[Total No. of Pages : 7 Roll N0_____

1(CCE-M)4

CHEMISTRY-I

[05]

Time : 3 Hours **Maximum Marks : 300**

INSTRUCTIONS

i) *Answer must be written in English.*

ii) *The number of marks carried by each question is indicated at the end of the question.*

iii) *The answer to each question or part there of should begin on a fresh page.*

iv) *Your answer should be precise and coherent.*

v) *The part/parts of the same question must be answered together and should not be interposed between answers to other questions.*

vi) ***Candidates should attempt any five questions.***

vii) *If you encounter any typographical error, please read it as it appears in the text book.*

viii) *Candidates are in their own interest advised to go through the General Instructions on the back side of the title page of the Answer Script for strict adherence.*

ix) *No continuation sheets shall be provided to any candidate under any circumstances.*

x) *Candidates shall put a cross (X) on blank pages of answer Script.*

xi) *No blank page be left in between answer to various questions.*

xii) *No programmable Calculator is allowed.*

xiii) *No stencil (with different markings) is allowed.*

1. a) Drive and solve the Schrodinger wave equation for a particle in an infinite one dimensional box, with potential energy zero inside the box.

b) Determine the term symbols for ground state electronic configurations of boron and carbon.

c) Construct the wave functions for the sp hybrid orbitals.

(20×3=60)

2. a) Give a brief account of the molecular arrangement, which exists in various states of liquid crystals. **(12×5=60)**

b) Calculate the interplanar spacing (d_{hpl}) for a cubic system between the following sets of planes : i) 110 ii) 111 iii) 222. Assume that a is the edge length of the unit cell.

c) Calculate Kp at 25°C and 325°C for the reaction NO (g) $+1/2O_2(g) \rightleftharpoons NO_2(g)$, if at 25°C, $\Delta H^o = -56.48$ KJ mol^{-1} and $\Delta G^o = -34.85$KJ mol^{-1}

d) What is Joule-Thomson effect? Explain the term Joule-Thomson Coefficient.

e) Define the term resonance, resonance hybrid and resonance energy. Why is the resonance stabilisation energy of carbonate ion more than that of carbonic acid?

3. a) The rate law for the decomposition of gaseous N_2O_5,

$N_2O_5 \longrightarrow 2NO_2 + 1/2O_2$ is observed to be r = - d $[N_2O_5]/dt = k[N_2O_5]$, A reaction mechanism which has been suggested to be consistent with this rate law is :

$N_2O_5 \underset{}{\overset{K}{\rightleftharpoons}} NO_2 + NO_3$ (fast equilibrium)

$NO_2 + NO_3 \xrightarrow{K_1} NO_2 + NO + O_2$ (slow)

$NO + NO_3 \xrightarrow{K_2} 2NO_3$ (fast) **[15×4=60]**

i) Show that the mechanism is consistent with the observed rate law.

ii) If $k = 5\times10^{-4}$ Sec^{-1}, Calculate the time required for the N_2O_5 concentration to be reduced to 10% of its original value.

b) Discuss in brief the collision theory of bimolecular reactions. What are the limitations of this theory?

c) Calculate the ionic strength, activity coefficient and the mean activity coefficient of $Cu(NO)_3$ at a molarity of 2×10^{-3}M.

d) What are fuel cells? Describe the functioning of coal- fired fuel cells.

4. a) Describe the bonding in $[Cu(NH_3)_4]^{2+}$ and $[Fe(CN)_6]^{3-}$ in terms of valence bond theory. **[10 marks×6]**

b) Calculate crystal field stabilizing energy for the following systems :

i) d^5 low spin octahedral

ii) d^4 tetrahedral

c) Draw the structures of the following :

i) $Mo_4 Cl_8 (PR_3)_4$

ii) $[Co_4 (CO)_{12}]$

d) Describe briefly the various methods used for the separation of lanthanides.

e) Determine the number of metal-metal bonds in the followings:

i) $[Co_2 (CO)_8]$

ii) $[Ni (CO)_{12}]^{2-}$

f) How does the valence bond theory account for the following facts :

i) $[Ni (CN)_4]^{2-}$ is diamagnetic and square planar.

ii) $[Ni (CO)_4]$ is diamagnetic and tetrahedral.

5. a) Give a brief account of concentration cells. Calculate the liquid junction potential at 25°C between two solutions of HCl having mean ionic activities of 0.01 and 0.001, respectively. The transference number H^+ ion (t_+) in HCl may be taken as 0.83. **[20 marks×3]**

b) i) Write the differential and integrated forms of zero order reaction.

ii) The $t_{1/2}$ of a reaction is halved as the initial concentration of the reactants is doubled. What is the order of reaction?

c) i) Give a brief account on limitation of Arrhenius theory of dissociation.

ii) What is electrophoretic effect?

6. a) i) Why sulphur has higher negative electron affinity than oxygen? **[20 marks×3]**

ii) Calculate the electronegativity of silicon using Allred-Rochow method. Covalent radius of silicon is 1.175 A^0.

b) i) Why ammonium salts are much more soluble in water than the corresponding sodium salts.

ii) Discuss the geometry of any molecule having two lone pairs and four bond pairs.

c) i) Explain on the basis of MO theory as to why hydrogen forms diatomic molecule while helium remains monoatomic.

ii) A metal complex having composition $Cr(NH_3)_4 Cl_2Br$ has been isolated in two forms (A) and (B). The form (A) reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate

soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridisation of chromium in each.

7. a) Explain the absorption laws. Calculate the absorbance, when a UV light is passed through the given solution, the radiant power is reduced to 75%.

[12 marks × 5]

b) Give the reasons for high and low quantum yields.

c) Give reasons of the following:

i) Strong oxidizing agents do not exist in liquid ammonia.

ii) Covalent compounds such as C_6H_6 and C_2H_5OH give conducting solution in liquid HF.

d) On radiation of propionaldehyde at 30°C with light of λ = 3020 A^0, the quantum yield for CO is found to be 0.54. The intensity of incident light is 15000 ergs per sec. What is the light intensity in einstein per sec? Also find out the rate of formation of CO?

e) Give the correct order of acidic strength of the following acids viz. HBr, H_2SO_4, $HClO_4$ and HCl in two different solvents.

i) In glacial acetic acid

ii) In water.

8. a) i) Which complex has larger crystal field splitting **[20 marks×3]**

$[CO(CN)_6]^{3-}$ or $[CO(NH_3)_6]^{3+}$

ii) Discuss the structure of complex (Fe $(NH_3)_6]^{2+}$ on the basis of the crystal field theory.

b) i) The complex ion $[CO(NH_3)_6]^{3+}$ is octahedral and diamagnetic, the complex ion $[CO F_6]^{3-}$ is also octahedral but paramagnetic. How does valence bond theory account for this observation?

ii) What is lanthanide contraction?

c) Complete the following reaction:

i) $AgNH_2 + KNH_2 \xrightarrow{liq.NH_3}$

ii) $HNO_3 + HF \longrightarrow$