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Total Pages : 7

# 337303

**December, 2019**

**B.Sc(Chemistry) - III SEMESTER**

**Physical Chemistry - III (BCH 303)**

Time : 3 Hours]

[Max. Marks : 75

*Instructions :*

1. *It is compulsory to answer all the questions (1.5 marks each) of Part -A in short.*
2. *Answer any four questions from Part -B in detail.*
3. *Different sub-parts of a question are to be attempted adjacent to each other.*
4. *Graph paper sheet be provided.*

## PART - A

**1.** (a) The slope of sublimation curve of any substance is greater than of its vaporization curve. Explain. (1.5)

(b) What is the role of salt bridge in electrochemical cells? (1.5)

(c) What is an azeotrope? If pure ethanol has a boiling point of 76.6 °C and its azeotrope has a boiling point of 76.2 °C. What would its graph look like? (1.5)



14/12

23

(d) Triethylene-water system exhibits a lower consolute temperature and above CST the two liquids become partially miscible. Give reasons. (1.5)

(e) Why can't we use a voltmeter to for measuring the voltage of a galvanic cell? (1.5)

(f) How will you distinguish between a compound and its eutectic mixture when they both have sharp melting point? (1.5)

(g) What is the effect of adding naphthalene on the CST of phenol-water system at constant pressure? Explain giving reason. (1.5)

(h) Most adsorption processes are exothermic in nature. Explain. (1.5)

(i) Adsorption of gases on solid surface is n monolayer at high temperature and low pressure. Give reason. (1.5)

(j) What is a standard hydrogen electrode? What is its electrode potential? (1.5)

## PART - B

**2.** (a) Draw and discuss the phase diagram of sulphur which exhibits the phenomenon of enantiotropy. (5)



(b) Phenol and water are partially miscible in each other. Write your observations on

(i) Number of phases and degrees of freedom

(ii) Composition of each phase

(iii) Quantities of layers if there is a phase separation

as phenol is added progressively to a definite quanitity, say 10 mL of water at constant temperature below its CST. (5)

(c) The vapour pressure of ethylene bromide and propylene bromide are 22.93 kPa and 16.93 kPa at 300 K. These two compounds form a nearly ideal mixture. When 3 moles of ethylene bromide and 2 moles of propylene bromide are mixed and allowed to attain equilibrium at 300 K, the total pressure is 20.4 kPa. Calculate the mole fractions of the two components in the liquid state. (5)

**3.** (a) Deduce Gibbs phase rule for a non-reactive system at equilibrium, in which one component is absent in one phase, while the other components are present in all phases. (5)

(b) Construct a labelled phase diagram for two component system consisting of A and B using the following data. Also comment on nature of the compound formed.

Melting point of A = 700 °C;

Melting point of B = 480 °C

One eutectic point is at 330 °C and 20 mol % of A

Another eutectic point is at 410 °C with 80 mol % of A

A solid compound AB2 is formed which melts at 590 °C. (5)

(c) Calculate the number of components in a solution containing $H^+$, $OH^-$, $Na^+$, $Cl^-$, $NO_3^-$, AgCl(s) and $H_2O(l)$. (5)

**4.** (a) State and explain Nernst distribution law and its limitations. (3)

(b) An aqueous solutions contains 10 g of solute per litre of solution. When 1 litre of solution is treated with 100 mL of ether, 6 g of the solute are extracted. Calculate the distribution coefficient, $K_D$ for the distribution of solute between ether and water. How much more solute would be extracted from the aqueous phase by adding a further 100 mL of ether. Assume that the molecular state of solute is same in both solvents. (6)



(c) Draw a labelled triangular phase diagram of chloroform acetic acid water system and explain various regions in it. (6)

**5.** (a) What is e.m.f. of a cell? Describe the method of measuring the e.m.f. of an electrochemical cell using a potentiometer. (5)

(b) The potential of a Harned cell at 25 °C are given below at various molalities of HCl :

$Pt(s) \mid H_2$ (g, 1 bar) | HCl (m) | AgCl(s) | Ag(s)

| $m/10^3$ | 3.215 | 5.619 | 9.138 |
|---|---|---|---|
| $E_{cell}/V$ | 0.52 | 0.49 | 0.47 |

Determine the standard electrode potential of silver-silver chloride electrode graphically. (5)

(c) Starting from Gibbs-Helmholtz equation and relation $\Delta G = -nFE$, derive the relations for $\Delta H$ and $\Delta S$ in terms of temperature coefficients of cell potential. What are the units of $\Delta H$ and $\Delta S$ if F is expressed in coulomb mol 1 and E in volt. (5)

**6.** (a) What is the principle of potentiometric titrations? What are the advantages of potentiometric titrations over the conventional volumetric titrations? (5)

(b) Write the cell with which the equilibrium constant of the following reaction can be determined

$$Cd^{2+} + 4NH_3 \leftrightarrow Cd(NH_3)_4^{2+}$$

Also, determine the standard equilibrium constant for the reaction at 298 K, given that

$E^\circ_{(Cd^{2+}/Cd)} = -0.4$ V and $E^\circ_{(Cd(NH3)4^{2+}/Cd)} = -0.6$ V. (5)

(c) Using Freundlich isotherm expressed in the terms of mass of solute adsorbed per kg of adsorbent ($x$) and concentration C in g/dm$^3$, i.e.,

$$x = k.C^{1/n}$$

Calculate the mass of acetic acid in grams that 900 g of charcoal would adsorb from 0.817 mol/dm$^3$ vinegar solution. The value of constants $k$ and $n$ are 0.16 and 2, respectively. (5)

Q7 (a) What are the assumptions of Langmuir adsorption theory? Using the basis of Langmuir theory of adsorption, show that

$$\theta = \frac{Kp}{1 + Kp} \quad (5)$$



(b) A concentration cell formed from a metal and its nitrate is given below :

$M(s) \mid M(NO_3)_x$ (0.01 M) $\parallel M(NO_3)_x$ (0.1M) $\mid M(s)$

The potential of the cell was found to be 0.0295 V at 298 K. Determine the molecular formula of the metal nitrate. (5)

(c) At 0 °C and 1 atm pressure, the volume of nitrogen gas required to cover a sample of silica gel assuming Langmuir monolayer adsorption is found to be 130 cm$^3$g$^{-1}$ of the gel. Calculate the surface area per gram of the silica gel. Given that area occupied by a $N_2$ molecule is 0.162 nm$^2$. (5)