

# Physical Chemistry

Lecture 5  
Theoretical chemical kinetics

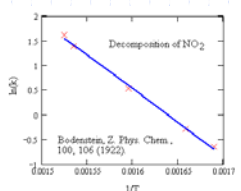
## Chemical kinetics

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

## Temperature dependence of rate constants

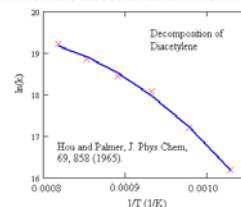
$$k(T) = A \exp(-E_a / RT)$$

- ◆ 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



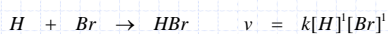
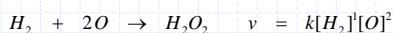
## Non-Arrhenius behavior

- ◆ 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
 
$$v \propto Z_{AB}$$

$$v_{\max} = Z_{AB} = \pi \sigma_{AB}^2 \overline{v_{AB}} n_A^+ n_B^+$$

$$= S_{AB} L_A \sqrt{\frac{8kT}{\pi \mu}} C_A C_B$$
- ◆ SCT: gas-phase reaction rate proportional to collision frequency
- ◆ SCT does not generally agree with experimental rates
 
$$S_{AB} = \pi \sigma_{AB}^2 \equiv \text{collision cross-section}$$
- ◆ Points out how to think about theory of chemical reactions
 
$$k_{\max} = S_{AB} L_A \sqrt{\frac{8kT}{\pi \mu}}$$

## "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

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

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

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

## 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

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

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

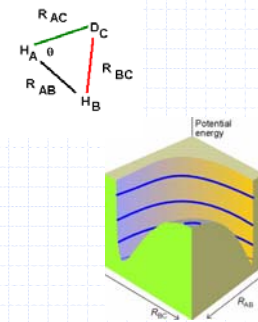
## Experimental SCT and Arrhenius parameters

Reaction	Range	In A	$E_a$	$p$
$H + D_2 \rightarrow HD + H$	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	$2.7 \times 10^{-5}$
$BH_3 + BH_3CO \rightarrow CO + B_2H_6$	273 - 333	19.34	29.3	$2.9 \times 10^{-4}$
$PH_3 + B_2H_6 \rightarrow PH_2BH_3 + BH_3$	249 - 273	14.97	47.7	$7.4 \times 10^{-6}$
$CO + O_2 \rightarrow O + CO_2$	2400 - 3000	21.97	213.4	$4.3 \times 10^{-3}$
$F_2 + ClO_2 \rightarrow F + FClO_2$	227 - 247	16.37	33.5	$5.2 \times 10^{-5}$

(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  $\text{kJ mol}^{-1}$ .

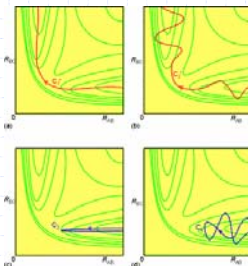
## Computer modeling of potential-energy surfaces

- ◆ 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

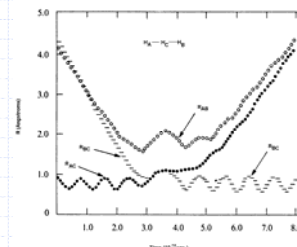
- ◆ Reactive encounters go through the reactive region
- ◆ Unreactive encounters go to the reactive region and return in the same channel



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

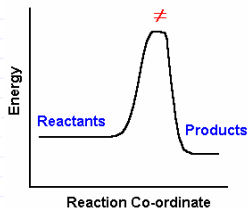
## Simulation of a reactive event

- ◆ 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 an activated complex, a precursor to products
- ◆ Only activated complex gives products by a first-order process



## Activated-complex mathematics

- ◆ Reaction velocity proportional to activated-complex concentration
 
$$v = f C_x \quad K_x = \frac{a_x}{a_A a_B} \cong C^{\theta} \frac{C_x}{C_A C_B}$$
- ◆ Quasi-equilibrium between reactants and activated complex
 
$$v = \frac{f K_x}{C^{\theta}} C_A C_B$$
- ◆ Statistical mechanics defines disappearance rate constant of activated complex,  $f$ 

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

## 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

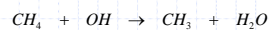
$$k_2 = \frac{R}{hLC^{\theta}} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) T \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)$$

- ◆ 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  $1/T$

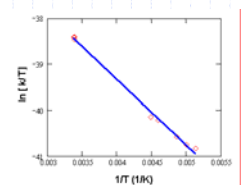
- ◆ Example



- ◆ 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. Vaghjani, 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, $A$
<b>Solution</b>	$\Delta H^{\ddagger} + RT$	$\frac{eRT}{hLC^{\theta}} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$
<b>Gas, unimolecular</b>	$\Delta H^{\ddagger} + RT$	$\frac{eRT}{hL} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$
<b>Gas, bimolecular</b>	$\Delta H^{\ddagger} + 2RT$	$\frac{e^2 RT}{hLC^{\theta}} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$
<b>Gas, termolecular</b>	$\Delta H^{\ddagger} + 3RT$	$\frac{e^3 RT}{hLC^{\theta 2}} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right)$

## 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