AUTUMN END SEMESTER EXAMINATION-2016

1st Semester B.Tech & B.Tech Dual Degree

CHEMISTRY

CH-1003

(Regular-2016 & Back-2015 Admitted Batch)

Time: 3 Hours **Full Marks: 60**

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) 10moles of an ideal gas expand isothermally from a volume of 2litres to 20litres. Find the entropy change accompanying the expansion. [2 × 10

(b) On the basis of molecular orbital theory, show that B_2 is more magnetic than C_2.

(c) Write down the electrode reactions taking place in H_2-O_2 alkaline fuel cell.

(d) Draw the band diagrams of intrinsic and extrinsic semiconductors.

(e) Show that for a first order reaction $t_{99.9\%} \approx 10\ t_{50\%}$.

(f) Anhydrous $CuSO_4$ is colorless-explain.

(g) Indicate whether the following vibrations will be IR active or inactive.
(i) SO_2 symmetric stretching
(ii) CO_2 asymmetric stretching

(h) What is energy of activation of a reaction? How does a catalyst affect the activation energy?

(i) For a solution of camphor in hexane in a 5 cm cell, the absorbance A was found to be 2.52 at 295nm with $\epsilon_{max} = 14$. What is the concentration of the solution?

(j) Can a solution of $NiSO_4$ be stored in copper vessel? Given $E^0_{Ni^{+2}/Ni} = -0.25V$ and $E^0_{Cu^{+2}/Cu} = 0.34V$.

2. (a) Calculate the vibrational absorption frequency of the -OH 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 C_3H_6O and the following IR spectral data. [4

(a) 1710cm^{-1} and (b) 3340cm^{-1} and 1640 cm^{-1}

3. (a) For the reaction, $2NO+Cl_2 \rightarrow 2NOCl$, the proposed mechanism is as follows: [4

$$NO+Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl_2$$

$$NO+ NOCl_2 \xrightarrow{k_2} 2NOCl$$

Show that the overall rate = $k[NO]^2[Cl_2]$, where $k= k_1k_2/k_{-1}$; assume $k_2[NO] << k_{-1}$.

(b) For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, the free energy changes at 25 ^{0}C and 35 ^{0}C are –3.98 and –3.37 Kcal respectively. Calculate the heat of reaction at 35 ^{0}C. [4

4. (a) Calculate CFSE and magnetic moment of the complex $[Cu(NH_3)_4]^{2+}$. [4

(b) Find the pH of a solution placed in a quinhydronehalf-cell which was coupled with standard calomel electrode. The [4

EMF of the combined cell was determined to be 0.123V at 25 ^{0}C. (Given $E_{calomel} = 0.2415V$, $E^0_{Q/H2Q} = 0.6996V$).

5. (a) Discuss the formation of bonding and antibonding molecular orbitals on the basis of LCAO principle. [4

   (b) The equivalentconductance of a very dilute solution of $NaNO_3$ at 298K is 105.2 ohm^{-1} cm^2 equiv^{-1}. If the ionic conductance of nitrate ion is 61.7 ohm^{-1} cm^2 equiv^{-1}, then calculate the transport number and ionic mobility of sodium ion in this solution. [4

6. (a) Predict the effect of increased pressure and temperature on the following reaction equilibria stating only if product formation will be favoured. [4

   (a) $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g) + 194.0$ kJ

   (b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 361.0$ kJ

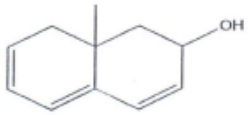
   (b) K_p for a reaction is 1.6×10^{-4} at 400^0 C. Find K_p at 500^0 C? Heat of reaction in this temperature range is –25.0 kcal. [4

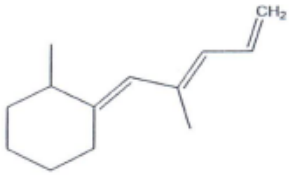
7. (a) The voltage of the cell $Pb/PbSO_4| Na_2SO_4.10\ H_2O| HgSO_4/Hg$ is 0.9647V at 25 ^{0}C. The temperature coefficient is 1.74×10^{-4} VK^{-1}. Calculate the value of ΔG, ΔS and ΔH. [4

   (b) Enthalpy and entropy changes of a reaction are 40.63KJ/mol and 108.8 J/molK respectively. Predict the feasibility of the reaction at 27 ^{0}C. [4

8. (a) Find the number of vibrational degrees of freedom for CH_4 and C_6H_6. [4

b) Calculate λ_{max} for the following compounds by using Woodward-Fieser rule. The increment for -OH being +5 nm. [4





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