

Chemistry 251: **Kinetics and Mechanism of Inorganic Reactions.**
Fall 2006

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Office Hours: every Wed 3:00-4:15 pm and by appointment.
- TA** Charles McCrory, cmccrory@stanford.edu
Office hours: TBA, including @ Gates Computer Science computer cluster
- Lectures** TTH 07:00PM-08:15PM BRAUN Lecture Hall
- Texts** *required:* Espenson, James, H. "Chemical Kinetics and Reaction Mechanisms"
2nd Edition; Stanford Bookstore or amazon.com. Call number: QD502 .E86 1995
recommended: Tobe, Martin L.; Burgess, John "Inorganic Reaction
Mechanisms". amazon.com. Call number: QD502.5 .T63 1999
Jordan, Robert B. "Reaction Mechanisms of Inorganic and Organometallic
Systems" 2nd Edition. Call number: QD502 .J67 1998
Wilkins, Ralph G. "Kinetics and Mechanisms of Reactions of Transition Metal
Complexes" 2nd Edition. Call number: QD474 .W53 1991
- Objectives** To master (1) essential tools of applied chemical kinetics as a universal means to elucidate reactivity and mechanism, and (2) fundamental aspects of structure, bonding and reactivity of coordination and organometallic complexes. The unifying goal of this course is to learn how to design insightful mechanistic inquiries. Starting with (a) an in-depth overview of applied chemical kinetics, we will proceed to examine in detail its applications in the studies of (b) ligand exchange, isomerization and (c) electron-transfer in transition metal complexes and related reactivity, while focusing on the underlying principles. A significant part of the course content will involve hands-on practice with computer analysis of kinetics data: in the form of homework assignments you will experience realistic challenges and intricacies of analyzing raw experimental data for plausible mechanistic conclusions and additional experimental tests.
- Grading** Six homeworks (60%), take-home midterm (20%) and an in-class final (20%).
- Resources** Computer-based portions of the homeworks will be tailored to MATLAB, available around the clock on the Linux machines in Gates Computer Science computer cluster. Detailed instructions for use of MATLAB will be distributed along with the assignments, and the course TA will be on hand at the computer cluster during three designated office hours.

Lecture notes, problem sets, MATLAB instructions and other relevant material will be posted on
<http://coursework.stanford.edu>

Chemistry 251: Kinetics and Mechanism of Inorganic Reactions.

Fall 2006 Approximate list of topics to be covered.

Lectures: 20	Topics
Wk 1; 9/26 Fundamentals of kinetics, elementary reactions.	Reactivity in perspective: structure in motion. PES profile as the realistic goal. Chemical kinetics on a macroscopic scale. Rate laws.
9/28 Simple rate laws, strategy of their experimental determination. <i>Receive HW 1.</i>	1st, 2nd, pseudo-first order kinetics. Strategic approaches to experimental determination of rate laws. Method of initial rates. Pseudo first-order conditions. Graphical analysis of potential dependencies (search for linear scatter plots), regression fits: examples, limitations.
Wk 2; 10/3 Complex reaction schemes. Simplifying approximations.	Relaxation kinetics. Parallel reactions. Consecutive first-order reactions. Consecutive first-order reactions with a reversible step. Steady-state approximation, examples. Rapid pre-equilibrium assumption, examples. Rate-determining step. Michaelis-Menten kinetics.
10/5 <i>HW 1 due, receive HW 2.</i>	Numerical integration of rate laws.
Wk 3; 10/10 Deduction of reaction mechanism from a rate law. Additional mechanistic probes.	Fundamental correspondence between mechanism and rate law. Mechanistic interpretation of rate laws, examples. Kinetically-indistinguishable mechanisms. Isotope labeling, trapping of intermediates, radical clocks. Mini review.
10/12 Transition state theory of reaction rates. Isotope effects.	Temperature dependence of reaction rates. Eyring, Arrhenius analysis. Chemical interpretation of activation parameters. Pressure dependence of rate constants. Analysis of composite rate constants. Principle of microscopic reversibility. Hammond postulate. Thermodynamic and kinetic isotope effects. Tunneling. Solvent KIE and proton inventory technique.
Wk 4; 10/17	
10/19 Diffusion control. pH, solvent, salt effects on reaction rates. <i>HW 2 due, receive HW 3.</i>	Bimolecular reactions in solution. Diffusion control of reaction rates. Upper limits on reaction rates. pH, solvent and salt effects on polar and ionic reactions.
Wk 5; 10/24 Principles of structure and bonding of inorganic complexes. Classification of inorganic reactivity.	Perspective on reactivity of inorganic coordination compounds. Formal characteristics of electronic structure and bonding. Ligand types. Coordination geometries. Correspondence between formal bonding characteristics and reactivity. Reactivity classification.
10/26 Classification of ligand substitution. Substitution at d^8 square planar M. <i>HW 3 due. Receive take-home midterm.</i>	Ligand substitution: perspective; basic concepts; classification; rate laws; simple trends. Substitutions in d^8 square-planar complexes: overview, classification, associative mechanism.
Wk 6; 10/31 Trans-effect, trans-influence. Dissociative mechanism.	Effects of ligands on ligand substitution kinetics of d^8 square-planar complexes: entering, spectator; trans-effect, trans-influence, cis-effect. Dissociative substitution.
11/2 Substitution in octahedral complexes. Crystal field theory. Catalysis of substitution. <i>Take-home midterm due. Receive HW 4.</i>	Crystal field theory essentials: CFSE, structure-specific d -orbital splitting patterns, CFAE. Examples: derivation of rate laws, assignments of mechanisms. Insight from computational studies. Catalyzed and promoted substitution.
Wk. 7; 11/7 Solvent exchange and complex formation. Stereochemical change, isomerization.	Influence of metal ion charge, size, d^n configuration, first-order Jahn-Teller distortions. Examples. Eigen-Wilkins mechanism of complex formation. Dissociative and associative activation. Classification. Pseudo-rotation by coordination number: 3, 4, 5, 6. Involvement of an intermediate of different coordination number: $4 \rightarrow 5 \rightarrow 4$ and $4 \rightarrow 3 \rightarrow 4$.
11/9 Redox reactions: overview. Inner-sphere electron-transfer. Mixed-valence complexes.	Oxidation-reduction reactivity: overview, fundamentals, examples, classification. ISET: Taube's experiment. Detailed mechanistic sequence of elementary steps possible during ISET. Examples. Mixed-valence complexes: classification + stability.
Wk. 8; 11/14	
11/16 Outer-sphere electron-transfer. Marcus theory basics. Inner vs outer sphere dichotomy. <i>HW 4 due, receive HW 5.</i>	Mechanistic sequence of elementary steps. Origins of the barrier to OSET. Marcus theory basics: parabolic free energy dependence on nuclear configuration. Electronic coupling between free energy surfaces. Kinetic limits and rate constants expressions. Reorganization parameters and energies. Marcus cross-relationship. Experimental tests of Marcus theory. Comparison of IS and OS ET; distinguishing between the two.
Wk. 9; 11/28	
11/30 Promotion of electron transfer. <i>HW 5 due, receive HW 6.</i>	Kinetic promotion of electron transfer by Brønsted acids, bases and ion-pairing interactions: examples.
Wk. 10; 12/5 Proton transfer.	Comparative recap of Marcus theory of OSET. Perspective on proton-transfer reactivity, evidence of tunneling from KIE. Medium polarization/proton tunneling theory. Kinetic limits. Tunneling distance and reorganization energy: examples. Inverted-region behavior of proton transfer rates.
12/7 Proton-Coupled Electron Transfer. Exit review.	Kinetic coupling of alternating charge transfer steps. Proton-coupled electron transfer. Examples. Transition state and medium reorganization/tunneling theories of reaction rates: recap & comparison.
12/12 Final exam. 7:00-10:00 pm. <i>HW 6 due</i>	