnetic. Calculate the bond order in O_2, O_2^+ and O_2^- and $O_2^{-\ -}$
Given-Atomic Number of O = 8. 10

(c) Discuss the basic properties of halogens. What are interhalogen compounds? How are they prepared? Give a brief account of polyhalides. 10

(d) Give the general comparisons of second and third transition series with the first transition series with special reference to radii, oxidation states, aqueous chemistry, M-M bonding and magnetic properties. 10

Marks

SECTION - B

4. Answer the following sub-questions:

(a) Explain the crystal field splitting in tetrahedral complexes with the help of diagram. What are the high-spin and low-spin complexes ? Calculate the CFSE for high-spin d^4 and low-spin d^7 tetrahedral complexes. **10**

(b) Derive the expression **10**

$$\mu_{eff}=2.84\sqrt{X_m^{corr}\cdot T}$$

for the transition metal complexes at the specified temperature. Explain the paramagnetism, ferromagnetism and antiferromagnetism with the help of diagram.

(c) (i) Discuss the electronic spectrum of $[Ti\ (H_2O)_6]^{3+}$. **5**

(ii) What is the lanthanide contraction? What are the causes of lanthanide contraction? Discuss the effect of lanthanide contraction on the lanthanide elements. **5**

(d) Name the actinides in order of their atomic numbers. Write their electronic configurations. Give a brief account of separation of Np, Pu and Am, from U. **10**

5. Answer the following sub-questions.

(a) What do you understand by 10 Dq or Δo ? How is it measured? Discuss the factors affecting the magnitude of 10 Dq or Δo. **10**

(b) Discuss the magnetic properties of transition metal complexes. Write the expression for magnetic moment in terms of spin and orbital quantum numbers. How is it converted to spin only formula? Using this formula, calculate magnetic moment values for $[Mn\ Cl_4]^{2-}$ and $[Co(NH_3)_6]^{3+}$ **10**

Given :- Atomic Numbers : Mn=25, Co=27

(c) (i) Discuss the electronic spectrum of $(V(H_2O)_6)^{3+}$ on the basis of Orgel diagram. **5**

(ii) Describe the ion exchange method for the separation of lanthanides **5**

(d) Discuss the similarities between the actinides and the lanthanides. Explain – actinides have a greater tendency to form complexes than lanthanides. Why do actinides show higher oxidation states than lanthanides. Give reason for the observation that a large number of oxides of actinides are non-stoiochiometric but the same is not true for lanthanides. **10**

Marks

(c) (i) Derive Van't Hoff equation showing he variation of equilibrium constant K with temperature. Also obtain its integrated form **6**

(ii) The equilibrium constant Kp for reaction **4**

$A + B \rightleftharpoons C + D$

is 10^{-12} at 327°C and 10^{-7} at 427°C. Calculate the enthalpy of the reaction. Given $R = 8.314$ J K^{-1} Mol^{-1}.

- o O o -

Marks

SECTION - C

6. Answer the following sub-questions:-

(a) (i) Discuss the Bronsted Lowry theory of acids and bases. Explain the conjugate acid-base pairs with suitable examples. Compare the Bronsted Lowry theory with Arrhenius theory. **5**

(ii) Explain the role of liquid ammonia as a solvent with respect to the following points:- Precipitation reactions, Solvolysis reactions and Acid-base reactions. **5**

(b) (i) Explain the deviation of real gases from ideal gas behaviour. Derive the van der Waal's equation for one mole of a gas. **6**

(ii) Calculate the pressure exerted by one mole of methane (CH_4) in a 250 ml container at 27°C using van der wall's equation. **4**

Given $a = 2.253\ L^2\ atm\ mol^{-2}$ $b = 0.0428\ L\ mol^{-1}$

$R = 0.0821\ L\ atm\ mol^{-1}\ K$

(c) What are liquid crystals ? Give the examples. Classify them according to their molecular arrangements. Discuss their characteristics and applications. **10**

(d) Give the evidence to establish that NaCl has face-centred cubic structure but CsCl has body-centred cubic structure. **10**

7. Answer the following sub-questions:

(a) (i) Explain the Lewis concept of acids and bases. What are the advantages and limitations of Lewis concept? **5**

(ii) Discuss the important reactions of liquid sulphur dioxide as non-aqueous solvent. **5**

(b) (i) Write down the expression for the Maxwell's law of distribution of velocities. Give the significance of the terms involved. Explain the terms average velocity, root mean square velocity and most probable velocity. **6**

(ii) Calculate the average velocity, root mean square velocity and most probable velocity for nitrogen molecule at 27°C. **4**

Given :- $_7N^{14}$

(c) What is poiseulle equation for the viscosity of a liquid? Explain the terms involved in it. What do you mean by coefficient of viscosity. Describe Ostwald's method for determining it. What is the effect of temperature on viscosity of a liquid? **10**

(d) Derive the Bragg's equation for the diffraction of X-rays by crystal lattice. What are the limitations of this method? Discuss the powder method of crystal analysis. **10**

P.T.O.

Marks

SECTION - D

8. Answer the following sub-questions:

(a) (i) Deduce the rate expression for second order reaction where both the concentration terms are same. Explain that half life period depends upon initial concentration of the reactants **11**

(ii) Hydrolysis of ethyl acetate by NaOH using equal concentrations of ester of NaOH, the following results are obtained. **4**

Time t (min)	0	5	15	25
HCl (ml)	16.00	10.24	6.13	4.32

Show that the reaction is of second order.

(b) (i) Show thermodynamically that for an ideal gas, $C_p - C_v = R$ **4**

(ii) Derive the Clausius-Clapeyron equation for the variation of vapour pressure with temperature. **7**

(iii) If the vapour pressures of water at 95°C and 100°C are 634 and 760 mm respectively. Calculate the latent heat of vaporization per mole. **4**

(c) (i) Define equilibrium constant. Show that it can have two different values depending upon how you express concentration. Derive the relationship between these two values. **6**

(ii) The value of Kp at 25°C for the reaction **4**

$2\,NO\,(g) + Cl_2\,(g) \rightleftharpoons 2\,NOCl\,(g)$

is $1.9 \times 10^3\ atm^{-1}$. Calculate the value of k_c at the same temperature.

9. Answer the following sub-questions :

(a) (i) Derive the rate equation for the first order reaction and show that **11**

(m) Half-life is independent of initial concentration

(n) Rate constant is independent of concentration.

(ii) A first order reaction is 1/5 th completed in 40 minutes. Calculate the time required for its 100% completion. **4**

(b) (i) State and Explain Joule Thomson effect **4**

(ii) Derive the expression for entropy change of an ideal gas when **7**

(m) its volume & temperature are changed.

(n) its pressure and temperature are varied.

(iii) Calculate the entropy change involved in thermodynamics expansion of 2 moles of a gas from volume of 5 litres to volume of 50 litres at 30°C. **4**