

- (d) A certain system absorbs  $3 \times 10^{18}$  Quanta of light per second. On irradiation for 20 minutes, 0.003 moles of the reactant was found to have reacted. Calculate the Quantum yield for the process.  
(Avagadro's number =  $6.02 \times 10^{23}$ ). 10
7. (a) How are lanthanides separated by ion exchange method ? 10
- (b) Explain the factors which favour the formation of ionic compounds. 10
- (c) What is lanthanide contraction ? Explain the consequences of lanthanide contraction. 15
- (d) Explain the main features of crystal field theory. Discuss the crystal field splitting in octahedral complexes. 15
8. (a) Discuss the properties of d-block elements with respect to :  
(i) Variable oxidation states  
(ii) Complex formation  
(iii) Catalytic property. 15
- (b) Discuss the bonding in olefin complexes. 15
- (c) Calculate CFSE and spin only magnetic moment of  $[\text{Co}(\text{CN})_6]^{-3}$  and  $[\text{Co F}_6]^{-3}$  on the basis of CFT. 10
- (d) Explain :  
(i) Neutralisation reaction and  
(ii) Precipitation reactions in liquid  $\text{NH}_3$  as solvent with suitable example. 10
9. (a) Explain crystal field splitting in tetrahedral complexes and calculate CFSE for  $d^3$  system. 10
- (b) Discuss the applications of emf measurements of fuel cells. 15
- (c) State and explain the III<sup>rd</sup> law of thermodynamics. 15
- (d) The rate constant of a first order reaction increases from  $2 \times 10^{-5} \text{ S}^{-1}$  to  $2 \times 10^{-4} \text{ S}^{-1}$  when temperature is increased from  $27^\circ\text{C}$  to  $47^\circ\text{C}$ . Calculate the activation energy of the reaction. 10

Roll No. ....

Total No. of Pages : 4

1(CCE.M)3

Chemistry-I  
(05)

Time : Three Hours]

[Maximum Marks : 300

**INSTRUCTIONS**

- (i) Answers 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 thereof 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 question no. **1** which is compulsory and any **four** more out of the remaining 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) What are Quantum numbers ? Explain and give their significance. 10
- (b) Explain the concept of resonance and resonance energy with suitable example. 10
- (c) Derive the relation between  $C_p$  and  $C_v$  for n moles of an ideal gas. 10
- (d) Discuss Schottky defect and Frenkel defect with respect to crystalline solids. 10
- (e) Discuss the kinetics of polymerisation with a suitable example. 10
- (f) Explain briefly bonding in metal carbonyls. 10
- (g) Write a note on Photoelectric Cells. 10
- (h) Explain the properties of lanthanides with respect to :
  - (i) Colour and
  - (ii) Magnetic Property. 10
- (i) Explain :
  - (i) Acid-base reactions and
  - (ii) Solvolytic reactions in liquid  $\text{SO}_2$  with suitable examples. 10
- (j) Explain Fajan's rule of Polarisation. 10
2. (a) Derive the expression for energy of the particle in one dimensional box from Schrodinger's wave equation. 15
- (b) Discuss the molecular orbital theory of chemical bonding. Write the M.O. diagram for CO and NO molecule. Calculate the bond order. 15
- (c) Construct Born-Haber cycle for 1 : 1 ionic compounds. Explain the steps involved. 10
- (d) What is covalent bond ? Explain the factors which favour the formation of covalent bond. 10
3. (a) State and explain the laws of thermochemistry. 15
- (b) Derive Gibbs Helmholtz equation. 15
- (c) Derive the Bragg's law of X-ray diffraction. 10

- (d) The heat of combustion of ethyl alcohol ( $\text{C}_2 \text{H}_5 \text{OH}$ ) is  $-1380.7 \text{ kJ/mol}$ . If the heats of formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are  $-394.5 \text{ kJ/mol}$  and  $-286.6 \text{ kJ/mol}$  respectively, calculate the heat of formation of ethyl alcohol. 10
4. (a) Explain the collision theory of reaction rates of bimolecular reactions. 10
- (b) What are liquid crystals ? Explain their types with examples. 10
- (c) Discuss the effect of temperature and catalysts on the reaction rates. 10
- (d) Derive the rate equation for second order reaction when  $a = b$ . 10
- (e) A first order reaction is 40% complete in 50 minutes. Calculate the rate constant for the reaction. In what time will the reaction be 80% complete ? 10
5. (a) Define free energy function. Explain the variations of free energy of a gas with temperature and pressure. 12
- (b) State and explain the laws of crystallography. 13
- (c) Discuss the Debye-Huckel theory of strong electrolytes. 15
- (d) 10 moles of an ideal gas at the initial pressure of one atmosphere at  $0^\circ\text{C}$  were expanded reversibly under isothermal conditions to a final pressure of 0.1 atmosphere. Calculate the work done by the gas, the change in internal energy and the heat absorbed by the system.
 

$(R = 8.314 \text{ JK}^{-1} \text{ deg}^{-1} \text{ mol}^{-1}).$  10
6. (a) The Quantum yield for
 
$$\text{H}_2 (\text{g}) + \text{Cl}_{2(\text{g})} \xrightarrow{h\nu} 2 \text{HCl}_{(\text{g})}$$
 is high but for
 
$$\text{H}_{2(\text{g})} + \text{Br}_{2(\text{g})} \xrightarrow{h\nu} 2 \text{H Br}_{(\text{g})}$$
 is low.
 

Discuss this with respect to the mechanism of these reactions. 15
- (b) State and explain Lambert-Beer's law. 15
- (c) What are the limitations of Arrhenius theory of dissociation ? 10