

Physical Chemistry

Lecture 5
Theoretical chemical kinetics

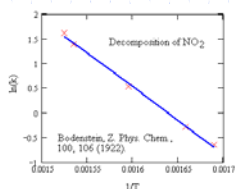
Chemical kinetics

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

Temperature dependence of rate constants

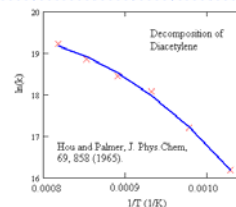
$$k(T) = A \exp(-E_a / RT)$$

- ◆ 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



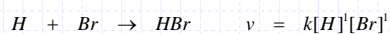
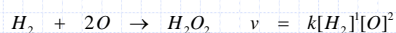
Non-Arrhenius behavior

- ◆ 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**



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

$$v_{\max} \propto Z_{AB} = \sigma_{AB} \bar{v}_{AB} n_A^+ n_B^+$$

$$= \sigma_{AB} L \sqrt{\frac{8kT}{\pi\mu}} C_A C_B$$

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

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

"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' improvement of the ideal-gas law

$$v = Z_{AB} p \exp(-E_{\min} / RT)$$

$$= p \sigma_{AB} L \sqrt{\frac{8kT}{\pi\mu}} \exp(-E_{\min} / RT) C_A C_B$$

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

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

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

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

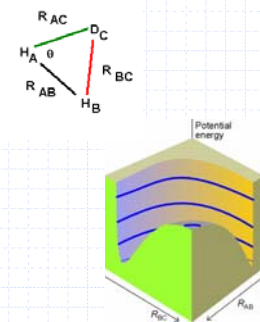
Experimental SCT and Arrhenius parameters

Reaction	Range	In 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
$O + O_2 \rightarrow 2 O_2$	273 - 900	23.21	20.0	0.037
$N + NO \rightarrow N_2 + O$	300 - 6000	23.28	-0	0.040
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	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}
$PH_3 + B_2H_6 \rightarrow PH_2BH_3 + BH_3$	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 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.
 (c) E_a is in kJ mol^{-1} .

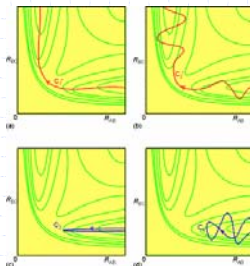
Computer modeling of potential-energy surfaces

- ◆ 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

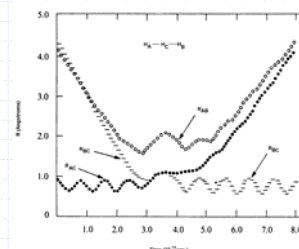
- ◆ Reactive encounters go through the reactive region
- ◆ Unreactive encounters go to the reactive region and return in the same channel



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

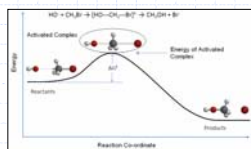
Simulation of a reactive event

- ◆ 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

$$v = f C_x$$

$$K_x = \frac{a_x}{a_A a_B} \cong C^0 \frac{C_x}{C_A C_B}$$
- Quasi-equilibrium between reactants and activated complex

$$v = \frac{f K_x}{C^0} C_A C_B$$
- Statistical mechanics defines disappearance rate constant of activated complex, f

$$= \frac{RT}{h L C^0} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) C_A C_B$$

Eyring's equation

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

$$k_2 = \frac{RT}{h L C^0} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right)$$

- This is not 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 $1/T$

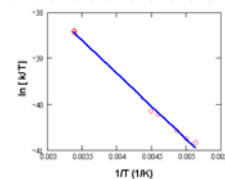
- Example



- From slope and intercept

- $\Delta H^\ddagger = 12.0 \text{ kJ/mol}$
- $\Delta S^\ddagger = -33.2 \text{ J/K-mol}$

- 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	$\Delta H^\ddagger + RT$	$\frac{eRT}{h L C^0} \exp\left(\frac{\Delta S^\ddagger}{R}\right)$
Gas, unimolecular	$\Delta H^\ddagger + RT$	$\frac{eRT}{h L} \exp\left(\frac{\Delta S^\ddagger}{R}\right)$
Gas, bimolecular	$\Delta H^\ddagger + 2RT$	$\frac{e^2 RT}{h L C^0} \exp\left(\frac{\Delta S^\ddagger}{R}\right)$
Gas, termolecular	$\Delta H^\ddagger + 3RT$	$\frac{e^3 RT}{h L C^0 2} \exp\left(\frac{\Delta S^\ddagger}{R}\right)$

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