(b) Give Orgel diagrams for $[Cu(H_2O)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ complexes and indicate the possible electronic d-d transitions. 25

10. (a) State and explain the third law of thermodynamics. 25

(b) Explain the evaluation of absolute entropy of gases at 1 atmospheric pressure and 25ºC. 25

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Chemistry

(05)

Paper—I

Time : Three Hours] [Maximum Marks : 300

Note :— (i) Answers must be written in English.

(ii) Number of marks carried by each question are indicated at the end of the question.

(iii) Part/Parts of the same question must be answered together and should not be interposed between answers to other questions.

(iv) The answer to each question or part thereof should begin on a fresh page.

(v) Your answers should be precise and coherent.

(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.

SECTION–A

1. (a) Derive the normalised wave function expression for particle in a one dimensional box. 10

(b) Explain the nature of ψ and ψ^2. 10

(c) Derive the Gibbs-Helmoltz equation and explain the terms in it. 10

(d) Sketch the Schottky and Frenkel defects in crystals. 10

(e) In a first order reaction A$\rightarrow$ products under what conditions the rate of reaction is equal to rate constant ? 10

(f) What is liquid junction potential and how is it eliminated ? 10

(g) What are photoelectric cells ? Illustrate with one example. 10

(h) Write the ionization of liquid SO_2 and explain an example of oxidation-reduction reaction in it. 10

(i) Explain Lanthanide contraction. 10

(j) Give the d orbital splitting in square planar complex. 10

2. (a) Write the Schrodinger wave equation for hydrogen atom in spherical polar co-ordinates and discuss its solutions. 25

(b) Give the MOEDs of NO and CO molecules and explain their bond orders and magnetic properties. 25

3. (a) Derive the expression for maximum work in isothermal reversible expansion of ideal gases. 25

(b) Derive the relationship between C_P and C_V for n moles of ideal gas. 15

(c) 280 grams of nitrogen absorbed 100 cals of heat without change in volume. The temperature of N_2 gas increased from 30ºC to 32ºC. Calculate the molar heat capacity (C_V). 10

4. (a) Derive Bragg's equation and its use in crystal structure determination. 25

(b) What are liquid crystals ? How many types of liquid crystals are there ? Give one example each and mention any two properties and applications of liquid crystals. 25

5. (a) Derive the rate equation for first order reactions and show that $t_{1/2}$ is independent of initial concentration. 25

(b) What are the limitations of Collision theory ? 10

(c) Explain the theory of absolute reaction rates. 15

6. (a) Explain the Debye-Huckel theory of strong electrolytes. 25

(b) What are fuel cells ? Explain their important features taking any two examples. 25

7. (a) State and explain the fundamental laws of photochemistry. 15

(b) What is quantum yield ? How is it determined experimentally ? 15

(c) In photochemical reaction $H_2 + Cl_2 \rightarrow 2HCl$, 2×10^{-10} moles of Cl_2 is converted to HCl with light of λ = 4000 Å. What is the quantum yield of reaction if light energy absorbed is 7.16×10^{-15} k cals. 20

8. (a) Discuss the colour property and magnetic property of tripositive lanthanide ions. 20

(b) Write the separation of trivalent lanthanide ions by ion-exchange method. 20

(c) Write :

(i) neutralization reaction and

(ii) precipitation reaction in liq. NH_3. 10

9. (a) Calculate the CFSE and spin only magnetic moment of complexes :

(i) $[Fe(H_2O)_6]^{2+}$

(ii) $[Fe(CN)_6]^{3-}$

(iii) $[Mn(H_2O)_6]^{2+}$

(iv) $[CoCl_4]^{2-}$ and

(v) $[Co(NH_3)_6]^{3+}$. 25