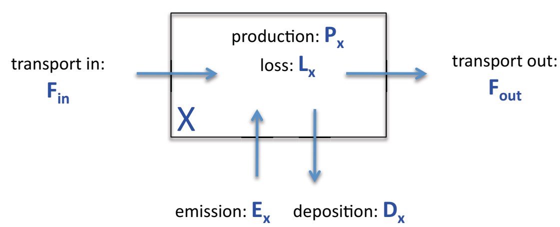
1.84/12.807 Lecture 2, 9/9/13: Kinetics of bimolecular reactions

- Lifetimes, kinetics basics
- Activation energy
- Collision theory
- Transition State Theory
- Experimental techniques

Lifetime, concentration

Atmosphere: set of compartments that are well-mixed



[*Note: Additional material is discussed here during lecture.*]

Basic concepts in kinetics

Complex reactions:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

rate = $-d[CH_4]/dt = d[CO_2]/dt = k\,[CH_4]^m\,[O_2]^n$

Elementary reactions:

$O(^1D) + H_2O \rightarrow OH + OH$

rate = $-d[O(^1D)]/dt = k\,[O(^1D)]\,[H_2O]$

Elementary unimolecular rxns:

$HOONO_2 \rightarrow HO_2 + NO_2$

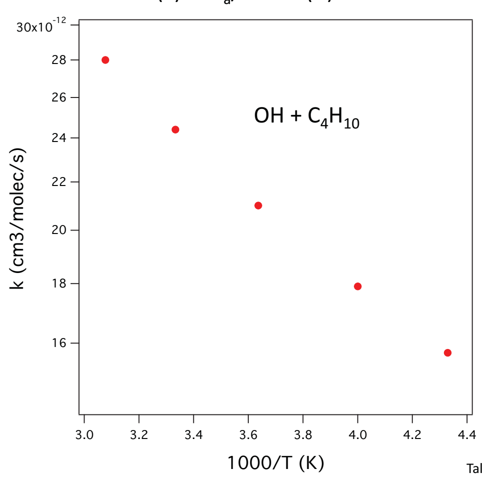
rate = $-d[HOONO_2]/dt = k\,[HOONO_2]$

$[HOONO_2]_t = [HOONO_2]_0\,e^{-kt}$

Temperature-dependence of reactions

Arrhenius Equation (1889): $k(T) = A\,e^{-E_a/RT}$

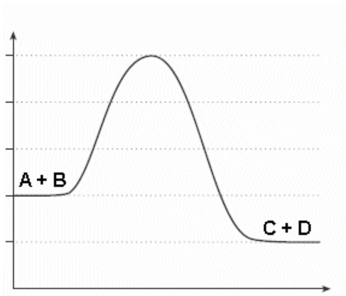
$ln(k) = -E_a/RT + ln(A)$



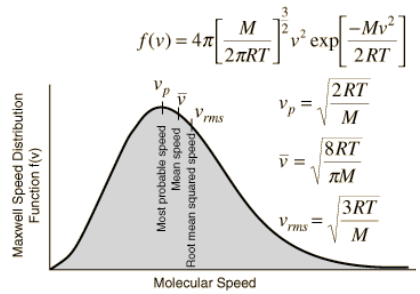
Talukdar et al, *Int. J. Chem. Kin.* 26:973 (1994)

Activation energy

Reaction coordinate: Only systems with enough energy ($E \geq E_a$) can react



Maxwell-Boltzmann Distribution: Distribution of energies (velocities, etc.) at a given T



http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/kintem.html

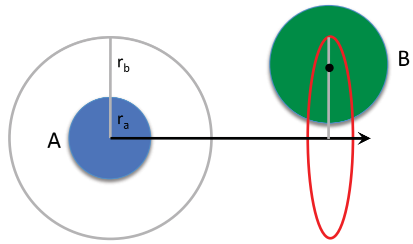
Online kinetics databases

IUPAC: Evaluated kinetic and photochemical data
http://www.iupac-kinetic.ch.cam.ac.uk/

JPL/NASA: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies
http://jpldataeval.jpl.nasa.gov/

NIST Chemical Kinetics Database on the Web
http://kinetics.nist.gov/kinetics/index.jsp
Note: NOT an evaluation!

Hard-sphere collision theory



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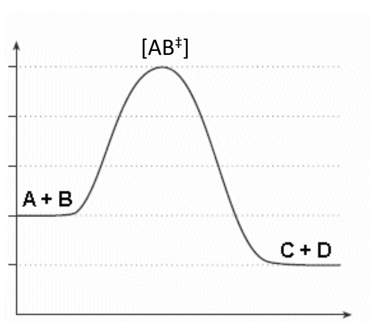
Transition state theory

Used to predict rates of molecules



Thermodynamic derivation:
Treat the transition state as a "real compound"

For a more thorough treatment, see
Steinfeld, Francisco and Hase, *Chemical Kinetics and Dynamics* (Prentice Hall 1998)
Pilling and Seakins, *Reaction Kinetics* (Oxford 1997)

What have we left out?

- Pressure effects (*next lecture*)
- Details of TST
- Quantum effects (tunneling)
- “Pre-reactive” complexes
- Ion-molecule, ion-ion reactions

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