2017

CHEMISTRY

[Honours]

PAPER – IV

Full Marks : 45

Time : 2 hours

The figures in the right hand margin indicate marks

[OLD SYLLABUS]

GROUP – A

Answer any **one** question : 15 × 1

1. (*a*) Discuss the physico-chemical principle involved in the measurement of pH of an aqueous solution by using a quinhydrone electrode. 6

(*b*) Explain why there occurs a lowering of vapour pressure of a solvent when a nonvolatile

solute is dissolved in it. How is relative lowering of vapour pressure measured experimentally by Walker's Dynamic Method ? 2 + 3

(*c*) In 20·0 ml of a 0·2 M acetic acid (pK = 4·8) is added (*i*) 5·0 ml and (*ii*) 10·0 ml of NaOH solution separately. Calculate the pH of the solution in the two cases and state with reason, in which case the buffer capacity will be greater. 3 + 1

2. (*a*) Derive thermodynamically the relation between the osmotic pressure of a solution and its molar concentration. 6

(*b*) Obtain the suitable expression for the experimental determination of the degree of hydrolysis of a salt of a strong acid and a weak base. 5

(*c*) Calculate the number of components in (*i*) KCl-NaCl-H_2O and (*ii*) KCl-NaBr-H_2O systems. 2 + 2

GROUP – B

Answer any **two** questions : 10 × 2

3. (*a*) Set up an appropriate cell and derive the expression for its emf, for the determination of the ionic product of water. 1 + 3

(*b*) Depict an approximate representation of the phase diagram of a system in which the two components form compounds with congruent melting points. 3

(*c*) Boiling point of benzene is 80°C and its latent heat of vapourisation is 94 cal g^{-1}. A solution of 9·504 g of a nonvolatile solute in 42·0 g of benzene boil at 80·38°C. Calculate the molar mass of the solute. 3

4. (*a*) Write down, without derivation, the expression for the emf of concentration cells with trasference and without transference and hence obtain the expression for the liquid *junction potential*. 4

(*b*) Define the term transference number of an ion and discuss the principle of its determination by the moving boundary method. 1 + 2

(*c*) Henry law constant for $H_2(g)$ in water is $5{\cdot}34 \times 10^7$ torr. Calculate the solubility of the gas in water at 25°C if its partial pressure over the solution is 760 torr. (Assume that density of the solution is the same as that of the solvent and no. of moles of the solute is negligible in comparison with those of solvent). 3

5. (*a*) State the Nernst Distribution law. How is this law derived from thermodynamic considerations ? 1 + 3

(*b*) Depict, with explanations, the nature of the conductometric titration curves for the titration of (*i*) HCl with NH_4OH as titrant and (*ii*) $AgNO_3$ with KCl as titrant. 3

(*c*) The standard redox potentials of Fe^{3+}, Fe^{2+}; Pt and Sn^{4+}, Sn^{2+}; Pt electrodes are respectively

0·77 V and 0·15 volt at 25°C. Depict the cell, with the cell reaction and calculate the equilibrium constant of the reaction that occurs in the cell. 3

6. (*a*) What is meant by the cryoscopic constant of a solvent ? Describe any method for its determination. 1 + 2

(*b*) The equivalent conductance values at infinite dilution in $ohm^{-1}cm^2 equiv^{-1}$ were found for the electrolytes KCl, NaCl, KNO_3 and $NaNO_3$ to be 149·9, 128·8, 145·0 and 123·9 respectively. Generalise the observation, with reason in the form of a law and give the statement of the law. 2

(*c*) Three separate plots of equivalent conductance against square root of concentration ($\sqrt{c}$) for three strong electrolytes. Sodium acetate, sodium chloride and hydrochloric acid yielded three intercepts in appropriate unit having values 91, 127 and 426 respectively.

A 0·2 M acetic acid in a conductivity cell of cell constant 0·36 cm^{-1} offered a resistance of 509 ohm at 25°C. Calculate the degree of dissociation of acetic acid. 5

GROUP – C

7. Answer any *five* questions : 2×5

(*a*) Suggest an experiment, based on emf measurement, to show that mercurous ion, is Hg_2^{++} and not Hg^{+}.

(*b*) Explain why KCl is used in the salt bridge for emf measurements.

(*c*) Give an example where abnormal value of transport number is observed. Discuss the reason for such observation.

(*d*) Consider two solution of KCl having concentration (*i*) 0·1 N and (*ii*) 0·01 N whose, conductance value(s) are measured by using a conductivity cell with cell constant 1·0 cm^{-1}. Comment on the value(s)

of measured conductance and calculated specific conductance and equivalent conductance assuming ideal behaviour of the two solutions.

(*e*) A solution is 0·5 M in $MgSO_4$, 0·1 M in $AlCl_3$ and 0·2 M in $(NH_4)_2SO_4$. Calculate the total ionic strength.

(*f*) Consider three solutions of (*i*) Urea (0·60 g) (*ii*) glucose(1·80 g) and (*iii*) KCl(0·74 g) per 100 ml of the solution at 25°C in each case state, with reason, which of the three pairs of solution will be isotomic.

(*g*) Calculate the temperature at which the osmotic pressure of a solution will be doubled.
