Registration No. :

Total number of printed pages – 3

Second Semester Examination – 2013

CHEMISTRY – I

QUESTION CODE : A 434

Full Marks – 70

Time : 3 Hours

*Answer Question No. 1 which is compulsory and any five from the rest.
The figures in the right-hand margin indicate marks.*

(Standard data : h=6.626×10^{-34}Js, m_e=9.1×10^{-31}kg, c=3×10^8ms^{-1}, R=8.314 JK^{-1}mol^{-1}, N=6.023×10^{23}mol^{-1}, 1amu =1.6605×10^{-27} kg, e=1.6×10^{-19}C)

1.   Answer the following questions :   2×10

   (a)   What are the bond orders of H_2 and H_2^+?

   (b)   Write down the Arrhenius equation and explain each term involved in it.

   (c)   Calculate the velocity of an electron that has been accelerated by a potential difference of 1 V.

   (d)   What are eigen values and eigen functions ?

   (e)   How is the theory of absolute rate superior to collision theory ?

   (f)   What is the difference between Triple point and eutectic point ?

   (g)   Why cannot all the phases of sulphur system co-exist at the same temperature and pressure ?

   (h)   What is a storage cell ? How does it differ from a fuel cell ?

   (i)   The ionic radii of Cs^+ and Br^- ions are 169 pm and 195 pm, respectively. What type of unit cell would be expected for CsBr crystals ?

   (j)   What are the criteria of spontaneity of chemical reactions ?

P.T.O.

2. (a) Write down the cell involving the reaction with the reactions at anode and cathode :

$Zn(s) + Fe^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Fe(s)$,

$E°(Fe^{2+},Fe) = -0.440V$ and $E_o(Zn^{2+},Zn) = -0.76V$.

Find out the $E°_{cell}$ of the cell. 3

(b) Find out the miller indices of crystal planes with intercepts 2a, 3b, c, and 6a, 3b, 3c. 3

(c) Write down the reactions involved in charging and discharging of lead storage cell. 4

3. (a) Explain why order of a reaction cannot be predicted from overall stoichiometry. 2

(b) A first order reaction is 20% complete in 10 minutes. Calculate

(i) rate constant, and

(ii) time taken for 75% completion. 4

(c) What are Schottky and Frenkel defects ? Explain with examples. 4

4.. (a) Draw a neat diagram and discuss the water equilibrium system. 4

(b) Which of the following molecules / ions are paramagnetic and diamagnetic ?

Calculate the bond order in each case. 6

(i) O_2

(ii) O_2^+

(iii) O_2^{2-}

(iv) O_2^-

(v) O_2^+

5. (a) What is the difference Between the Eutectic reaction, peritectic reaction and Eutectiod reaction and perictiod reaction Explain with Example. 4

(b) (1)$Cp - Cv = [P + \{\partial U/\partial V\}_T][\partial V/\partial T]p$ 4

(c) If $T = f(P, V)$ Then prove that dT is a Perfect differential. 2

6. (a) Show that for a first order reaction the time required for the successive reduction in the concentration of A by a constant factor is independent of the initial concentration of A. 3

    (b) The pseudo-first order rate constant for an acid hydrolysis reaction, $S + H_2O + H^+ \rightarrow P$, is $1.8 \times 10^{-5}\ s^{-1}$. Calculate the true rate constant, given $[H^+] = 0.1\ M$, and $[H_2O] = 55.6\ M$. 4

    (c) Explain the metallic bonding with reference to Electron Gas Model. 3

7. (a) Calculate the distance between Na^+ and Cl^- in NaCl crystal, if its density is $2.165\ gm\ cm^{-3}$. NaCl has fcc structure (Mass of Na = 23, Cl = 35.5) 3

    (b) Calculate the change in emf with temperature of the fully charged lead acid storage cell, if $\Delta S = 2.72\ kJmol^{-1}$ for the cell reaction :

    $PbO_2(s) + Pb(s) + 2H_2SO_4 \rightarrow 2\ PbSO_4(s) + 2H_2O(l)$ 3

    (c) On the basis of the uncertainty principle explain why electrons cannot exist within the nuclei of atoms. 4

8. (a) A hydrogen electrode and a normal calomel electrode ($E° = 0.28\ V$) had a voltage of 0.435V, when placed in a solution at 298K. Calculate the pH of the solution. 3

    (b) Calculate the change in free energy accompanying the vaporization of one mole of liquid water at 100°C and 0.1 atm pressure. Will the process be spontaneous ? 4

    (c) If $\partial U = T \partial S - P \partial V$ Then Show that $(\partial T / \partial V)_S = -(\partial P / \partial S)_V$. 3

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