

Kinetics

CHEM 323 Physical Chemistry I

Background

- Chemical Reactions cause Composition of Systems to change over Time
 - Chemical potential goes to zero (equilibrium)
 - At equilibrium microscopic change occurs
- Field of Kinetics studies how Chemical Reactions occur
 - Tied to, but independent of, thermodynamics
 - Thermodynamics is path-independent
 - Kinetics path-dependent

The Kinetics Experiment

- Measure Change in Composition as a Function of Time
 - Monitor pressure, concentration, etc.
- Real-Time Methods
 - Direct monitoring
 - Flow/stopped-flow methods
 - Pulse methods (flash photolysis, T-jump)
- Quench Methods
 - Standard/flow methods
 - Freeze quench

Rate of Reaction

- Definition of Reaction Rate

$$v = \frac{d\xi}{dt} = \frac{1}{\nu_J} \frac{dn_J}{dt}$$

- Products versus reactants
- Heterogeneous versus homogeneous
- Rate Law
 - Experimentally determined expression not from balanced chemical equation
 - Rate constant
 - Reaction order (overall and partial orders)

Determining the Rate Law

- Full Differential Equations
- Isolation Method
 - Pseudo-order rate laws
 - Extracting order with respect to other species
- Method of Initial Rates
- Integrated Rate Laws
 - Simplest cases with solvable differential equations (one or two reactants)
 - See Table 22.3 in Atkins and de Paula
 - Used in conjunction with isolation method

Relationship of Kinetics to Thermodynamics

- Equilibrium Constant

$$K = \frac{k_{forward}}{k_{reverse}}$$

- Activation Energy

- Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT} \quad k = Ae^{-E_a/RT}$$

- Reaction potential energy profiles/surfaces
- Hammond postulate

Relationship of Kinetics to Thermodynamics

- Transition State Theory
 - What is a transition state?
- Eyring Equation
 - Relates k to $\Delta^\ddagger G$, $\Delta^\ddagger S$ and $\Delta^\ddagger H$
 - Correspondence to Arrhenius equation (meaning of A and E_a)

$$k = \frac{k_b T}{h} e^{\Delta^\ddagger S/R} e^{-\Delta^\ddagger H/RT} = \frac{k_b T}{h} e^{-\Delta^\ddagger G/RT}$$

$$k = \frac{k_b T}{h} K^\ddagger$$

Complex Reactions

- Preceding strictly applies only to Reactions with a single Step
- Many Reactions consist of many Elementary Steps
 - Reaction mechanism (stoichiometric/intimate)
 - Rate law of elementary step
 - Molecularity
- Studied using standard Kinetic Methods
 - Complex rate laws and overall orders

Complex Reactions

- Multi-step Mechanisms require Formation of Intermediates
- Rate-Determining Step
 - Slowest elementary step in mechanism
 - Determines how fast reaction can occur
 - Determines form of the rate law
- Converting Mechanism to Rate Law
 - Steady-state approximation
 - Predicted rate law must match experimental
 - Mechanism is not a probe of structure

Examples

- Single-Step Reactions
 - Irreversible (rate laws, S_{N2})
 - Reversible
- Consecutive Reactions
 - Pre-equilibrium followed by slow step
 - Dissociative substitution reaction (S_{N1})
 - Associative substitution reaction
 - Competitive pathways

More on Complex Reactions

- Kinetic Isotope Effect
 - Primary kinetic isotope effect
 - Secondary kinetic isotope effect
 - Most important for H/D
- Activation Energy of a Multi-Step Reaction
 - Each k has Arrhenius behavior
 - Total E_a is sum of E_a in numerator less sum of E_a in the denominator
 - Total E_a can be negative!

$$k = \frac{k_1 k_2}{k_{-1}} = \frac{A_1 A_2}{A_{-1}} e^{-(E_{a1} + E_{a2} - E_{a-1})/RT}$$

More on Complex Reactions

- Microscopic Reversibility
- Role of Solvent
 - Polar solvents stabilize charge
 - Lewis bases
- Influence of Ionic Strength
 - Reactions with neutral species unaffected
 - For reactions involving ions in aqueous solution the following applies ($I \leq 0.1$)

$$\log k = \log k_0 + 1.02 z_A z_B \sqrt{I}$$

Catalysts

- Definition
 - Decreases E_a by changing mechanism
- Important Terms
 - Homogenous/heterogeneous
 - Turnover number/efficiency
 - Catalyst poisoning/inhibition
- Autocatalysis
 - Oscillating chemical reactions
 - Bistability
 - Chemical chaos
