

This question paper contains 4 printed pages]

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S. No. of Question Paper : 2419

Unique Paper Code : 2172501

F-4

Name of the Paper : Paper-2, Thermodynamics, Equilibrium and Electrochemistry

Name of the Course : Allied Course : Biochemistry

Semester : IV

Duration : 3 Hours

Maximum Marks : 75

*(Write your Roll No. on the top immediately on receipt of this question paper.)*

Attempt five questions in all including

Question No. 1 which is compulsory.

Scientific calculator is allowed

1. Explain the following (any five) :

- (a) The energy required to break O–H bond in water is  $498 \text{ kJ mol}^{-1}$  while in the hydroxyl radical it is  $430 \text{ kJ mol}^{-1}$ .
- (b)  $\text{H}_2\text{S}$  is passed through an acidified solution to precipitate cations of the second group whereas in the fourth group it is passed through an alkaline solution.
- (c) First law of thermodynamics is incapable of predicting the direction of a process.
- (d) A mixture of ammonium chloride and ammonium hydroxide resists changes in its pH value on adding acid or base.

P.T.O.

(e) Ionic molar conductivity at infinite dilution increases in order  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  ?

(f) Variation of molar conductivity of a weak electrolyte with dilution. 3×5

2. (a) Prove that :

$$(i) \left( \frac{\partial H}{\partial p} \right)_T = 0 \text{ for an ideal gas}$$

$$(ii) \left( \frac{\partial E}{\partial V} \right)_P = \frac{C_v}{nR} P$$

(b) State second law of thermodynamics. Prove that  $dS$  is an exact differential.

(c) Derive Gibbs-Helmholtz equation :

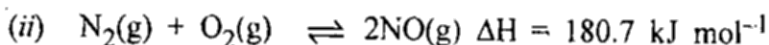
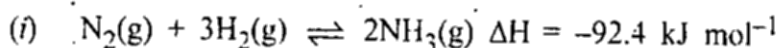
$$\left[ \frac{\partial \left( \frac{\Delta G}{T} \right)}{\partial T} \right]_P = - \frac{\Delta H}{T^2}$$

(d) Prove  $(dG)_{T,P} = (dw)_{\text{net}}$ . 4,4,4,3

3. (a) Two moles of HI were heated in a sealed bulb at  $444^\circ\text{C}$  till equilibrium state was reached and was found to be 22% dissociated at that time. Calculate the equilibrium constant for the dissociation and synthesis reaction.

(b) Derive relation between  $K_c$ ,  $K_p$  and  $K_x$ .

(c) State the effect of the pressure and temperature on the following equilibrium reactions :



(d) What is a chemical equilibrium ? Give characteristics of chemical equilibrium. 5,3,4,3

4. (a) Show that pH of a solution of a salt of strong acid and weak base is given by :

$$\text{pH} = 1/2(\text{pk}_w - \text{pk}_b - \log_{10} C).$$

- (b) Define solubility product of sparingly soluble salt. Calculate molar solubility of  $\text{PbI}_2$  :

(i) In water

(ii) In 0.20 M NaI

Given :  $K_{\text{sp}}(\text{PbI}_2) = 7.9 \times 10^{-9} \text{ M}^3$ .

- (c) What is meant by ionic product of water ? Discuss the effect of temperature on ionic product of water.

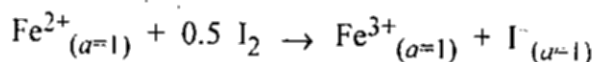
- (d) Define buffer capacity and buffer index.

4,6,3,2

5. (a) Define ionic mobility. Derive the relation of ionic mobility in terms of molar conductivity.

- (b) Define electrode potential and standard electrode potential. Absolute value of an electrode potential cannot be determined. Why ?

- (c) For the reaction :



Write the cell and the two half cell reactions. Calculate its standard e.m.f. Indicate whether the cell reaction represented is spontaneous or not.

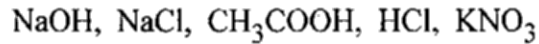
- (d) At 298 K, molar conductivities at infinite dilution for  $\text{AgNO}_3$ ,  $\text{KCl}$  and  $\text{KNO}_3$  are 133.5, 149.9 and  $144.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , respectively. What is the molar conductivity of  $\text{AgCl}$  at infinite dilution ?

4,3,5,3

P.T.O.

6. (a) Calculate the equilibrium constant of a reaction at 300 K if  $\Delta G^\circ$  at this temperature is  $29.4 \text{ kJ mol}^{-1}$ .

(b) Classify the following as strong and weak electrolytes :



(c) State and explain Hess law of constant heat of summation.

(d) Describe hydrogen gas electrode and write Nernst equation for it.

(e) Define transport number.

3,3,4,4,1

7. Write short notes on any *three* of the following :

(a) Kirchhoff's law

(b) Conductometric (acid-base) titration curves

(c) Kohlrausch's law of independent migration of ions

(d) Ostwald's dilution law.

3×5