

1[CCE.M]1

Chemistry-I

(05)

Time : Three Hours

Maximum Marks : 300

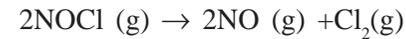
INSTRUCTIONS

- (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 answers 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** 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.

- (ii) $\text{Ir}_4(\text{CO})_{12}$
- (iii) $\text{Fe}_3(\text{CO})_{12}$ 21
- (b) Give evidence to establish that metal ligand bonding in coordination complexes is not purely electrostatic in nature as is assumed in Crystal Field Theory. 9
- (c) What is crystal field theory ? How does it differ from Valence Bond Theory ? How does this theory differ from the Valence Bond Theory ? How does it account for the fact that $[\text{CoF}_6]^{3-}$ is paramagnetic but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic, though both are octahedral ? 20
7. (a) How do lanthanides occur in nature ? Briefly describe the procedure generally adopted for their separations. 25
- (b) With the help of suitable examples describe the colour property and magnetic property of tripositive lanthanide ions. 25
8. (a) Discuss the applications of e.m.f. measurement of fuel cell in brief. 40
- (b) What are the limitations of Arrhenius Theory of Dissociation ? 10
9. (a) Discuss the following types of reactions in liquid ammonia as non aqueous solvent with suitable examples.
- (i) Precipitation reactions.
- (ii) Acid base reactions.
- (f) What are concentration cells ? Derive expression for the emf of concentration cell. 10
- (g) A sample of gaseous HI was irradiated by light of wavelength 253.7 nm when 307J of energy was found to decompose 1.30×10^{-3} , calculate quantum yield for the dissociation of HI. 10
- (h) Explain lanthanide contraction. 10
- (i) Find the expression for CFSE of d^5 , d^6 system in weak and strong octahedral fields in terms of Dq and pairing energy. 10
- (j) The heat of reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ at 27°C was found to be -21.976 kcal. What will be the heat of reaction at 50°C ? The molar heat capacity at constant pressure and at 27°C for N_2 , H_2 and NH_3 are 6.8, 6.77 and 8.86 $\text{cal mol}^{-1} \text{K}^{-1}$. 10
2. (a) Discuss the four quantum numbers and their significance. 10
- (b) Discuss the electronic configuration of NO, CO and HF molecules in terms of molecular orbital approach. 9
- (c) What is meant by bond order ? Calculate the bond order of He_2^+ , O_2^- and O_2^+ molecular ions. 11
- (d) Draw the shapes of d-orbitals. Discuss the related interconversion and splitting of d orbitals. 10

- (e) In what way does the Heisenberg uncertainty principle contradict the concept of stationary orbit for electrons as suggested by Bohr ? 10
3. (a) Describe Nernst Heat Theorem. How does Nernst Heat Theorem lead to the enunciation of the Third Law of Thermodynamics ? Explain how the absolute entropy of a substance is determined with the help of Third Law of Thermodynamics. 22
- (b) Find the entropy change of the following reaction,
- $$2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$$
- Entropies of formation of CO, O₂ AND CO₂ are 197.6, 205.03 and 213.6 JK⁻¹ mole⁻¹ respectively at 25°C. 10
- (c) Discuss the determination of rate of reaction i.e. third order reaction in the A+B+C → Products the variation of three concentrations terms it is a process of third order and three different cases arise,
- Three terms may be equal
 - Two may be equal and one different
 - All three may be different. 18
4. (a) Discuss in brief the Debye Huckel Theory of strong electrolyte and its quantitative treatment. 15
- (b) What is equilibrium constant K for the following reaction at

400 K :



Given $\Delta H^\circ = 77.2 \text{ kJ mole}^{-1}$

$\Delta S^\circ = 122 \text{ J K}^{-1} \text{ mole}^{-1}$ at 400 k,

$R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$. 15

- (c) Define Free Energy Function. Discuss the variation of free energy of a gas with temperature and pressure. Also deduce Gibbs Helmholtz equation. 20
5. (a) Discuss the defects in crystals with a suitable example in which these are present. 30
- (b) Describe lattice structure of CsCl so as to bring out the answer to the following :
- Nature of unit cell.
 - Number of formula unit per unit cell.
 - Edge length of unit cell in terms of radius of Cs⁺ and Cl⁻. 13
- (c) Derive an expression for the chemical potentials described by Gibbs. 7
6. (a) Draw the structure by calculating total no. of metal-metal bond in cluster and metal-metal bond for each metal for the following :
- Mn₂(CO)₁₀

- (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.

1. (a) Give the Schrodinger's wave equation for H atoms in Cartesian and polar co-ordinate. With the help of a diagram show the relation between the two co-ordinates. 10
- (b) Why value of C_p is greater than C_v ? Derive the relation between C_p and C_v for n moles of an ideal gas. 10
- (c) Calculate the angle at which first and second reflections are obtained from planes 500 pm apart, using X-ray of wavelength 100 pm. 10
- (d) What is meant by the terms rate constant and order of a reaction ? Starting from the rate equation, derive the units of rate constant (K) for a zero-order, first order, second order and a half-order reaction. 10
- (e) Explain the term specific conductance and molar conductance as applied to solution of electrolytes. Also give their units. How do specific conductance and molar conductance change on dilution ? 10

- (iii) Protolysis of urea, acetamide, sulphamide in liquid ammonia.
- (iv) Ammonolysis reaction.
- (v) Complex formation reactions. 35

- (b) Discuss acid–base reactions, complex formation reaction and redox reaction in liquid sulphur dioxide as non aqueous solvent.

15