[97] SEAT No._____ No. of Printed Pages: 2

[97] SARDAR PATEL UNIVERSITY

M.Sc. (Chemistry) Examination, Fourth Semester

Wednesday, Date: 20-03-2019

Time: 2.00 p.m. to 5.00 p.m.

Subject: Electro-Analytical Methods Paper: PS04CANC22

[Total Marks: 70]

N.B. (1) Figures to the right indicate full marks.
(2) Attempt all questions.

Q.1 Select the correct answer from each of the following: (08)

1. The internal filling solution in the glass membrane electrode is
   (a) HCl (b) KI (c) aqueous salt solution (d) none of these

2. In amperometric titration, the results of the titration are independent of the _____.
   (a) concentration (c) capillary characteristic
   (b) potential (d) diffusion co-efficient

3. Potentiometric titration can be carried out on micro-level up to _____M.
   (a) 10^{-4} (b) 10^{-5} (c) 10^{-6} (d) 10^{-7}

4. In high frequency method, the titrimeter can be easily connected to a potentiometic recorder, so that the variation of _____ current may be plotted as a function of time.
   (a) Oscillator (b) Inductive (c) Capacitative (d) Diffusion

5. Conductometric cells with _____paths are used for concentrated solutions, so that the resistance to be measured may be of convenient magnitude
   (a) short (b) equal (c) long (d) not equal

6. Only when written as a _____reaction will the sign of the e.m.f. of the half-reaction corresponds to the sign of the electrode potential.
   (a) oxidation (b) reduction (c) redox (d) all of above

7. The DME can not be used at potentials more positive than 0.3 V because Hg _____ at such potentials.
   (a) reduce (b) oxidize (c) remains inert (d) remains active

8. Calcium selective electrode is an example of _____electrode.
   (a) Glass membrane (b) Solid-state (c) Molecular selective (d) Liquid

Q.2 Answer the following: **(Any Seven)** (14)

[i] Write down ILKOVIC equation and explain terms involved in it.

[ii] Define the terms: Ionic conductance and migration current.

[iii] Discuss alkaline error and acid error.

[iv] Explain the basic principles involved in amperometry.

[v] Differentiate: Galvanic and electrolytic cell.

[vi] Discuss in brief on polarographic maxima.

[vii] Write the advantages of high frequency conductance method.

[viii] Define: Electrode potential and Diffusion potential.

[ix] Derive: $E^\circ = (RT/nF) \ln k$

(P.T.O)

Q.3 [a] Discuss on solid state and liquid membrane ion selective electrode. **(6)**

[b] Answer the followings: **(6)**

[i] Write the advantages and disadvantages of hydrogen electrode.

[ii] Give the classification and advantages of electro analytical methods.

OR

[b] Answer the followings: **(6)**

[i] Determination of dissociation constant for monobasic weak base.

[ii] Why calibration of glass electrode is required?

Q.4 [a] Differentiate between amperostatic coulometry and potentiostatic coulometry. **(6)**

[b] Answer the followings: **(6)**

[i] HCl is titrated coulometrically with electrolytically generated ion OH^- at a constant current of 10 mA. The point of equivalence on the titration of 5 ml. of solution being analytical is reacted for 3 min. and 10 sec. Calculate the titer of HCl solution with respect to NaOH.

[ii] Differentiate between direct potentiometry and potentiometric titration.

OR

[b] Write in brief on advantages of potentiometric titration and applications of an ion selective electrodes. **(6)**

Q.5 [a] Answer the followings: **(6)**

[i] Give the method to determine ionic product of water using conductometer.

[ii] Discuss about the cells used in high frequency conductance method and mention the advantages and disadvantages of high frequency titration.

[b] Write the principle of conductometric titration and discuss the following nature of curves with proper explanation: **(6)**
(1) Weak acid Vs. Strong Base (2) Weak acid Vs. Weak Base (3) Complexometric titration

OR

[b] Let us consider that one is titrating 100 ml of 0.01N HCl solution with 0.1N NaOH in the cell whose cell constant is 1.0 cm^{-1}, under this condition find out the conductance at (i) at the start (ii) after addition of 9 ml NaOH solution (iii) at the equivalence point (iv) after addition of 11ml of the NaOH. (λ_{H^+} = 350, λ_{Cl^-} = 76, λ_{Na^+} = 50, λ_{OH^-} = 198) **(6)**

Q.6 [a] Answer the followings: **(6)**

[i] Explain the basic principle in polarography. How is the technique useful in qualitative and quantitative analysis?

[ii] Give an account of the DME along with their advantages and limitation.

[b] Write short note on: **(6)**

[i] Titration with Rotating platinum microelectrode.

[ii] Cyclic Voltametry.

OR

[b] The following data were obtained on the rising portion of a polarographic wave for the reduction of 4.20 mM nitrate in DMF at 25 °C on the plateau of the polarographic wave. The drop time was 34.9 sec. for 10 drops and 20 drops had a mass of 0.1296 gm. The diffusion current was 14.25 μA. Determine $E_{½}$, n and D for nitrate in DMF. All current measurements were made at the top of the undamped records trace. **(6)**

E vs. $Ag/AgNO_3$ (0.01M) V	-2.400	-2.420	-2.440	-2.460	-2.480	-2.460
i, μA	1.00	2.28	3.50	6.00	9.00	11.17

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