

Chemistry 722
Reaction Kinetics and Dynamics

Spring 2003
Ian Harrison

Nature of the Course

Chemistry 722 provides an introduction to the practice and theory of modern chemical kinetics with emphasis on reactions occurring in gases, liquids, and on catalytic surfaces. The basic principles of chemical kinetics are developed and current experimental and analytic techniques are described. The microscopic reaction dynamics underlying the macroscopic kinetics are discussed in terms of reactive potential energy surfaces. Statistical theories of reactions are developed which simplify the description of the overall reaction dynamics. These include transition state theory, Rice-Ramsperger-Kassel-Marcus (RRKM) theory for unimolecular reactions, Kramers' theory, Marcus electron transfer theory, and information theory. Current topics in reaction kinetics and dynamics from the literature will be discussed. Applications of the basic principles will be illustrated through problem-solving exercises. Some computer programs for kinetics will be made available (for PCs or IBM RISC-6000s).

Textbook

- 1) "Chemical Kinetics and Dynamics" by J.I. Steinfeld, J.S. Francisco, W.L. Hase, 2nd ed., Prentice Hall Publ., Upper Saddle River, N.J., 1999.

Recommended References

- 1) "Unimolecular Reaction Dynamics: Theory and Experiments", Tomas Baer and W.L. Hase, Oxford University Press, NY, 1996.
- 2) "An Introduction to Statistical Thermodynamics", T.L. Hill, Dover Publ., NY, 1986

Resources

- 1) Reserve books in Chem. Library, Rm. 259
- 2) 20 Pentium computers in Rm. 266-268 with Mathcad and Gaussian '98 Prgms., and ethernet access to campus mainframe computers and the WWW.

Course Calendar

1) Course Meeting Times:

Mondays, Wednesdays, & Fridays 9-10 am. in Rm. 262 of the Chemistry Building

2) Marking Scheme

Problem Sets (4)	60% (Feb. 17, March 10, April 7, April 25)
Midterm	10% (March 21)
Final Exam (Take-home)	30%

Professor Harrison's office is Rm. 154
labs are Rm. 160, 162, 204
secretary is Shirley Fuller in Rm. 140
email: harrison@virginia.edu

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Tentative Sequence of Topics to be Presented

	<u>Text</u>
1) Macroscopic Kinetics	
Basic Concepts of Kinetics	Chapters 1-5
Complex Reactions	
Kinetic Measurements	
Reactions in Solutions	
Catalysis	
2) Microscopic Reaction Kinetics/Dynamics	
a) Potential Energy Surfaces, Scattering Theory	Chapters 6-9
Relation between Cross Section and Rate Coefficient	
Microscopic Reversibility and Detailed Balancing	
Potential Energy Surfaces: Ab Initio and Semi-Empirical (LEPS)	
Dynamics of Bimolecular Collisions	
Experimental Techniques for State-to-State Kinetics	
b) Statistical Approach to Reaction Dynamics: Transition State Theory	Chapter 10
Derivation of TST from Statistical Mechanics,	
Thermodynamic Formulation of TST	
Microcanonical and Variational TST	
c) Unimolecular Reaction Dynamics: RRKM Theory	Chapter 11
Lindemann-Hinshelwood Theory of Unimolecular Reactions	
Sum and Densities of States	
Derivation of RRKM theory from Statistical Mechanics	
Intermolecular Energy Transfer	
Product Energy Partitioning	
Apparent and Intrinsic Non-RRKM Behavior	
d) Solvent/Medium Effects	Chapter 12
Potential of mean force	
Effect of friction on TST rates: Kramers Theory	
e) Information Theory	Chapter 13
Maximum-Entropy Postulate	
Surprisal Analysis and Synthesis	
3) Selected Applications	
Microcanonical unimolecular rate theory at surfaces (e.g., J. Chem. Phys. 118 , 843 (2003))	
Marcus electron transfer theory; Application to dissociative adsorption on metals	
Gas-phase protein kinetics in ICR mass spectrometers (e.g., JACS 118 , 10640 (1996))	
Kinetic Isotope Effects	
Non-adiabatic reaction dynamics	
Reaction kinetics/dynamics of systems of interest to the class	

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Reserve Books for Chem. Library

- 1) "Chemical Kinetics and Dynamics" by J.I. Steinfeld, J.S. Francisco, W.L. Hase, Prentice Hall Publ., Englewood Cliffs, N.J., 1989.
- 2) "Unimolecular Reaction Dynamics: Theory and Experiments", Tomas Baer and W.L. Hase, Oxford University Press, NY, 1996.
- 3) "Theory of Unimolecular and Recombination Reactions", R.G. Gilbert and S.C. Smith, Blackwell Sci. Publ., Boston, 1990.
- 4) "Chemical Kinetics", 3rd ed., K.J. Laidler, Harper Row Publ., NY, 1987.
- 5) "Introduction to Molecular Dynamics and Chemical Kinetics", G.D. Billing and K.V. Mikkelsen, John Wiley & Sons, NY, 1996.
- 6) "Advanced Molecular Dynamics and Chemical Kinetics", G.D. Billing and K.V. Mikkelsen, John Wiley & Sons, NY, 1997.
- 7) "Principles of Chemical Kinetics", J.E. House, Wm. C. Brown Publ., Dubuque, IA, 1997.
- 8) "Reaction Kinetics", M.J. Pilling and P.W. Seakins, Oxford Science Publ., NY, 1995.
- 9) "Thermochemical Kinetics", 2nd ed., S.W. Benson, John Wiley & Sons, NY, 1976.
- 10) "Kinetic Systems", C. Capellos and B.H.J. Bielski, Wiley-Interscience, NY, 1972.
- 11) "Chemical Kinetics and Catalysis", R.A. van Santen and J.W. Niemantsverdriet, Plenum Press, 1995.
- 12) "Molecular Reaction Dynamics", R.D. Levine and R.B. Bernstein, Oxford Univ. Press, Oxford, 1974.
- 13) "Molecular Reaction Dynamics and Chemical Reactivity", R.D. Levine and R.B. Bernstein, Oxford Univ. Press, NY, 1987.
- 14) "Catalytic Chemistry", B.C. Gates, John Wiley & Sons, NY, 1992.
- 15) "Heterogeneous Reaction Dynamics", S.L. Bernasek, VCH Publ., NY, 1995.
- 16) "Surface Science: Foundations of Catalysis and Nanoscience", K.W. Kolasinski, John Wiley & Sons, NY, 2002.
- 17) "An Introduction to Statistical Thermodynamics", T.L Hill, Dover Publ., NY, 1986. (at \$12.95 a terrific buy for a fine and very readable reference text which was originally published in 1960 yet remains a standard reference in the current literature)
- 18) "Physical Chemistry", 5th ed., P. Atkins, W.H. Freeman & Co., NY, 1994.