This question paper contains 4 printed pages]

Code No. : 05(I) *Roll No. .....*

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CHEMISTRY

Paper : I

Time Allowed : 3 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) Candidate should attempt Question No. 1 which is compulsory and any four out of the remaining questions.

P. T. O.

1. (a) Set up the Schrodinger equation for a particle i one dimensional box and then derive th expression for energy of the particle. 1

(b) Explain the formation of HF molecule on the basi of molecular orbital approach. 1

(c) The enthalpy change accompanying complet combustion of graphite, hydrogen gas, and liqui ethanol at 25°C to form $CO_2(g)$ and $H_2O(l)$ ar 393.5, 285.8, and 1366.9 kJ mol^{-1}, respectively Calculate the enthalpy of formation, ΔH_f^o, fo liquid ethanol. 1

(d) Draw the faces of a cubic crystal with Mille indices (101), (100) and (200). 1

(e) By what factor would the rate of a reaction fo which the activation energy is 51.85 kJ mol^{-1} b increased by a temperature rise of 10°C from 25 t 35°C. 1

(f) What are fuel cells ? Describe the constructio and working of $H_2 - O_2$ fuel cell. 1

(g) A monochromatic radiation is incident on a solution of known concentration wherein 10% o the light gets absored. What fraction of the ligh will be absorbed by the same solution in a cel two times as long ? 1

(h) Calculate the crystal field stabilization energy o d^8 Ni^{++} ion in an octahedral complex. 1

(i) Write a comparative account of ionic radii and oxidation states of later lanthanides and actinides. 1

(j) Discuss redox, precipitation and solvolytic reaction in liquid SO_2. 10

2. (a) Derive the expressions of wave functions and associated energies of H_2^+. 25

(b) A particle of mass 2.0×10^{-29} Kg is confined in a one dimensional box of length 4.0 nm. Find the frequency and wave length of the photon emitted when the particle goes from $n = 3$ to $n = 2$ level. ($h = 6.626 \times 10^{-34}$ Js) 25

3. (a) Explain the Joule-Thomson expansion. Show that the Joule-Thomson coefficient for an ideal gas is zero. 25

(b) The free energy change for a reaction is expressed as a function of temperature by the equation : 25

$$\Delta G^\circ \text{ (J mol}^{-1}) = 18660 - 14.40\ T \log T - 6.07\ T + 8.24 \times 10^{-3}\ T^2$$

Find ΔG° and ΔH° at 25°C.

4. State the third law of thermodynamics. Describe as how the absolute entropy of a substance is evaluated using the heat capacity (C_p) data. 10 + 40

5. (a) Derive the relation between equilibrium constant K_p and K_c. Under what condition $K_p = K_c$? 25

(b) Derive Bragg's equation and explain how the crystal structure is determined using this equation. 25

6. (a) Show that the expression for the second order r constant (k_2) of the reaction $2A \rightarrow P$ is :

$$k_2 = \frac{1}{t}\left[\frac{1}{C_t} - \frac{1}{C_0}\right]$$

(C_0 and C_t are the concentrations of the reactant zero and time t, respectively).

(b) Derive the expression for the half-life of an order reaction.

7. (a) Give a quantitative treatment of the Deb Huckel theory of 1 : 1 strong electrolytes.

(b) Calculate the mean activity coefficient $(\nu_{\pm})$ Na_2SO_4 at a molality of 2×10^{-3} in aque solution at 25°C. (A value of water = –0.509).

8. Give an example each of concentration cells with without transport and then derive the equation of of the former type. 5 + 5 +

9. Discuss the kinetics and derive expressions for rates of the following reactions :

(i) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$

(ii) $H_2(g) + Br_2(g) \xrightarrow{h\nu} 2HBr(g)$

Explain why the quantum yield of reaction

(i) is very large (= 10^5) in comparison to reaction (ii) (= 0.01). 22 + 22

10. Discuss the crystal field theory. In what way different from the valence bond theory ?
