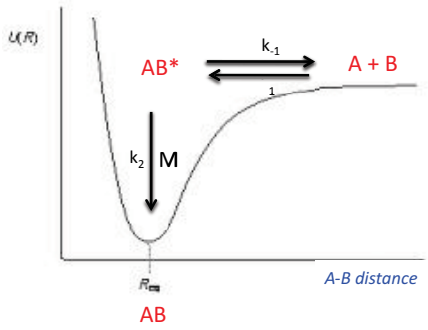
1.84/12.807 Lecture 3, 9/11/13: Beyond bimolecular collisions

- sample presentation: kinetics measurements
- Termolecular rxns
- Unimolecular rxns

PSet1 (due 9/25) posted online today

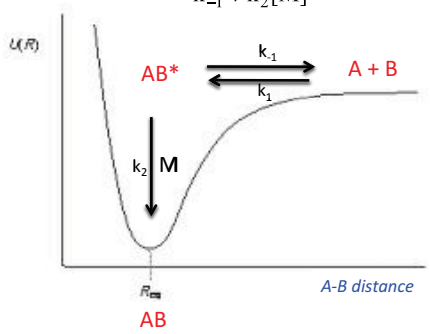
Termolecular reactions



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

Lindemann-Hinshelwood: low P

$$k_{L\text{-}H} = \frac{k_1 k_2 [M]}{k_{-1} + k_2 [M]}$$

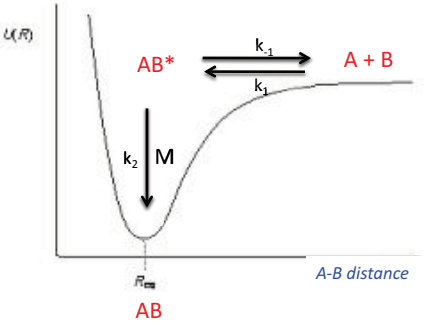


Values of k_0: $H + H + M \rightarrow H_2 + M$ $k_0 = 8 \times 10^{-33}$ cm^6 molec^{-2} s^{-1}

$CH_3 + CH_3 + M \rightarrow C_2H_6 + M$ $k_0 = 2 \times 10^{-25}$ cm^6 molec^{-2} s^{-1}

Lindemann-Hinshelwood: high P

$$k_{L\text{-}H} = \frac{k_1 k_2 [M]}{k_{-1} + k_2 [M]}$$



Values of k_∞: barrierless, fast → approaching collision rate (~10^{-10} cm^3 molec^{-1} s^{-1})

Lindemann-Hinshelwood: in between k_0 and k_∞

$$k_{L-H} = \frac{k_0 k_\infty [M]}{k_\infty + k_0 [M]}$$

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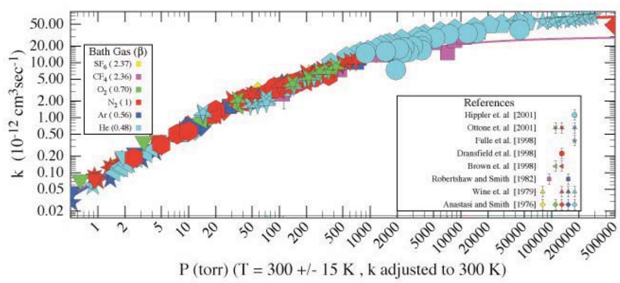
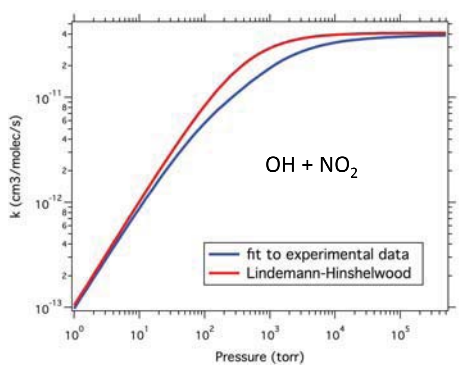


"Softer" collisions



Average amount of energy lost depends on bath gas:

- He: 200 cm^{-1}
- O_2, N_2: 300-350 cm^{-1}
- H_2O, SF_6: 600-800 cm^{-1}
- cyclohexane: 1200 cm^{-1}

(1 kcal/mol ~ 350 cm^{-1})

"Softer" collisions

To take into account the fact that not all collisions are fully deactivating, J. Troe developed a modification to the Lindemann-Hinshelwood rate expression [J. Phys. Chem. 83:114, 1979] :

$$k_{Troe} = k_{L-H} F = \frac{k_\infty k_0[M]}{k_\infty + k_0[M]} F$$

in which F is the "broadening factor":

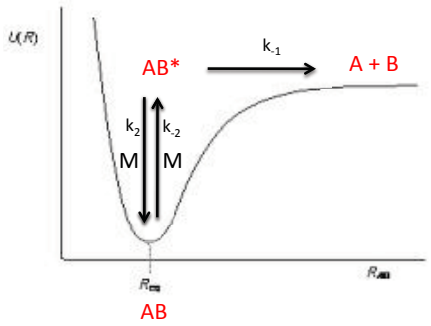
JPL recommendation: $$F = 0.6^{\left(1+\left(\log_{10}\left[k_0[M]/k_\infty\right]\right)^2\right)^{-1}}$$

IUPAC recommendation: $$F = F_c^{\left(1+\left(\log_{10}\left[k_0[M]/k_\infty\right]/N\right)^2\right)^{-1}} \qquad N = 0.75 - 1.27\log_{10}F_c$$

F_c is a fitted parameter

Pressure-dependent reaction rate data can generally be fit well to either expression.

Unimolecular reactions



use values for k_0 and k_∞ for unimolecular reaction (IUPAC)
relate unimolecular and termolecular reactions using eq. constant K (JPL)

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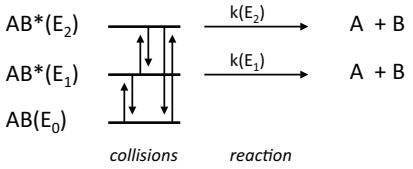
Online kinetics databases

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/

Explicit treatment of "soft" collisions

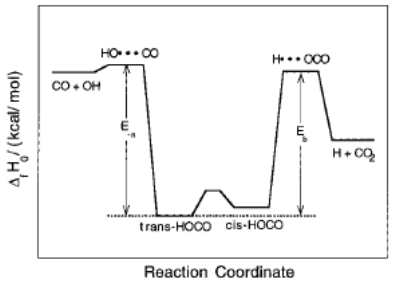
- The Troe expression approximates "soft" collisions; it essentially models some fraction of the collisions as deactivating
- To model the *explicit* effects of "soft" collisions on unimolecular reactions, need to account for AB* at multiple energy levels:



$$\text{rate} = \sum_i \left([\text{AB*}](E_i) \times k(E_i) \right)$$

- More energy levels used → more accurate description of reaction
- Using 100's-1000's of energy levels gives reasonable results. This can be done using matrices: "Master equation"

More complex potential energy surfaces



Golden et al., *J. Phys. Chem. A,* 102:8603 (1998)

1.84J / 10.817J / 12.807J Atmospheric Chemistry
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