

Chemistry 4011/8011*Mechanisms of Chemical Reactions*

Fall 2006

MWF 10:10 am – 11:00 am, Smith 331
and optional review sections,

M 11:00 am – 12:00 pm, Kolthoff S132

M 6:00 pm – 7:00 pm, Kolthoff S136

Legend for Readings:

"MPOC": Anslyn & Dougherty, *Modern Physical Organic Chemistry*
("App": Appendix)"Kinetics": Wright, *Introduction to Chemical Kinetics*"L & R": Lowry & Richardson, *Mechanism and Theory in Organic Chemistry*

Schedule		Instructor	
W	Sep 6	Introduction to course <i>Complete online scheduling form at course website</i>	Andy
F	Sep 8	Electronics and thermodynamics: Bonding and orbital mixing; electron pushing <i>Required Reading: MPOC 1.0-1.1, 1.3-1.5, App5.0-App5.7</i> <i>Post Problem Set 1</i>	Andy
M	Sep 11	<u>Problem Solving Workshop 1:</u> Electron pushing	Marc
M	Sep 11, 11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136		Section, Marc <i>Mol. Orbitals</i>
W	Sep 13	Electronics and thermodynamics: Energies in reaction coordinates, potential energy surfaces <i>Required Reading: MPOC 2.0-2.1.5</i>	Andy
W	Sep 13, 4:30 – 5:30 pm, Kolthoff 481		Office Hours, Andy
Th	Sep 14, 12:00 – 1:00 pm, Kolthoff 70		Marc
F	Sep 15	<u>Problem Solving Workshop 2:</u> Bond energies, intermediates and transition states <i>Post Problem Set 2</i>	Andy & Marc

M	Sep 18	Electronics and thermodynamics: Solvation, weak interactions, chelation/multivalency, preorganization <i>Required Readings: MPOC 3.0-3.2, 4.0-4.2</i> <i>Recommended Reading:</i> Meyer, E. A. et al., <i>Angew. Chem. Int. Ed.</i> 2003 , 42, 1210-1240. (http://dx.doi.org/10.1002/anie.200390319) Williams, D. H. et al., <i>Chem. Soc. Rev.</i> 1998 , 27, 57-63. (http://dx.doi.org/10.1039/a827057z) <i>Problem Set 1 Due</i>	Andy
M	Sep 18, 11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136		Section, Marc <i>Problem Set 1</i>
W	Sep 20	<u>Problem Solving Workshop 3:</u> Host-guest, noncovalent interactions	Andy
W	Sep 20, 4:30 – 5:30 pm, Kolthoff 481		Office Hours, Andy
Th	Sep 21, 12:00 – 1:00 pm, Kolthoff 70		Marc
F	Sep 22	Phenomenological kinetics: Basic concepts, reaction order, method of initial rates <i>Required Reading: MPOC 7.0-7.1, 7.4</i> <i>Recommended Reading: Kinetics 3.0-3.7</i> <i>Problem Set 2 Due</i> <i>Post Problem Set 3</i>	Andy
M	Sep 25	Phenomenological kinetics: Integrated rate expressions, elementary reaction steps, first-order reactions <i>Recommended Reading: Kinetics 3.8-3.10</i>	Andy
M	Sep 25, 11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136		Section, Marc <i>Problem Set 2</i>
W	Sep 27	Phenomenological kinetics: Reaction half-lives, fitting experimental kinetic data <i>Recommended Reading:</i> Harris, D. C. <i>J. Chem Ed.</i> 1998 , 75, 119-121. (See course site for link.)	Andy
W	Sep 27, 4:30 – 5:30 pm, Kolthoff 481		Office Hours, Andy
Th	Sep 28, 12:00 – 1:00 pm, Kolthoff 70		Marc

F	Sep 29	Phenomenological kinetics: Second-order kinetics <i>Problem Set 3 Due</i>	Andy
M	Oct 2	<u>Problem Solving Workshop 4:</u> Introductory kinetics	Andy & Marc
M	Oct 2,	11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136	Section, Marc <i>Problem Set 3</i>
W	Oct 4	Phenomenological kinetics: Pseudo-first-order kinetics <i>Recommended Reading: Kinetics 3.11-3.17</i>	Andy
W Th	Oct 4, Oct 5,	4:30 – 5:30 pm, Kolthoff 481 12:00 – 1:00 pm, Kolthoff 70	Office Hours, Andy Marc
F	Oct 6	Midterm exam review <u>Post Problem Solving Workshop 5:</u> <i>Integrated Rate Laws</i>	Andy
M	Oct 9,	10:10 am – 12:10 pm, Kolthoff S132 6:00 pm – 8:00 pm, Kolthoff S136	Midterm Exam 1 <i>(Covers Sep 6 – Oct 4)</i>
W	Oct 11	Phenomenological kinetics: Complex reactions <i>Recommended Reading: Kinetics 3.18</i>	Andy
W Th	Oct 11, Oct 12,	4:30 – 5:30 pm, Kolthoff 481 12:00 – 1:00 pm, Kolthoff 70	Office Hours, Andy Marc
F	Oct 13	Phenomenological kinetics: Steady-state and pre-equilibrium assumptions <i>Required Reading: MPOC 7.5</i> <i>Recommended Reading: Kinetics 3.19-3.22</i> <i>Post Problem Set 4</i>	Andy
M	Oct 16	Phenomenological kinetics: Numerical methods Case study: Atmospheric reactions	Andy
M	Oct 16,	11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136	Section, Marc <i>Exam 1</i>

W	Oct 18	<u>Problem Solving Workshop 6:</u> Complex kinetics	Andy & Marc
W Th	Oct 18, Oct 19,	4:30 – 5:30 pm, Kolthoff 481 12:00 – 1:00 pm, Kolthoff 70	Office Hours, Andy Marc
F	Oct 20	Theoretical kinetics: Collision theory <i>Recommended Reading: Kinetics 4.0-4.2</i> <i>Problem Set 4 Due</i> <i>Post Problem Set 5</i>	Andy
M	Oct 23	Theoretical kinetics: Transition-state theory and activation parameters <i>Required Reading: MPOC 7.2</i> <i>Recommended Reading: Kinetics 4.3-4.4</i>	Andy
M	Oct 23,	11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136	Section, Marc <i>Problem Set 4</i>
W	Oct 25	Theoretical kinetics: Hammond Postulate, Curtin-Hammett Principle, More O’Ferrall- Jencks plots <i>Required Reading: MPOC 7.3</i>	Andy
W Th	Oct 25, Oct 26,	4:30 – 5:30 pm, Kolthoff 481 12:00 – 1:00 pm, Kolthoff 70	Office Hours, Andy Marc
F	Oct 27	Theoretical kinetics: Case studies; “kinetic” vs. “thermodynamic” products, Principle of Microscopic Reversibility <i>Recommended Reading:</i> Noyori, R., 2001 Nobel Prize Lecture. (http://nobelprize.org/chemistry/laureates/2001/noyori-lecture.html) Keith, J. M. et al. <i>Adv. Synth. Catal.</i> 2001 , 343, 5- 26. (<a href="http://dx.doi.org/10.1002/1615-4169(20010129)343:1<5::AID-ADSC5>3.0.CO;2-I">http://dx.doi.org/10.1002/1615-4169(20010129)343:1<5::AID-ADSC5>3.0.CO;2-I) <i>Problem Set 5 Due</i> <i>Post Problem Set 6</i>	Andy
M	Oct 30	<u>Problem Solving Workshop 7:</u> Applying kinetic theories	Andy & Marc
M	Oct 30,	11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136	Section, Marc <i>Problem Set 5</i>

W	Nov 1	Theoretical kinetics: Marcus Theory <i>Required Reading: MPOC 7.7</i>	Andy
W Th	Nov 1, Nov 2,	4:30 – 5:30 pm, Kolthoff 481 12:00 – 1:00 pm, Kolthoff 70	Office Hours, Andy Marc
F	Nov 3	Theoretical kinetics: Implications of Marcus Theory: Photosynthesis <i>Required Reading: MPOC 7.8</i> <i>Recommended Reading:</i> Moser, C. C. et al. <i>Nature</i> 1992 , 355, 796. (http://dx.doi.org/10.1038/355796a0) <i>Problem Set 6 Due</i> <i>Select Group Presentation Topic</i>	Andy
M	Nov 6	<u>Problem Solving Workshop 8:</u> Marcus Theory & substituent effects	Andy & Marc
M	Nov 6,	11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136	Section, Marc <i>Problem Set 6</i>
W	Nov 8	Experimental kinetics: Substituent effects and linear free-energy relationships <i>Required Reading: MPOC 8.2-8.3, 8.6</i>	Andy
W Th	Nov 8, Nov 9,	4:30 – 5:30 pm, Kolthoff 481 12:00 – 1:00 pm, Kolthoff 70	Office Hours, Andy Marc
F	Nov 10	<u>Problem Solving Workshop 9:</u> Substituent effects	Andy & Marc
M	Nov 13,	10:10 am – 12:10 pm, Kolthoff S132 6:00 pm – 8:00 pm, Kolthoff S136	Midterm Exam 2 (Covers Oct 6 – Nov 8)
W	Nov 15	Experimental kinetics: Equilibrium and primary kinetic isotope effects <i>Required Reading: MPOC 8.1</i> <i>Recommended Reading: L & R 2.9</i>	Andy
W Th	Nov 15, Nov 16,	4:30 – 5:30 pm, Kolthoff 481 12:00 – 1:00 pm, Kolthoff 70	Office Hours, Andy Marc
F	Nov 17	Experimental kinetics: Secondary kinetic isotope effects; KIE theory <i>Post Problem Set 7</i>	Andy

M	Nov 20	<u>Problem Solving Workshop 10:</u> Kinetic Isotope Effects	Andy & Marc
M	Nov 20,	11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136	Section, Marc <i>Exam 2</i>
W	Nov 22	Experimental kinetics: Tunneling <i>Post Problem Set 8</i>	Andy
F	Nov 24	<i>Holiday.</i>	
M	Nov 27	Experimental kinetics: Miscellaneous experimental methods in kinetics <i>Required Reading: MPOC 8.8</i> <i>Problem Set 7 due</i>	Andy
M	Nov 27,	11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136	Section, Marc <i>Problem Set 7</i>
W	Nov 29	Catalysis: Thermodynamic principles, entropic catalysis <i>Required Reading: MPOC 9.0-9.2</i>	Andy
W	Nov 29,	4:30 – 5:30 pm, Kolthoff 481	Office Hours, Andy Marc
Th	Nov 30,	12:00 – 1:00 pm, Kolthoff 70	
F	Dec 1	Catalysis: Enthalpic catalysis <i>Required Reading: MPOC 9.3</i> <i>Problem Set 8 Due</i> <i>Post Problem Set 9</i>	Andy
M	Dec 4,	10:10 am – 11:00 pm, Smith 331	Section, Marc <i>Problem Set 8</i>
W	Dec 6	<u>Problem Solving Workshop 11:</u> How to make a better catalyst	Marc
W	Dec 6,	6:00 – 8:00 pm, MCB 3-120	Group Presentations (8011 only)
W	Dec 6,	4:30 – 5:30 pm, Kolthoff 481	Office Hours, Andy Marc
Th	Dec 7,	12:00 – 1:00 pm, Kolthoff 70	

F Dec 8 Catalysis: Enzymes Andy
Required Reading: MPOC 9.4
Recommended Reading:
 Garcia-Viloca, M. et al., *Science* **2004**, 303, 186-195. (<http://dx.doi.org/10.1126/science.1088172>)
Problem Set 9 Due

M	Dec 11, 10:10 – 11:00 am, Smith 331	Group Presentations (8011 only)
M	Dec 11, 11:00 am – 12:00 pm, Kolthoff S132 6:00 pm – 7:00 pm, Kolthoff S136	Section, Marc <i>Problem Set 9</i>
W	Dec 13, 10:10 – 11:00 am, Smith 331 <i>Post Group Presentation Quiz</i>	Group Presentations (8011 only)
W	Dec 13, 4:30 – 5:30 pm, Kolthoff 481	Office Hours, Andy Marc
Th	Dec 14, 12:00 – 1:00 pm, Kolthoff 70	
M	Dec 18, 1:30 pm – 3:30 pm, Smith 331 <i>Group Presentation Quiz Due (8011 only)</i> <i>Group Presentation Essay Due (8011 only)</i>	Midterm Exam 3 (Covers Nov 10 – Dec 8)