QTC

2009

CHEMISTRY - I (Optional)

100093

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.*

1. Answer ***any four*** of the following : **(40 marks)**

(a) Calculate the Effective Atomic Number for the diamagnetic complex $[CO(NH_3)_6]Cl_3$. Write the IUPAC name of the complex. Using valence bond theory, show the type of hybridization present in the complex using orbital box diagram and predict its shape (At. No. of CO : 27). **10**

(b) Write the mechanism for the hydrogenation of propylene using homogeneous $RhCl(PPh_3)_3$ catalyst. Indicate the important steps involved in the mechanism. **10**

(c) Write three important molecules involving CO, Mg and Fe in biological processes. **10**

P.T.O.

Marks

(d) (i) State the Gibb's phase rule and explain the terms. For the equilibrium, $Ca\,CO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$, identify the number of phases and number of components. **10**

(ii) Sketch the phase diagram of water. Label the phases present in the areas, along the curves on the diagram. Label the triple point and state the number of degrees of freedom at this point.

(e) (i) What are primary and secondary air pollutants ? Classify H_2SO_4 and CO as primary and secondary pollutants. **10**

(ii) Explain the terms COD and BOD of water.

(iii) What is soil pollution ? Give one example.

SECTION - A

2. Answer the following sub - questions :

(a) (i) State the Heisenberg's uncertainty principle. An electron of mass 9.10×10^{-31} kg moves with a velocity of 2.188×10^{6} m/sec. Calculate the de Broglie wave length of this electron. (Planck's constant $h = 6.62 \times 10^{-34}$ J. sec). **10**

(ii) Explain why and how does lithium resemble magnesium.

(b) Draw the M.O. energy level diagram of NO molecule. Predict the bond order and number of unpaired electrons in the NO molecule. **10**

(c) (i) Draw the shapes of the following molecules indicating the positions of the lone pairs of electrons and also arrange them in the increasing reactivity order. IF_5, IF_7, $Cl\,F_3$, $Br\,F_3$. **10**

(ii) Explain why iodine is almost insoluble in water, but dissolves readily in an aqueous solution of KI.

Marks

(d) Define transition elements and explain how the following properties vary in transition elements ? **10**

(i) Ionic character

(ii) Basic properties

(iii) Stability of various oxidation states

(iv) Ability to form complexes

3. Answer the following sub - questions :

(a) (i) Write all the elements of group I with their outer shell electronic configuration. Arrange them in the order of increasing hydration and ionic mobility with suitable explanation. **10**

(ii) Write the electronic configuration of Fe^{2+} (Atomic No. of Fe = 26). State Pauli's exclusion principle. What is the shape of an 'S' orbital ?

(b) State the Valence Shell Electron Pair Repulsion Theory. The bond angle in NH_3 is 107.3° and that in H_2O is 104.4°. Explain why ? Discuss the hybridization and shape of SF_4 and $Cl\ F_3$. **10**

(c) Draw the structures of the following compounds : **10**

(i) $P_4\ O_{10}$ (ii) $P_3\ N_3\ Cl_6$ (iii) $H_3\ P_3\ O_9$

(d) (i) Explain why Zn, Cd, Hg do not show the characteristics of transition elements. **10**

(ii) Write the outer shell electronic configuration of Cr (Atomic No. = 24) and Cu (Atomic No. = 29).

SECTION - B

4. (a) (i) What are the major limitations of Valence Bond Theory ? **10**

(ii) Draw the shapes of the various *d* orbitals and explain why they are split into two groups t_{2g} and e_g in an octahedral ligand field.

(b) Calculate the spin only magnetic moment of the following complex ions and show the arrangement of electrons in *d* orbitals using crystal field theory. **10**

(i) $[\ Fe\ (II)\ (H_2O)_6\ ]^{2+}$ (ii) $[\ Fe\ (II)\ (CN)_6\ ]$

Marks

(c) (i) [Ti $(H_2O)_6$]$^{3+}$ has maximum absorption in the d-d peak at 20 300 cm^{-1} and hence predict where the peaks will appear for [Ti $(CN)_6$]$^{3-}$ and [Ti $(Cl)_6$]$^{3-}$. **10**

(ii) Why is it difficult to separate the compounds of lanthanide elements ? Outline the methods for the separation of lanthanides.

(d) What are the principles upon which separation of Np, pu and An from *U* are made ? **10**

5. (a) Draw the energy level diagrams and indicate the occupancy of the orbitals in the following complexes : **10**

(i) d^9, octahedral with tetragonal elongation.

(ii) d^6, octahedral, low spin. Why does the splitting of d orbitals vary with geometry of the complexes ?

(b) The complex ion [Ni $(CN)_4$]$^{2-}$ is diamagnetic while [Ni $(cl)_4$]$^{2-}$ is paramagnetic and has two unpaired electrons. Explain with *d* orbital energy diagram. Deduce the structure of the two ions. **10**

(c) (i) Why d-d transitions are weak ? How does Δ_o change in going from one octahedral complex to the other with the same ligand set but (i) M^{3+} in place of M^{2+} (ii) a second and third transition element (eg., Ru^{n+} or OS^{n+}) in place of first series element (eg., Fe^{n+}). **10**

(ii) Write a short note on 'Lanthanide contraction'.

(d) Draw the structure of uranyl nitrate. Explain its importance in purification of Uranium. **10**

SECTION - C

6. (a) (i) Define a Lewis acid and a Lewis base. Identify the Lewis acid and Lewis base in the reaction, $Al^{3+}_{(aq)} + 6\ H_2O_{(l)} \rightarrow Al\ (H_2O)_{6(aq)}$. **10**

According to Lux Flood definition, which is the acid in the reaction between MgO and CO_2 to form Mg CO_3 ?

(ii) Write the equation for the auto dissociation of NH_3. How do $NaNH_2$ and NH_4Cl react in liquid NH_3 ? Explain why Na NH_2 acts as a base in liquid NH_3.

Marks

(b) (i) Which assumptions of the kinetic theory are responsible for the deviation of gases from ideal behaviour ? What is the value of $(\delta P/\delta V)$ at T_c ? **10**

(ii) The van der Waal's constants 'a' and 'b' of H_2O are 5.46 lit^2. atm. $mole^{-2}$ and 0.031 lit. $mole^{-1}$ respectively. Calculate the Critical pressure P_c, Critical temperature T_c and Critical volume V_c of H_2O. ($R = 0.082$ lit. atm/K. mol).

(c) (i) Compare with reasoning the liquid and gaseous states of matter with respect to density and diffusion. What is meant by vapour pressure of liquid ? **10**

(ii) Discuss the ordering in nematic and cholesteric type liquid crystals. Which one of these types is used in liquid crystal display ?

(d) (i) Define plane of symmetry and centre of symmetry of a crystal. The intercepts made by a plane of a crystal on the three crystallographic axes are a, b and 2/3 c where a, b and c are the unit cell dimensions. What are the corresponding Miller indices ? **10**

(ii) What is the number of atoms present in one unit cell of Copper which crystallizes in an FCC structure ?

7. (a) (i) Classify BF_3 and H_2O as lewis acid or lewis base with reasoning. In the reaction $H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$, identify the conjugate acid and conjugate base of the reactants. In the reaction between NH_3 and HCl, identify the lewis base among the products. **10**

(ii) Classify hexane, dimethyl formamide and ethanol as suitable type of solvents. Write the reaction for the auto ionization of the solvent $Br F_3$.

(b) (i) What is meant by mean free path and collision number ? **10**

(ii) Calculate the most probable velocity, mean velocity and root mean square velocity of H_2 at 0°C. ($R = 8.314$ J. K^{-1}. mol^{-1}; Molecular mass of $H_2 = 2.016 \times 10^{-3}$ kg.mol^{-1}).

(c) (i) Explain why liquids do not have a shape of their own and assume that of the container and why they are not compressible as gases ? **10**

(ii) H_2O is a liquid and H_2S is a gas at room temperature. Explain why ?

Marks

(d) (i) What are the seven crystal types ? In SnO_2 crystal, the unit cell edges and the interfacial angles are as follows : **10**

$a = b \neq c$; $\alpha = \beta = \gamma = 90°$. What is the crystal type of SnO_2 ?

(ii) When X rays of wave length 5800 A° are diffracted, the (200) first order reflection of NaCl occurs at an angle of 5.91°. Calculate the length and volume of NaCl unit cell.

SECTION - D

8. (a) (i) An elementary reaction is of the type : $A \rightarrow$ products. Derive the expression for the rate constant of the reaction in terms of the concentration of A. **15**

(ii) Explain how the method of half life can be used to determine the order of a reaction.

(iii) For the alkaline hydrolysis of ethyl acetate, the initial concentrations of both the ester and the alkali are 0.08 M. If the rate constant of the reaction at 25°C is $1.02 \times 10^{-2}\ M^{-1}\ sec^{-1}$, calculate the time taken for 50% and 75% conversion of the reaction.

(b) (i) State the first law of thermodynamics. Show that for an ideal gas, $C_p - C_v = R$. **15**

(ii) The enthalpy changes for the complete combustion of one mole of glucose and the complete combustion of one mole of maltose are $^{-}2810$ kJ/mol and $^{-}5645$ kJ/mol. respectively. Molecular formulae of glucose and maltose are $C_6H_{12}O_6$ and $C_{12}H_{22}O_{11}$. Write the corresponding stoichiometric equations for the combustion reaction and thus calculate the enthalpy change for the conversion of one mole of glucose. ($C_6H_{12}O_6$) into maltose ($C_{12}H_{22}O_{11}$) and H_2O.

(iii) What is Joule Thomson effect ? Helium gets warmed on Joule Thomson expansion. Why ?

(c) (i) State the Le chatelier's principle. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $\Delta H^{\circ} = {}^{-}92$ kJ/mol. What is the effect of increasing the temperature and pressure on the formation of NH_3 ? **10**

(ii) Derive the expression for the equilibrium constant, K_c for the reaction equilibrium $A + B \rightleftharpoons C + D$, from the law of mass action.

Marks

9. (a) (i) Define order and rate constant. What is the unit of rate constant for a zero order reaction ? **15**

(ii) The first order decomposition reaction of N_2O_5 is 50% complete in 1 *h*. Calculate the time required for 90% completion of the reaction.

(iii) What is a pseudo first order reaction ? Which function of concentration of the reactant is plotted Vs time to determine the rate constant if the reaction is (i) 1^{st} order (ii) 2^{nd} order ?

(b) (i) State the expression of Gibb's free energy (G) in terms of enthalpy and entropy. What is the condition of equilibrium in terms of G ? Define entropy and state its unit. **15**

(ii) A heat engine operates between 150°C and 25°C and takes 500 J of heat from the high temperature source. Calculate the efficiency of the engine and work done by the engine.

(iii) What is entropy of mixing ? Exactly 1.0 L of a 0 – 1M solution of substance A is added to 3.0 L of 0.05 M solution of substance B. Calculate the entropy of mixing.

(c) (i) A mixture of CO, H_2 and CH_3OH with partial pressures 10 bar, 1.0 bar 0.1 bar respectively is passed over a catalyst at 500 k. Calculate the free energy change for the formation of CH_3OH and thus predict whether more CH_3OH can be formed under the given conditions ($\Delta^\circ G_r$ 21.21 kJ/mol). **10**

(ii) State the Clapeyron - Clausius equation and give any two applications of this equation.

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