2016

CHEMISTRY

[Honours]

PAPER – IV

Full Marks : 45

Time : 2 hours

The figures in the right hand margin indicate marks

[OLD SYLLABUS]

GROUP – A

Answer **one** of the following : 15×1

1. (*a*) How would you identify the following three identical looking liquids ?

(*i*) pure metal *A* (*ii*) eutectic mixture of two metals *A* and *B* (*iii*) non-eutectic mixture of metals *A* and *B*. Explain with suitable diagrams. 5

(*b*) Determine the degrees of freedom of the mixture having eutectic composition. 2

(*c*) What is Van't Hoff factor ? Can it be integrable ? 3

(*d*) The solubility product of CaF_2 at 27° C is $3{\cdot}55 \times 10^{-1}$. Calculate the solubility of CaF_2 at 27° C in moles/litre. 2

(*e*) The specific conductance of a saturated solution of AgCl is $1{\cdot}55 \times 10^{-6}$ mho.cm^{-1}. The mobilities of Cl^- and Ag+ ions are $5{\cdot}6 \times 10^{-4}$ cm·sec^{-1} and $6{\cdot}8 \times 10^{-4}$ cm·sec^{-1} respectively under unit potential gradient. Calculate the solubility product of AgCl. 3

2. (*a*) 1 % solution of $AgNO_3$ is isotonic with the 2% solution of glucose. Calculate the degree of dissociation of $AgNO_3$ given that atomic weight of Ag = 107·8 gm. 3

(*b*) Derive the relation between ionic mobility with its conductance mentioning assumptions, if any. 4

(*c*) The specific conductances of a saturated solution of $SrSO_4$ and water are $1{\cdot}482 \times 10^{-4}$ mho.cm^{-1} and $1{\cdot}5 \times 10^{-6}$ mho.cm^{-1} respectively at 25° C. If the ion conductances of Sr^{+2} and SO_4^{-2} are 59·46 mho.cm^2.gm.eq^{-1} and 79·8 mho.cm^2.gm.eq^{-1} respectively at this temperature, calculate the solubility of the salt in gm.l^{-1} given that molecular weight of $SrSO_4$ = 182 gm. 4

(*d*) Water-phenol system shows upper consolute temperature. Determine its degree of freedom. How would (*i*) pressure on the system and (*ii*) small amount of NaCl in water affect upper consolute temperature ? Explain with plausible reasons. $1+1\frac{1}{2}+1\frac{1}{2}$

GROUP – B

Answer any **two** questions : 10×2

3. (*a*) "In a solution if solvent obey Rault's law, solute must follow Henry's law.— Justify. 3

(*b*) Melting point of ice decreases with increase in pressure whereas others show opposite. Explain with suitable diagrams. 4

(*c*) The plot of $\frac{1}{\wedge}$ vs. $\wedge c$ for a weak electrolyte has unit slope. Express dissociation constant of the weak electrolyte in terms of α and $\wedge$. Here all the symbols carry usual significances. 3

4. (*a*) 200 ml of 0·002 (M) NaCl is added to 200 ml of 0·004 (M) $AgNO_3$. Calculate the specific conductance of the mixture. Given, $\lambda_{Na^+} = 50{\cdot}1$, $\lambda_{Cl^-} = 76{\cdot}3$, $\lambda_{Ag^+} = 61{\cdot}9$, $\lambda_{NO_3^-} = 71{\cdot}4$. 3

(*b*) Construct a reversible cell without transference for the process

$$HCl(a_2) \rightarrow HCl(a_1)\ a_1 < a_2$$

and find the e.m.f. of the cell. 3

(*c*) Set up a reversible cell for the reaction $H_2(g) + O_2(g) \rightarrow H_2O(l)$ at 25° C. If for the

reaction, $\Delta G^{\circ} = -237{\cdot}2$ kJ and $\Delta H^{\circ} = -285{\cdot}9$ kJ, find (*i*) E° of the cell (*ii*) the rate at which E° changes with temperature at 25° C. 4

5. (*a*) Derive Nernst equation for the emf of a cell where the following reaction takes place.

$$\gamma_1 A + \gamma_2 B \rightleftharpoons \gamma_3 C + \gamma_4 D$$ 2

(*b*) Draw conductometric titration curve for the titration of equimolar mixture of strong acid and weak acid by NaOH. Both the acids are monobaric. Give plausible explanation. 4

(*c*) Solubility of AgCl in water is 10^{-5} mole/litre. Arrange the solubility of AgCl in increasing order in (*i*) 0·01 (M) $NaNO_3$ (*ii*) 0·01 (M) $Ca(NO_3)_2$ (*iii*) water (*iv*) 0·01 (M) NaCl. Give plausible reasons without calculating the solubility of AgCl in all the solutions. 4

6. (*a*) What is a buffer solution ? How does it act ? 2 + 2

(*b*) You are supplied with two weak acids *A* and *B* of pKa of the acids are 4·8 and 5·8 respectively. Which one would you prefer to prepare a buffer solution of pH 4·0 ? 2

(*c*) Show graphically the variation of equivalent conductance with the concentration of (*i*) CH_3COOH (*ii*) HCl. 2

(*d*) Mixture of tolune and benzene form ideal solution. Draw a figure showing variation of partial pressures of the components and total vapour pressure with variation of concentration of one component. Where benzene is more volatile than tolune ? 2

GROUP – C

Answer any **five** questions : 5×2

7. (*a*) Mixture of acetone and chloroform shows negative deviation in vapour pressure vs. concentration curve. Mention the name of the law followed by each component when mole fraction of chloroform is close to 1– where acetone is more volatile than chloroform.

(*Continued*)

(*b*) "Volatile solute dissolved in a solvent can never lead to elevation of boiling point of the solvent." Justify or criticize.

(*c*) Why the transport number of an ion can never be greater than 1 ? Explain.

(*d*) Why does Li^+ ion move slower than K^+ ion in water ?

(*e*) Using Debye-Hückel limiting law calculate mean acitivity coefficient of 0·001 (M) aqueous solution of $K_4[Fe(CN)_6]$. Given that Debye-Hückel constant is 0·51.

(*f*) "The standard electrode potential of the Fe^{+3}/Fe^{+2} is 0·77 volt." State the meaning of the statement.

(*g*) Can we write for an irreversibel cell $nFE^\circ = RT\ln K_{eq}$? Explain.
