SPRING END SEMESTER EXAMINATION-2018 2nd Semester B. Tech

CHEMISTRY CH-1003

(For 2017 Admitted Batch)

Time: 3 Hours Full Marks: 50

Answer any SIX questions including question No. 1 which is compulsory. The figures in the margin indicate full marks. Candidates are required to give their answers in their own words as far as practicable and all parts of a question should be answered at one place only.

- 1. (a) For the dissociation reaction of a metal oxide, $\Delta H=35$ [1×10] KJ/mol and $\Delta S = 0.08$ KJ/K at 1 atm pressure. Find the temperature up to which the reaction would not be spontaneous?
 - (b) On the basis of molecular orbital theory, show that HF is diamagnetic.
 - (c) [Ni(CN)₆]²⁻ is colorless. Explain.
 - (d) Explain sacrificial anodic protection.
 - (e) Explain bathochromic shift with suitable example.
 - Explain the effect of concentration on molar conductance (f) of NH₄OH.
 - (g) CO₂ is non polar but IR active. Explain.
 - (h) A reaction proceeds 3 times faster at 37 °C than it does at 27 °C. Find the activation energy.
 - For a solution of camphor in hexane in a 5 cm cell, the absorbance A was found to be 2.52 at 295nm with €max =14. What is the concentration of camphor?

(j) Predict whether the cell reaction

$$2Ag(s) + Zn^{2+}(aq) \longrightarrow 2Ag^{+} + Zn(s)$$
 is feasible or not.

Given
$$E^0_{Ag/Ag}^+ = -0.8V$$
 and $E^0_{Zn/Zn}^{+2} = 0.76V$.

- 2. (a) Calculate the vibrational absorption frequency of the -NH group while that of -CH group is 3023 cm⁻¹, keeping same value of force constant. [4]
 - (b) Deduce the structure of the isomeric compounds 'A' and 'B' having molecular formula C₃H₆O and the following IR spectral data.
 For 'A' a characteristic peak is at 1710 cm⁻¹ whereas for 'B' two peaks at 3340 cm⁻¹ and 1640 cm⁻¹.
- (a) For the reaction 2O₃ → 3O₂ the following mechanism [4] has been proposed

$$O_3 \stackrel{k_1}{\rightleftharpoons} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

Show that,
$$-\frac{d[O_3]}{dt} = k \frac{[O_3]^2}{[O_2]}$$

where
$$k = \frac{k_1 k_2}{k_{-1}}$$
 assuming that, $k_{-1}[O_2] >> k_2[O_3]$

(b) What is time lag theory? On the basis of the same, develop the condition for a uni molecular reaction to follow 2nd order kinetics.

- 4. (a) Calculate CFSE for the complex $[Co(NH_3)_6]^{3+}$. Given octahedral splitting energy is 21,400 cm⁻¹ and the pairing energy is 27,800cm⁻¹.
 - (b) Find the pH of a solution placed in a quinhydrone half-cell which was coupled with standard calomel electrode. The EMF of the combined cell was found to be 0.123V at 25 °C. (Given, E_{calomel} = 0.2415V, E⁰ = 0.6996V).
- 5. (a) Discuss the scheme of hybridization and predict the shape for the complex [Ni(CO)₄]. The complex is found to be diamagnetic. [4]
 - (b) The equivalent conductance of a very dilute solution of KNO₃ at 298K is 105.2 ohm⁻¹. cm² equiv⁻¹. If the ionic conductance of nitrate ion is 61.7 ohm⁻¹. cm² equiv⁻¹, then calculate the transport number and ionic mobility of potassium ion in this solution.
- 6. (a) Predict the effect of increased pressure and temperature on the following reaction equilibria. [4]

(i)
$$2SO_{2(g)} + O_{2(g)}$$
 \longrightarrow $2SO_{3(g)} + 194.0 \text{ KJ}$

(ii)
$$N_{2(g)} + O_{2(g)} = 2NO_{(g)} - 361.0 \text{ KJ}$$

- (b) Kp for a reaction is 1.6×10^{-4} at 400^{0} C. What will be the Kp at 500^{0} C? Heat of reaction in this temperature range is -25.0 kcal.
- 7. (a) Calculate the number of binary collisions per cc of a nitrogen sample at STP. Given diameter of N₂ molecule is 3.7 A⁰.
 - (b) Discuss the working principle of Ni-MH battery. [4] Mention two advantages of the same.

- 8. (a) Find the entropy change accompanying the mixing of [4] 4 g of H2 and 4 g of He at STP.
 - (b) Calculate λ_{max} for the following compound by using [4] Woodward-Fieser rule.
