This question paper contains **4** printed pages]

Roll No. | | | | | | | | | | | |

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 kJ mol^{-1} while in the hydroxyl radical it is 430 kJ mol^{-1}.

   (*b*) H_2S 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.

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(*e*) Ionic molar conductivity at infinite dilution increases in order Li^+, Na^+, K^+, Rb^+ ?

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

2. (*a*) Prove that :

(*i*) $\left(\frac{\partial H}{\partial p}\right)_T = 0$ 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 $(dG)_{T,P} = (dw)_{net}$. 4,4,4,3

3. (*a*) Two moles of HI were heated in a sealed bulb at 444 °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 :

(*i*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92.4$ kJ mol^{-1}

(*ii*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = 180.7$ kJ mol^{-1}

(*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 :

$$pH = 1/2(pk_w - pk_b - \log_{10} C).$$

(*b*) Define solubility product of sparingly soluble salt. Calculate molar solubility of PbI_2 :

(*i*) In water

(*ii*) In 0.20 M NaI

Given : $K_{sp}(PbI_2) = 7.9 \times 10^{-9}\ M^3$.

(*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 :

$$Fe^{2+}_{(a=1)} + 0.5\ I_2 \rightarrow Fe^{3+}_{(a=1)} + I^-_{(a=1)}$$

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 $AgNO_3$, KCl and KNO_3 are 133.5, 149.9 and 144.9 $\Omega^{-1}\ cm^2\ mol^{-1}$, respectively. What is the molar conductivity of AgCl at infinitedilution ? 4,3,5,3

P.T.O.

6. (*a*) Calculate the equilibrium constant of a reaction at 300 K if ΔG° at this temperature is 29.4 kJ mol^{-1}.

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

$NaOH$, $NaCl$, CH_3COOH, HCl, KNO_3

(*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