

## CHEM.774 Electrochemistry for Chemists.

Winter 2010-2011.

*"Everything you always wanted to know about electrochemistry but were afraid to ask"* (with apologies to W. Allen)

**Usual instructor:** Prof. A. W. Addison. (AddisonA@drexel.edu; 12-418; x2646).

This course incorporates both lecture sessions (Weds. & Fri.) and laboratory activities (Fridays). Your grade will be based on your treatment of your experimental data/results, and on the homework assignments; I do not plan a final exam. The coverage is aimed at using electrochemical techniques to reveal the thermodynamic and kinetic properties of molecules, rather than for quantitative chemical analysis (determination of concentration/amount).

### Text sources:

- C.M.A. Brett & A.M.O. Brett, "Electrochemistry: Principles, Methods & Applications", Oxford U.P. 1993 [hc]. QD553.B74.1993.

Fairly wide coverage, though some methods are short on detail/examples. Nonetheless it's fairly readable, and costs a fair bit less than the alternatives, so if you want to buy a book that has general utility, this is a reasonable choice. Another nice little bok with a good summary of matters electrodic is:

- A.C. Fisher, "Electrode Dynamics", Oxford University Press 1996, #34 in the "oxford Chemistry Primers" series, [pb] \$30. If you want something more comprehensive than Brett/Fisher, then:

- A.J. Bard, L.R. Faulkner, "Electrochemical Methods: Fundamentals & Applications", Wiley 2001, ISBN 0471043729 [hc] \$115. QD553.B37.2001, which is more or less 'the bible' of electrochemical theory and methods. *On reserve in Hagerty Library.*

- C.H. Hamann, A. Hamnett & W. Vielstich, "Electrochemistry", Wiley-VCH 2007, \$80. ISBN= 978-3-527-31069-2. Fairly comprehensive, but a bit thin on how to use various instrumentation-based methods, with more coverage of 'applied' and of 'traditional' electrochem. theory. Better than the original 1998 edition, which had lots of typos.

- D.T. Sawyer, A. Sobkowiak & J.L. Roberts, "Electrochemistry for Chemists" (Hardcover), Wiley-Interscience 1995. Hardcover, ISBN 0-471-59468-7, \$120, QD553.S32.1995. Fairly practical, with a chapter on examples, though there are a few things I don't "get" just yet ...

- R. Holze, "Experimental Electrochemistry: a Laboratory Textbook". Wiley-VCH 2009 [pb], ISBN= 978-3-527-31098-2, \$40. Quite a few nice experiments one could do, but thin on what for me passes as "theory".

- K. Izutsu, "Electrochemistry in Nonaqueous Solutions", Wiley-VCH Weinheim, 2002, QD555.6.N56.I98.2002. Not bad - both practical stuff and useful theory - easier than HH&V.

- P.T. Kissinger & W.R. Heineman, "Laboratory Techniques in Electroanalytical Chemistry", Second Edn., Marcel Dekker, 1996, \$100. This has been a pretty good book, though I've not seen this 2<sup>nd</sup> edition yet (it's checked out of Hagerty right now)

- Eds. Weissberger and Rossiter, "Techniques of Chemistry" —> "Physical Methods of Chemistry" —> "Electrochemical Methods": Wiley-Interscience: supposedly at QD61.P47.1986; 2-4 volumes on electrochemical data and methods for analytical, organic chemistry. Volume-1, Part-IIA is on various electrochemical techniques.

Volume-2 is about properties of solvents - a useful lab volume.

Volume-5, Part-II: Ed. Weinberg: pp667-1056, H. Siegerman, "Oxidation & Reduction Potentials of Organic Compounds" (Tables); QD251.W362

- "Electrochemistry at Solid Electrodes", R.N. Adams, Marcel Dekker New York, NY, 1969. A still-useful classic with definitive info about doing voltammetry & RDE polarography.
- F.C. Anson, "Electroanalytical Chemistry", ACS Audio Course (six one-hour audio cassettes and workbook): Hagerty Library Non-Print Division, *Phonotape E387*.
- L. Meites, "CRC Handbook Series in Organic Electrochemistry" CRC Press, 1977. Tables of organic redox potentials; QD272.E4.C17x, four volumes. Its classic forebear is
- W.M. Clark, "Oxidation-Reduction Potentials of Organic Systems", Williams & Wilkins, Baltimore, 1960. Has many short data tables; expounds on several principles, and was The Source for early practitioners of biological redox chemistry; QD281.09.C55
- L. Meites, "CRC Handbook Series in Inorganic Electrochemistry" CRC Press, 1980. Tables of redox potentials for inorganic ions and complexes; QD557.C73, five volumes.
- Eds. A. J. Bard, R. Parsons & J. Jordan, "Standard potentials in aqueous solution". M. Dekker, New York, 1985. QD571.S74 1985. A bigish book with many inorganic redox potentials.

**Topics.** *The order, accentuation and coverage is not set in stone, though the more 'fundamental' stuff obviously needs to come first.*

- Some simple electrochemical thermodynamics reviewed: Nernst eqn., cells, half-cells, standard cells, the SHE & standard electrode potentials.
- Units & definitions. Redox indicators, redox buffers.
- Kohlrausch's laws, ion mobility, LJP's, intro. to nonaqueous.
- LUMO/HOMO correlation with  $E^\circ$ . Electrical double layer.
- Reference electrodes.
- Potentiometry, diffusion layer, migration current.
- Chronoamperometry, Cottrell Eqn.,  $iQ$  plots, capacitive current.
- Electrode & cell technology, solvents, supporting electrolytes, nonaqueous solutions; reference electrodes, diffusion coefficients, viscosities, Walden's Rule. The unfortunate consequences of solution resistance;  $iR$  compensation.
- Dropping mercury electrode polarography, Ilkovič equation.
- Rotating disk electrode, Levich eqn., Gregory/Riddiford eqn. Reversible & irreversible processes, electron-transfer rates. The ring-disk electrode, kinetics studies.
- Heterogeneous electron-transfer kinetics.
- Cyclic voltammetry: Randles/Sevcik & Nicholson/Shain results for planar and spherical electrodes. Potential and current characteristics.
- CV for simple (binding) equilibria; some structural influences on  $E_{1/2}$ 's.
- CV at cylindrical electrodes by Stephens/Moorhead, Aoyagi/Matsuda & Addison models.
- Sequential processes, stripping voltammetry. Contrast CV with RDE.
- Pulse methods: pulse polarography/voltammetry, Tast polarography, Osteryoung square-wave voltammetry.
- AC techniques: phase-selected results in AC voltammetry.
- Chronocoulometry: analyte adsorption. Double potential step chronocoulometry for reversible processes.
- Chronopotentiometry.
- CV for quasireversible, irreversible & EC processes.
- Electron-transfer kinetics by Nicholson/Shain & Matsuda/Ayabe methods.

- Electron-transfer kinetics by DPSCC.
- CV for EC & CE processes, adsorption.
- DPSCC for EC processes.
- Spectroelectrochemistry

**Goals of the course:**

To learn how to do electrochemical experiments which reveal the thermodynamic, kinematic and kinetic properties of molecular systems, through analysis of the experimental data and interpretation of the results.