



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FOURTH SEMESTER – APRIL 2017

CH 4814- ELECTROCHEMISTRY

Date: 20-04-2017
Time: 09:00-12:00

Dept. No.

Max. : 100 Marks

Part-A

Answer ALL questions.

(10 x 2= 20)

1. Write an expression for the mean ionic activity of Na_2CrO_4 in terms of its molality and mean ionic activity coefficients.
2. How is van't Hoff factor related to degree of dissociation constant?
3. Write the derived differential capacitance of Gouy-Chapman-Stern double layer.
4. How does electroosmosis help to improve separation efficiency in capillary electrophoresis?
5. Draw the general pattern of the plot of current density versus overvoltage for an electrode with symmetry factor 0.75.
6. What do you mean by the low field approximation of the Butler-Volmer equation?
7. The Tafel slope of the plot of $\ln i$ vs η for positive overpotential was found to be 58.42. Obtain the corresponding transfer coefficient.
8. Predict the condition for the net current density to be independent of symmetry factor.
9. What are faradaic and condenser currents?
10. Calculate the reduction potential of $\text{Cr}_2\text{O}_7^{2-}|\text{Cr}^{3+}$ reaction at a pH of 3. Given SRP of $\text{Cr}_2\text{O}_7^{2-}|\text{Cr}^{3+} = 1.33\text{V}$.

Part-B

Answer any EIGHT questions.

(8 x 5= 40)

11. Acetic acid associates and forms dimer. 1.60 g of acetic acid when dissolved in 100 g of benzene raised the boiling point by 0.35 K. Calculate the van't Hoff factor and degree of association of benzoic acid. The molal elevation constant, K_b for benzene is $2.57 \text{ K Kg mol}^{-1}$.
12. Explain the influence of relaxation and electrophoretic effects on the conductivity of a dilute solution of strong electrolyte.
13. What is zeta potential? Write the significance and applications of zeta potential.
14. Discuss the Gouy-Chapman diffuse-charge model of the double layer.
15. Compare the following HFA plots (i) $\ln i$ vs +ve η (ii) $\log i$ vs -ve η .
16. Derive an expression for the anodic current density across an electrode as a function of applied potential for an electrode process involving more than one electron in overall reaction.
17. Distinguish between polarizable and non-polarizable electrodes.
18. Explain anodic and cathodic rectification behavior of electrodes.
19. Deduce Nernst equation from Butler-Volmer equation.
20. The exchange current density of $\text{Pt}|\text{H}_2, \text{H}^+$ is 0.79 mA cm^{-2} at 25°C . Calculate the current density across it when the over potential is i) 100 mV ii) -200 mV.
21. Discuss the following i) diffusion current ii) limiting current
22. Explain the mechanism of electrochemical reduction of nitro compound with an example.

Part-C

Answer any FOUR questions.

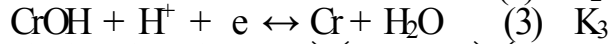
(4 x 10= 40)

23. Derive an expression for Debye-Huckel limiting law.
24. Discuss the Bjerrum theory of ion association.

25. How is the capacitance of an electrified interface determined using parallel-plate condenser model?
26a. How are the transfer coefficients evaluated theoretically for the reduction of iron when the second step is treated as the slowest step. (6)

b. How will you compare the kinetics of hydrogen evolution reaction over the surfaces of Tl and Rh. (4)

27. The reduction of Cr^{2+} to Cr follows the following mechanism



Calculate the values of $\vec{\gamma}$; $\tilde{\gamma}$; v ; r ; $\vec{\alpha}$; $\tilde{\alpha}$ if step 2 is treated as the rate determining step.

- 28a. Discuss the types of voltage sweeps used in polarography.

b. Describe the importance of Pourbaix diagram to understand the thermodynamic stability of iron at different pH values.

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