Analytical Electrochemistry Topics and Reading Assignments

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1.
         Electrochemical cell -- B&F 2.1, (2.2)
                   Physical description of cell
                   Measure potential
                   Calculate potential
                   Notation for cell, sign conventions
                   Why don't we just "ground the solution?"
                   Galvanic cell
                   Electrolytic cell
2.
         Charge transfer in a cell / equivalent circuit -- B&F 1.1-1.3
                   Concept of R<sub>internal</sub> of a cell
                   Physical processes in cell: Eeq, Rct, Rmt, Cedl, Rs, Eappl, V, i
                   Equivalent circuit
                   Application of Kirchhoff's 2nd law to equivaent circuit
                             direction of i
                             resistors
                             battery symbol
         Thermodynamics -- B&F 2.1
                   Reversibility
                   \Delta G^{\circ} = -nE^{\circ}F = -RT \ln K
                   Sum of E°'s
3.
         Mass transfer I - R<sub>s</sub> (migration only) -- B&F 1.4.1; 2.3.3
                   Nernst Planck equation
                   Derive specific conductivity (k) from N-P equation
                   Practical conductivity: calculate \kappa from \lambda
                   Define transport number, t<sub>i</sub>
4.
         Mass transfer II - R<sub>mt</sub> (diffusion only, time-dependent solution) -- B&F 1.4.2; 5.2.1
                   Ficks laws
                   Relation of current to flux
                   Semi-infinite boundary conditions
                   Cottrell equation
5.
         Mass transfer III - R<sub>mt</sub> (diffusion and advection, steady state solution) -- B&F 1.4.2; 5.1.1; 5.4.3-5.4.4
                   Derivation of I vs E curves
                             R insoluble
                             R initially absent
                             R initially present
                   Significance of i_l, E_{eq}, and E_{\frac{1}{2}}
                   Relation of ss-model to RDE, DME, and stagnant boundary layer (Nernst diffusion layer)
         Kinetics - R<sub>ct</sub> - phenomenological approach -- B&F 3.1-3.4; 3.5
6.
                   Observables: overpotential, i vs. E curves
                   Homogeneous kinetics
                   Heterogeneous electochemical kinetics
                   Butler-Volmer equation
                   High overpotentials: Tafel plot
                   Low overpotentials: Rct
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Combined effects of Rct and Rmt

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7. Electric double layer -- B&F 1.2; 13.1-13.3

Importance in electroanalytical chemistry: conductometry, polarography, adsorption

Experimental data for $\,C,\,q,\,\gamma\,$

Gibbs equation to relate C, q, γ

Helmholtz model

Gouy Chapman model, low potential limiting case and full case

Stern model, limiting cases for differential capacitance

(Adorption isotherms - linear, Langmuir, Frumkin)

8. Potentiometry -- B&F 2.4, 2.3

Overview

Noncrystalline

Crystalline

Calculation of E^{0'} from thermodynamic constants

Other: gas, enzyme

Examples of diffusion potentials

Derivation of Henderson equation

pH meter circuit and calibration

9. Voltammetric techniques -- B&F 6.1-6.2; 6.5; 7.3.5; 11.8

LSV

CV

Square wave

Stripping

10. Instrumentation -- B&F 1.3.4; 15.1-15.4; 15.6

Need for 3-electrode cell

Fundamental op-amp circuits

Potentiostat

11. Special Topics ...

Donnan potential and suspension effect

Corrosion

Sensors

Environmental electrochemistry

Fuel cells