# 2015

## CHEMISTRY

**[ Honours ]**

PAPER – IV

*Full Marks* : 45

*Time* : 2 hours

*The figures in the right-hand margin indicate marks*

*Candidates are required to give their answers in their own words as far as practicable*

*Illustrate the answers wherever necessary*

## GROUP – A

Answer any **one** question

**1.** (*a*) Derive thermodynamically the van't Hoff equation for osmotic pressure. 6

(*b*) Draw a schematic phase diagram for a two component system in which the components

form a stable compound with congruent metting point. 4

(*c*) The specific conductance of water is $7{\cdot}6 \times 10^{-2}$ $Sm^{-1}$ and the same for 0·1 M aqueous solution of KCl is 1.1639 $Sm^{-1}$. A conductivity cell, when filled with (*i*) 0·1 M KCl solution and (*ii*) 0.1 M acetic acid solution separately recorded resistances of 33·20 Ω and 300 Ω respectively. Calculate the molar conductance of acetic acid. 5

2. (*a*) Explain what is meant by pH of an aqueous solution and discuss the physico-chemical principle for its measurement by using a quinhydrone electrode. 2 + 4

(*b*) Derive the Nernst distribution law from thermodynamic consideration. 4

(*c*) A 0·5 percent aqueous solution of KCl was found to freeze at – 0·24°C. Calculate the van't Hoff factor and the degree of dissociation of the solute at this concentration. (Given $K_f = 1{\cdot}86$ K kg $mol^{-1}$) 3 + 2

## GROUP – B

Answer any **two** questions

3. (*a*) State Raoult's law for vapour pressure of binary solutions of volatile liquids. Show that, if in any solution, the solvent obeys Raoult's law, the solute will obey Henry's law. 2 + 4

(*b*) The standard reduction potentials of $Ce^{4+}$, $Ce^{2+}$; Pt and $Fe^{3+}$, $Fe^{2+}$, Pt electrodes are respectively 1·61 and 0·77 volts respectively at 25°C. Predict the cell, write the cell reaction and calculate the equilibrium constant of the reaction. 1 + 1 + 2

4. (*a*) Discuss the principle of measurement of the relative lowering of vapour pressure by Walker's dynamic method. 6

(*b*) Calculate the ionic strength of a solution containing 0·2 M KCl, 0·1 M $MgSO_4$, 0·05 M $Na_3PO_4$ and 0·2 M urea. 4

5. (*a*) Explain why the nature of the conductometric titration curves of sulphuric acid and oxalic acid with NaOH are different although both of these acids are dibasic. Depict the nature of the curves schematically with brief explanations. 2 + 2 + 2

(*b*) Calculate the pH of a buffer solution which contains 0·20 mole $NH_4OH$ and 0·25 mole of $NH_4Cl$ per litre. (Given : dissociation constant = $1{\cdot}81 \times 10^{-5}$) 4

6. (*a*) Define the term ionic mobility and establish its relation with molar ionic conductance at infinite dilution. 1 + 5

(*b*) The solubility product of magnesium hydroxide at 25°C is $1{\cdot}4 \times 10^{-11}$. Calculate the solubility of this compound in grams per litre. 4

## GROUP – C

7. Answer any *five* questions from the following : 2 × 5

(*a*) Calculate the number of components for the

system NaCl(s), KCl(s), $Na^+(aq)$, $Cl^-(aq)$, $H_2O(l)$, $H_2O(g)$

(*b*) Suggest an experiment to show that mercurous chloride is $Hg_2Cl_2$ and not HgCl.

(*c*) Explain why KCl is used as a salt bridge in certain polentiometric experiments.

(*d*) Solutions *A* and *B* cartain 1·2 g urea and 1·8 g glucose per litre respectively. Solution *B* is maintained at a temperature of 327°C. Calculate the temperature at which solution *A* should be maintained for *A* and *B* to be isotonic.

(*e*) Calculate the standard emf for the reaction from the following data :

$$Fe^{3+} + 3e \rightarrow Fe(s)$$

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

$$Fe^{2+} + 2e \rightarrow Fe(s)$$

$$\varepsilon_1^0 = 0{\cdot}77 \text{ V}$$

$$\varepsilon_2^0 = -0{\cdot}44 \text{ V}$$

(*f*) Calculate the degree of hydrolysis($x$) of 0·10 M solution of sodium acetate at 25°C. Assume $x$ to be small and $K_a = 1{\cdot}75 \times 10^{-5}$.

(*g*) Discuss briefly how the equivalent conductance at infinite dilution of a strong electrolyte is measured experimentally.

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