CHEMISTRY-I

FULL MARK : 70

Standard data:

h=6.626x10^{-34} Js, R=8.314 JK^{-1}mol^{-1}, c=3x10^{8} ms^{-1}, 1 amu=1.6605x10^{-27} Kg, Atomic weights: C=12.000, O=15.9994.

1. **2x10**

a)What is de Broglie relation ?

b)Arrange the following in the increasing order of energy,

(i)IR, (ii) UV-visible, (iii) microwave, and (iv) X-ray.

c)Which of the following pairs is isoelectronic?

(i) N_2 and CO, (ii) O_2 and N_r ,(iii) Li and Be.

d)Which of the following are close close-packed arrangements:

(i)ABCABC……(ii)ABAC…….

(iii)ABBA……(iv)ABCCB……. ?

e)What is the coordination number of Na^+ in NaCl crystal ?

f)Which of the following three conditions is valid for a spontaneous reaction;

(i)ΔG>0, (ii)ΔG=0, (iii)ΔG<0 ?

g)What happens to the entropy of a system at equilibrium?

h)Which of the following conditions will shift the equilibrium of an exothermic reaction towards right :

(i)Lowering , (ii)increasing , or (iii) keeping fixed the temperature?

i)Write down the relation between the rate constant and the temperature of a reaction .

(j)Which of the following relations between the standard free energy change (ΔG^0) and E^0 is correct : (i) $\Delta G^0=nFE^0$, (ii) $\Delta G^0=-nFE^0$, (iii) $\Delta G^0=nE^0$?

2.

(a)For one mole of an ideal gas T=f(P,V). Show that dT is a perfect differential. 3

(b)Show that $C_p-C_v=[V-[\frac{\partial H}{\partial P}]_r]\{\frac{\partial P}{\partial T}\}_v$ 4

(c)A particle is moving with velocity of 65×10^6m sec^{-1} and the wave length associated with the particle is 50×10^{-12}m. Find out the momentum of the particle. 3

3.

(a)If dU=TdS-PdV, then show that,

$(\frac{\partial T}{\partial V})_s=-(\frac{\partial P}{\partial S})_v$ 3

(b)Which of the following molecules will be rotationally active and why?

(i)H_2 (ii)NO (iii)HCl and (iv) F_2 2

(c)Calculate A S,A A , and A G for the vaporization of 2 moles of liquid benzene at its-boiling point of 80.2°C. Assume ideal gas behavior for the benzene vapour. (Given, the latent heat of vaporization ,L_v=101cal gm^{-1}, Mol.wt.of benzene =78)

5

4.

(a)What do you mean by a 'zero order reaction'? What is the activation energy for a reaction?

(b)From the standard reduction potentials:

(i)$Ce^{3+}+3e\rightarrow Ce$ $E^0=-2.48V$

(ii)$Ce^{4+}+e\rightarrow Ce^{3+}$ $E^0=1.61V$

Calculate the reduction potential for the half cell Pt Ce, Ce^{4+} 3

(c)For the reaction : $2NO+Cl_2\leftrightarrow 2NOCl$, following mechanism has been proposed.

Step-1: $NO+Cl_2\leftrightarrow NOCl_2$;

Step-2 : $NO+NOCl_2\rightarrow 2NOCl$

Show that the overall rate of the reaction is :$k[NO]^2[Cl_2]$, where ,$k=k_1k_2/k_{-1}$ (assume that $k_2[NO]<<k_1$)

5.

(a)Write down the reactions at the following two electrodes as well as the full cell reactions:

(i)$Fe|Fe^{2+}||Fe^{2+}\text{-}Fe^{3+}|Pt$

(ii)$Zn|ZnO_2^{2-}$, OH-/HgO(s)|Hg 2

(b)Consider a gaseous decomposition reaction :A→Products ,at 500^oC and at an initial pressure of 350torr. The rate of the reaction was 1.07 torr sec^{-1} when 5% of the decomposition was over and 0.76 torr sec^{-1} when 20% was over. Determine the order of the reaction. 4

(c)Write down the Nernst equation and calculate the reduction potential for the reduction of O_2 at pH=7.

(Given : Partial pressure of O_2 {$p(O_2)$}=0.20 bar and E^0=1.229 Vat pH=7.) 4

6.

(a)Consider the following esterification reaction.

$CH_3COOH+C_2H_5OH \leftrightarrow CH_3COOC_2H_5+ H_2O$, 1 mole of the acid and 1 mole of the alcohol are mixed at a temperature of 25^0C. At equilibrium, 0.667 moles of the acid have reacted . Calculate the equilibrium constant ,Kc. How much ester would be obtained if 2 moles of the acid were mixed with 1 mole of the alcohol under identical condition? 4

(b)The solubility of a sparingly soluble salt,silver chromate (Ag_2CrO_4) is $7.5x10^{-5}$ mol lit^{-1}.Assuming complete dissociation, calculate the solubility product of the salt. 2

(c)Draw a schematic phase diagram of the different phases(solid,liquid, and vapour) of a substance. What is a 'triple point'?

7.

(a)5 moles of monatomic ideal gas are compressed reversibly and adiabatically. The initial volume is $6dm^3$ and the final volume is $2dm^3$. The initial temperature is 27^0C.

(i)What would be the final temperature in this process?

(ii)Calculate w,q,and ΔU for the process ,Given C_v=20.91 $Jmol^{-1}K^{-1}$. 4

(b)Calculate the energy per photon for radiation of wavelength 650nm. 2

(c)Write down the molecular orbital electronic configuration foe O_2 and O_3 and compare the bond length and predict their magnetic property. 4

8.

(a)Calculate the frequency of the J=3←2 transition in the pure rotational spectrum of $^{12}C^{16}O$. The equilibrium bond length is 112.81pm. 4

(b)The wave number of the fundamental vibration of $^{79}Br,^{81}Br$ is $323.2cm^{-1}$. Calculate the force constant of the bond [m(^{79}Br)=78.9183 amu, m(^{81}Br)=80.9163 amu). 3

(c)At NTP 2.8 litres of oxygen were mixed with 19.6 litres of hydrogen. Calculate the increase in entropy (Assume ideal gas behaviour). 3