No. of printed pages: 3

[A-22]

SARDAR PATEL UNIVERSITY

M. Sc. (Semester –IV) Examination

Saturday, 25th APRIL 2015

10.30 a.m. to 01.30 p.m.

PS04CPHC03: ELECTRO ANALYTICAL METHODS

Note: Figures to the right indicate full marks. Total Marks: 70

Q. 1 Select the correct answer: (08)

[1] The emf of the cell Tl / Tl^{+} (0.001M) // Cu^{+2} (0.01M) /Cu is 0.83 V.The cell emf can be increased by

(a) Increasing concentration of Tl^{+} **(b) Increasing concentration of Cu^{+2}**

(c) Increasing concentration of Tl^{+} and Cu^{+2} **(d) None**

[2] If a salt bridge is removed from the two half cells, the voltage

(a) Drops to zero **(b)Does not change**

(c) Increases slowly **(d) Increases Rapidly**

[3] The number of coulombs required for the deposition of 107.80 gms of silver is

(a) 96500 **(b) 10,000**

(c) 48250 **(d) 93000**

[4] A current of 2.6 ampere was passed through $CuSO_4$ solution for 380 second .The copper deposited is (Cu = 63.5)

(a) 0.3250 **(b) 0.635**

(c) 6.35 **(d) 3.175**

[5] What is the P^{H} of a solution having H+ ion concentration of 3.3×10^{-11}

(a) 10.48 **(b) 8.5**

(c) 8.4815 **(d) 6.4**

[6] When P^{H} of a solution decreases , its H^{+} ion concentration

(a) Decreases **(b) Increases**

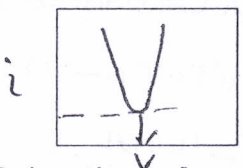
(c) Remains constant **(d) Increases rapidly**

[7] The two Pt electrodes filled in the conductance cell are 1.5 cm apart, having cross sectional area of each electrode is 0.75cm^2. The cell constant value is

(a) 1.25 cm^{-1} **(b) 0.5 cm^{-1}**

(c) 2.0 cm^{-1} **(d) 0.2 cm^{-1}**

[8] For the following amperometric curve



(a) sample is active and reagent is inactive

(b) sample and reagent is both

(c) sample and reagent both inactive

(d) sample is inactive and reagent is active

Q . 2 Answer any seven of the following: **(14)**

(a) For the cell, $Mg_{(s)} + 2Ag^{+}\ (0.0001M) \rightarrow Mg^{2+}\ (0.13M) + 2\ Ag_{(s)}$.

Calculate E_{cell} if $E^{0}_{cell} = 3.17$ v.

(b) State Faraday's laws of electrolysis.

(c) Differentiate between Galvanic and electrolytic cell.

(d) State forces apply on electrode surface during electrolysis in polarography. How these forces can be minimize?

(e) Using $\Delta E = q + w$, Obtain $\Delta G = W_{electrical}$

(f) A solution of $P^{H} = 9$ is one thousand times as basic as solution. Calculate the P^{H} of the solution.

(g) Obtain P^{H} = — log Ka for monobasic weak acid.

(h) A solution containing 0.25 gms of Cu^{+2} requires 20 minutes for complete deposition Of Copper at 1.25 A. Calculate coulomb requires for the deposition.
(Cu = 63.54.F = 96500)

(i) Calculate equilibrium constant for the reaction : $Cu_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Cu^{2+} + 2Ag_{(s)}$

(Given : $E^{0}_{cell} = 0.46$ v, where $E_{cell} = 0$)

Q. 3

(a) Discuss factors affecting P^{H} measurement with glass electrode. **(06)**

Why calibration of glass electrode is required ?

(b) Calculate P^{H} during the titration of 50 ml of 0.05 M HCl with 0.1 M NaOH at different addition of NaOH solution. i.e. 0.0 ml, 10 ml , 25 ml , and 25.5 ml. **(06)**

OR

(b) Discuss hydrogen electrode and antimony electrode. **(06)**

Q.4 (a) Outline electrochemical cell. Discuss electrolytic concentration cell without and with liquid junction potential.(Reversible to Cation and Reversible to anion) **(06)**

(b) Obtain the relations: (i) $\Delta H = nF\ [\ T\ (\partial E/\partial T\ )_P$ — E] (ii) $E^{0} = RT/nF$ ln K and (iii) $\log K_{sp} = E^{0}_{cell} / 0.0591$ **(06)**

OR

(b) For a cell Zn / $ZnCl_{2\,(aq)}$ / $AgCl_{(s)}$ / Ag, the emf is 1.02V at 0^{0}C and 1.0196 V at 1^{0}C. **(06)**

Write down cell reaction and calculate ΔG, ΔS and ΔH for the reaction.(F = 98485)

Q.5 (a) Write down mathematical form of Kohlarausch's law of independent migration of Ions. Discuss its applications. (06)

(b) State advantages and disadvantages of high frequency conductance method. (06)

OR

(b) (i) A 0.180 grams of organic acid was titrated coulometrically with OH^- ions Produced in 5 minutes by constant current of 0.514 ampere. Calculate the mass of the acid (n = 1, and F = 96500) (06)

(ii) Calculate equivalent conductance of acetic acid at infinite dilution if ionic conductance's at 25^0C for HCl =349.8, NaCl =126.4, and NaAc= 91.00

Q.6 (a) The diffusion current of Pb^{+2} in an unknown solution is 5.6 μA. 1 ml of 1.0×10^{-3} M Pb^{+2} solution is added to 10 ml of unknown solution and the diffusion current of the Pb^{+2} is increased to 12.0 μA.. (06)

What is the concentration of Pb^{+2} in the unknown solution.

(b) P- Phylene diamine, present in 0.488 mM concentration and having an applied current of 29.0 μA,had transition time of 76.8 second.What is the electron change Involved if the electrode had surface area of 1.72 cm^2 and D =0.92×10^{-5} (F = 96500 and π = 3.14) (06)

OR

(b) (i)Discuss current sample and cyclic voltametry. (03)

(ii) State applications of amperometry. (03)

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