

CHEMISTRY-I

FULL MARK : 70

Standard data:

$h=6.626 \times 10^{-34}$ Js, $R=8.314$ JK⁻¹mol⁻¹, $c=3 \times 10^8$ ms⁻¹, 1

amu= 1.6605×10^{-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) N₂ and CO, (ii) O₂ 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) $\Delta G > 0$, (ii) $\Delta G = 0$, (iii) $\Delta G < 0$?

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

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

3.

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

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad 3$$

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

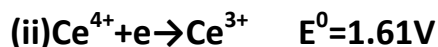
(i) H_2 (ii) NO (iii) HCl and (iv) F_2 2

(c) Calculate ΔS , ΔA , and ΔG 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, $L_v = 101 \text{ cal gm}^{-1}$, Mol.wt. of benzene = 78)

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:



Calculate the reduction potential for the half cell Pt | Ce, Ce⁴⁺ 3

(c) For the reaction : $2\text{NO} + \text{Cl}_2 \leftrightarrow 2\text{NOCl}$, following mechanism has been proposed.

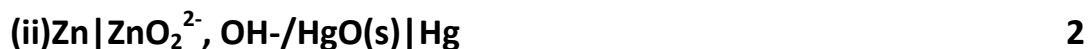
Step-1: $\text{NO} + \text{Cl}_2 \leftrightarrow \text{NOCl}_2$;

Step-2 : $\text{NO} + \text{NOCl}_2 \rightarrow 2\text{NOCl}$

Show that the overall rate of the reaction is $k[\text{NO}]^2[\text{Cl}_2]$, where $k = k_1 k_2 / k_{-1}$ (assume that $k_2[\text{NO}] \ll k_{-1}$)

5.

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



(b) Consider a gaseous decomposition reaction : $\text{A} \rightarrow \text{Products}$, at 500°C and at an initial pressure of 350 torr. 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 O₂ at pH=7.

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

6.

(a) Consider the following esterification reaction.

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$, 1 mole of the acid and 1 mole of the alcohol are mixed at a temperature of $25^\circ C$. At equilibrium, 0.667 moles of the acid have reacted. Calculate the equilibrium constant, K_c . 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 7.5×10^{-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 $6 dm^3$ and the final volume is $2 dm^3$. The initial temperature is $27^\circ C$.

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

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

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

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

8.

(a) Calculate the frequency of the $J=3 \leftarrow 2$ transition in the pure rotational spectrum of $^{12}C^{16}O$. The equilibrium bond length is 112.81 pm. 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 [$m(^{79}\text{Br})=78.9183\text{ amu}$, $m(^{81}\text{Br})=80.9163\text{ amu}$]. 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

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