Physical Chemistry

Lecture 5

Theoretical chemical kinetics

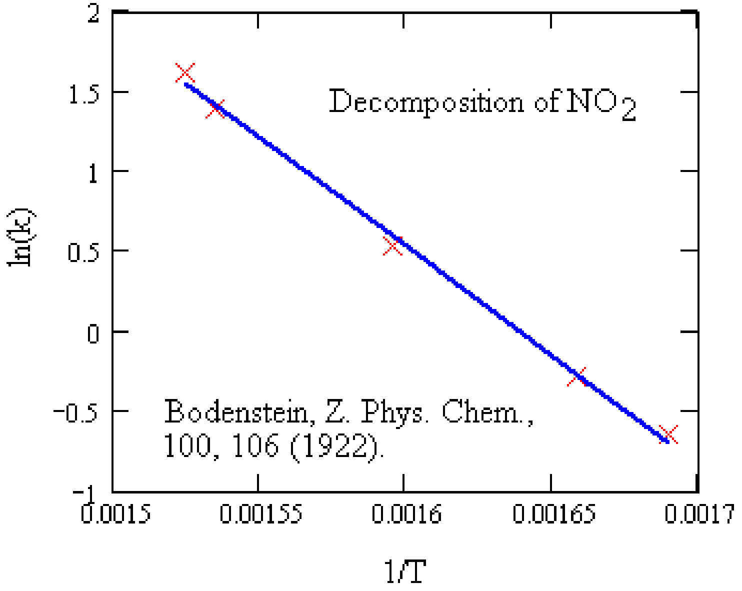
Chemical kinetics

- Understand the nature of reactions
- Predict reaction outcomes based on
  - Reactants
  - Conditions
- Requires integration of theory and experimental results

Temperature dependence of rate constants

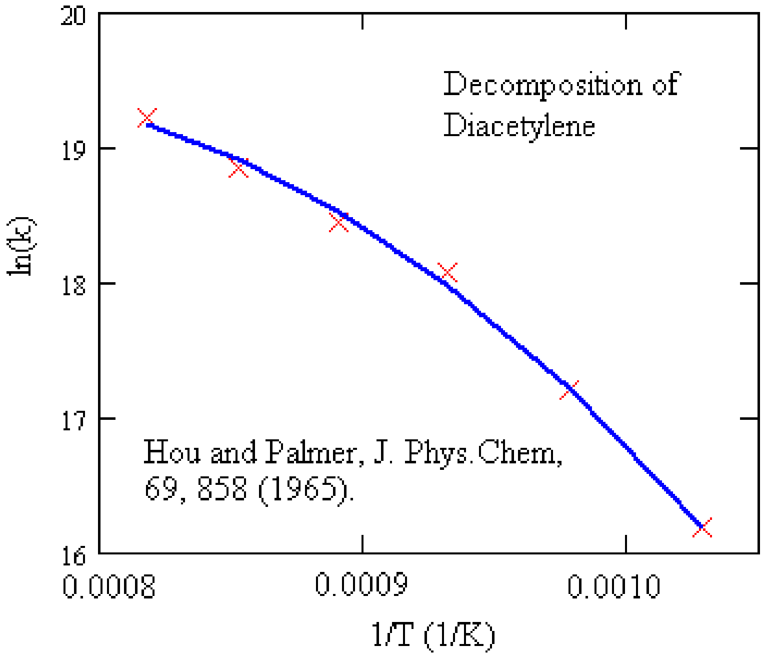
$$k(T) \quad = \quad A\exp(-E_a/RT)$$

- Empirical theory of Arrhenius gives a useful way to parameterize rate constants
  - A ≡ pre-exponential factor
  - E_a ≡ activation energy
- Often seen in analysis of kinetic data



Non-Arrhenius behavior

- Arrhenius behavior is empirical
- For some reactions the temperature dependence of the rate constant is not exponential
- Theory does not easily predict Arrhenius form
- Amazing that Arrhenius behavior is so often seen



Elementary reactions

- Chemical reactions are often more complex than presented and do not occur as a single step
- Some reactions do occur in a single step -- elementary reactions
  - Generally involve simple mono- or bimolecular interactions
  - Order in elementary reactions is the stoichiometry number, called molecularity

$$H_2 \quad + \quad 2O \quad \rightarrow \quad H_2O_2 \qquad v \quad = \quad k[H_2]^1[O]^2$$

$$H \quad + \quad Br \quad \rightarrow \quad HBr \qquad v \quad = \quad k[H]^1[Br]^1$$

Simple collision theory of gas-phase kinetics

- To participate in a bimolecular reaction, molecules must approach each other
- SCT: gas-phase reaction rate proportional to collision frequency
- SCT does not generally agree with experimental rates
- Points out how to think about theory of chemical reactions

$$\begin{aligned} v &\propto \langle Z_{AB} \rangle \\ v_{\max} &= \langle Z_{AB} \rangle = \sigma_{AB} \langle v_{AB} \rangle n_A^* n_B^* \\ &= \sigma_{AB} N_0 \sqrt{\frac{8kT}{\pi\mu}} C_A C_B \end{aligned}$$

$$\sigma_{AB} = \pi d_{AB}^2 \equiv \text{collision cross} - \text{section}$$

$$k_{\max} = \sigma_{AB} N_0 \sqrt{\frac{8kT}{\pi\mu}}$$

“Correcting” simple collision theory

- SCT neglects two features
    - Collision must be sufficiently energetic to cause reaction
    - Molecules must have proper orientation to allow reaction
- Empirically add two factors to account for these features
    - p ≡ steric factor
    - E_{min} ≡ minimum energy for reaction
- Like van der Waals’s improvement of the ideal-gas law

$$
\begin{aligned}
v &= \langle Z_{AB} \rangle\, p \exp(-E_{\min}/RT) \\
&= p\,\sigma_{AB} N_0 \sqrt{\frac{8kT}{\pi\mu}} \exp(-E_{\min}/RT)\, C_A C_B
\end{aligned}
$$

$$
k = p\,\sigma_{AB} N_0 \sqrt{\frac{8kT}{\pi\mu}} \exp(-E_{\min}/RT)
$$

Relation of SCT parameters to Arrhenius parameters

- Many experimental data reported as Arrhenius behavior
- Comparison with SCT necessary to connect theory and experiment
- Predicts a temperature-dependent activation energy and pre-exponential factor (which may not be the observation)

Arrhenius behavior

$$\frac{\partial \ln k}{\partial T} = \frac{E_a}{RT^2}$$

By comparison of differentials

$$E_a = E_{\min} + \frac{RT}{2}$$

$$A = p\, e^{1/2} k_{\max}$$

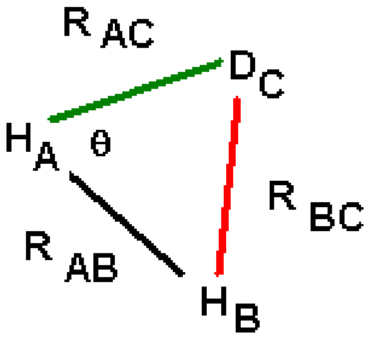
Experimental SCT and Arrhenius parameters

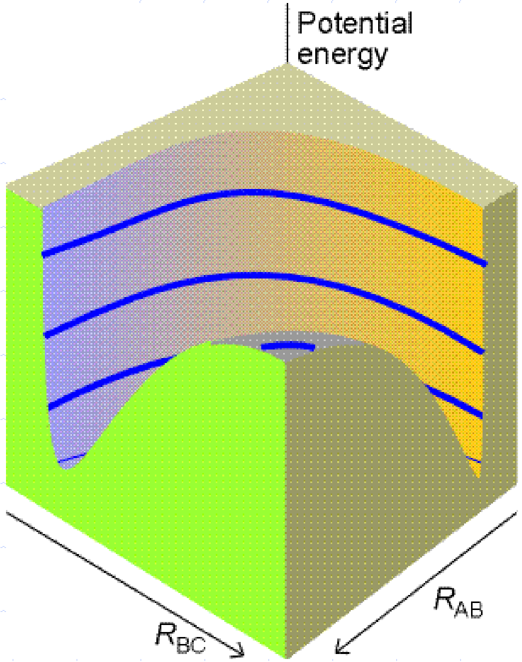
Reaction	Range	ln A	E_a	p
$H + D_2 \rightarrow HD + D$	300 – 750	24.61	39.3	0.088
$H + HCl \rightarrow H_2 + Cl$	200 – 500	23.85	14.6	0.039
$H + HBr \rightarrow H_2 + Br$	1000 - 1700	25.42	15.5	0.076
$O + O_3 \rightarrow 2\ O_2$	273 –900	23.21	20.0	0.037
$N + NO \rightarrow N_2 + O$	300 – 6000	23.28	~ 0	0.040
$CH_3 + C_6H_6 \rightarrow CH_4 + C_6H_5$	456 – 600	17.04	38.5	2.7×10^{-5}
$BH_3 + BH_3CO \rightarrow CO + B_2H_6$	273 – 333	19.34	29.3	2.9×10^{-4}
$PH_3 + B_2H_6 \rightarrow PH_3BH_3 + BH_3$	249 – 273	14.97	47.7	7.4×10^{-6}
$CO + O_2 \rightarrow O + CO_2$	2400 – 3000	21.97	213.4	4.3×10^{-3}
$F_2 + ClO_2 \rightarrow F + FClO_2$	227 – 247	16.37	33.5	5.2×10^{-5}

(a) The range of validity is expressed in kelvins.
(b) A is in $dm^3\ mol^{-1}\ s^{-1}$.
(c) E_a is in $kJ\ mol^{-1}$.

Computer modeling of potential-energy surfaces

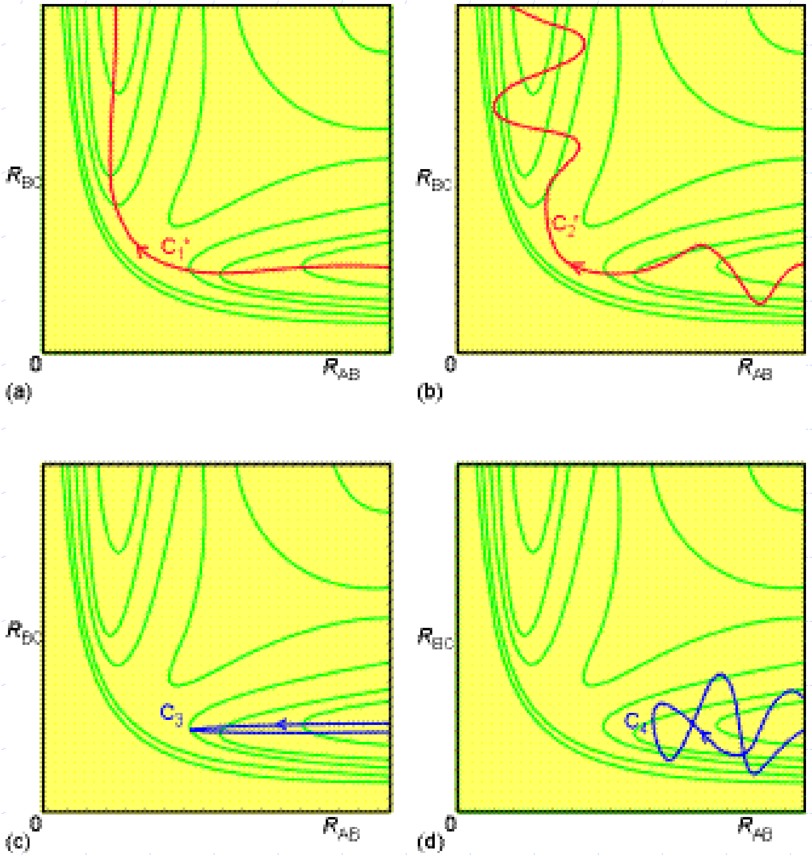
- Potential energy of configuration of molecules controls interaction
- Model time-dependent approach of molecules with (classical or quantum) simulation
- Example:
  - $D + H_2 \rightarrow HD + H$
- Several parameters
  - Distances
  - Angles





Computer simulation of reaction

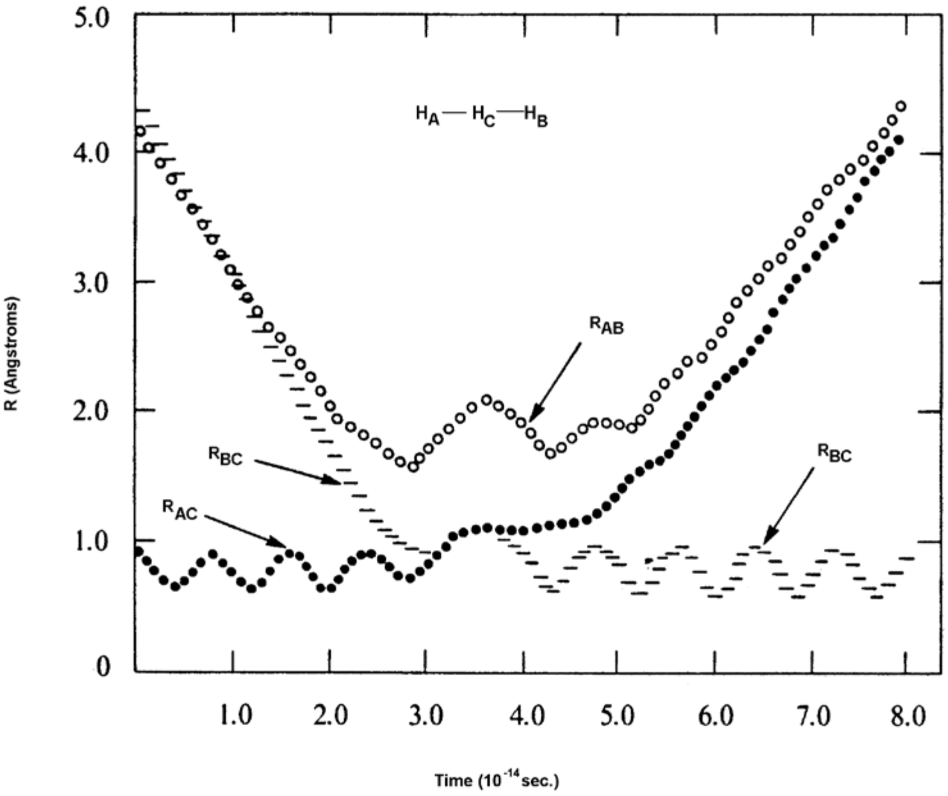
- Reactive encounters go through the reactive region
- Unreactive encounters go to the reactive region and return in the same channel



M. Karplus, R. N. Porter, and R. D. Shamra, J. Chem. Phys., 43,3258 (1965).

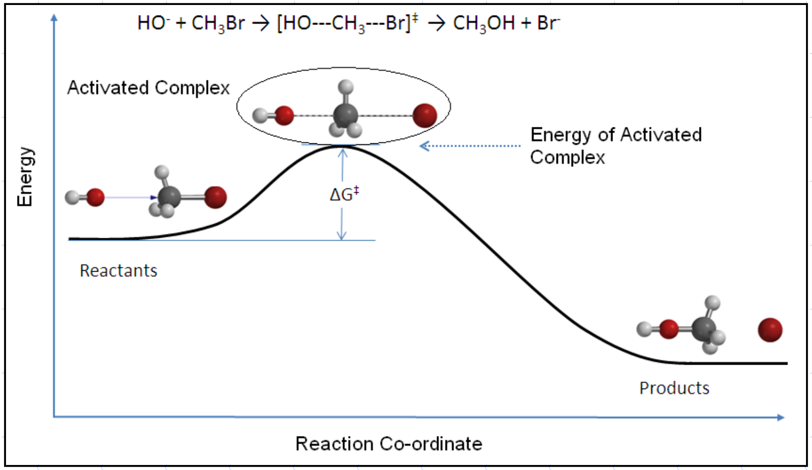
Simulation of a reactive event

- Follow the time course of the approach
- Atoms exchange partners
- Time scale is very short
- Repeat many times and measure fraction of times that reactive events happen



Activated-complex theory

- Theory developed by H. Eyring, M. Evans, and M. Polanyi
- Proposed the existence of an activated complex, a precursor to products
- The activated complex forms product(s) by a first-order process



Activated-complex mathematics

- Reaction velocity proportional to activated-complex concentration
- Quasi-equilibrium between reactants and activated complex
- Statistical mechanics defines disappearance rate constant of activated complex, f

$$v = f\,C_{\neq}$$

$$K_{\neq} = \frac{a_{\neq}}{a_A a_B} \cong C^{\theta}\,\frac{C_{\neq}}{C_A C_B}$$

$$v = \frac{fK_{\neq}}{C^{\theta}}\,C_A C_B$$

$$= \frac{RT}{hN_0 C^{\theta}} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right) C_A C_B$$

Eyring's equation

- Activated-complex theory gives a form for the biomolecular rate constant, k_2, in terms of the parameters of the activated complex

$$k_2 = \frac{RT}{hN_0C^{\theta}} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right)$$

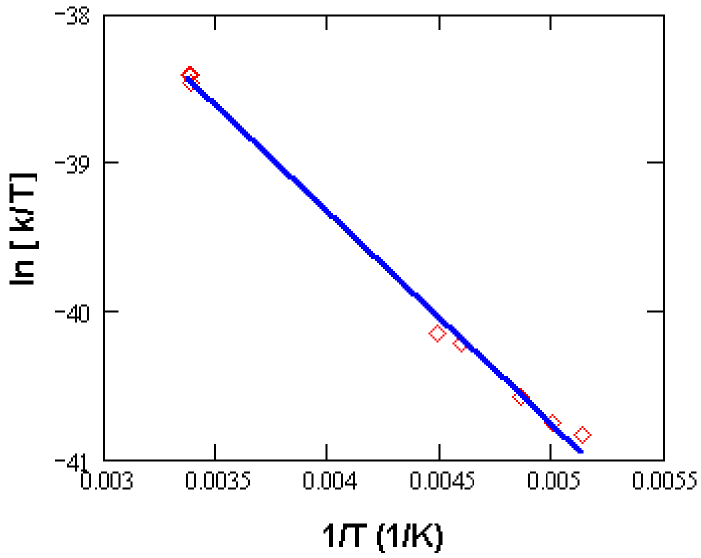
- This is <u>not</u> Arrhenius-like behavior
- Difficult to distinguish from Arrhenius behavior under many circumstances
- Different way to parameterize the SCT rate constant

Evaluation of Eyring parameters

- Evaluate by plotting ln(k/T) versus 1/T
- Example

$$CH_4 \quad + \quad OH \quad \rightarrow \quad CH_3 \quad + \quad H_2O$$

- From slope and intercept
  - ΔH≠ = 12.0 kJ/mol
  - ΔS≠ = -33.2 J/K-mol
- Alternative to Arrhenius parameters



T. Gierczak, R. Talukdar, S. Herndon, G. Vaghjiani, A. Ravishankara, J. Phys. Chem, 101A, 3125 (1997).

Relation of Eyring and Arrhenius parameters

- Need to be able to convert between the two parameterizations of kinetic data
- Use differential of Eyring form to show relationships

Phase/Molecularity	Activation Energy, E_a	Pre-exponential factor, A
Solution	$\Delta H^{\neq} + RT$	$\frac{eRT}{hN_0C^{\theta}}\exp(\frac{\Delta S^{\neq}}{R})$
Gas, unimolecular	$\Delta H^{\neq} + RT$	$\frac{eRT}{hN_0}\exp(\frac{\Delta S^{\neq}}{R})$
Gas, bimolecular	$\Delta H^{\neq} + 2RT$	$\frac{e^2RT}{hN_0C^{\theta}}\exp(\frac{\Delta S^{\neq}}{R})$
Gas, termolecular	$\Delta H^{\neq} + 3RT$	$\frac{e^3RT}{hN_0C^{\theta 2}}\exp(\frac{\Delta S^{\neq}}{R})$

Summary

- Theories of simple reactions
  - Simple collision theory
  - Modified collision theory
  - Computer simulation
  - Activated-complex theory
- Parameterization of reaction dynamics
  - Activation energy and pre-exponential factor
  - Equilibrium thermodynamic properties of activated complex