

Chemistry 120

Kinetics

Kinetics and Thermodynamics

- Thermodynamics
 - Predicts permissible changes
 - Gives direction of a permissible change
 - Does not answer how change occurs
- Kinetics
 - Concerned with how change occurs
 - Measures change in concentration with time (*rate* of a chemical reaction)
 - Relates this to chemical change on the microscopic level

Rate of Reaction

- For General Reaction: $aA + bB \rightarrow cC + dD$
Rate of Reaction is related to Concentration Change by

$$\text{rate} = -\frac{1}{a} \cdot \frac{d[A]}{dt} = -\frac{1}{b} \cdot \frac{d[B]}{dt} = \frac{1}{c} \cdot \frac{d[C]}{dt} = \frac{1}{d} \cdot \frac{d[D]}{dt}$$

- These are *instantaneous rates* for measurable change, use *average rate*

$$\text{rate} = -\frac{1}{a} \cdot \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \cdot \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \cdot \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \cdot \frac{\Delta[D]}{\Delta t}$$

Rate Law/Rate Equation

- Relates Reactant Concentrations to Rate of Reaction
- For Reaction: $aA + bB + cC \rightarrow \text{products}$, Rate Law is: $\text{rate} = k[A]^x[B]^y[C]^z$
 - x, y, z (*order of reaction* with respect to reactant) may not be equal to a, b, c
 - k is the *rate constant*
 - Sum of superscripts is *overall order*
- Rate Law is not derivable from balanced Equation, it must be found Experimentally

Determining the Rate Law

- *Method of Initial Rates*
 - Determine reaction rate over a short time
 - Systematically vary concentrations and determine how rate of reaction changes
 - Determine rate law

Concentration Change	Rate Change	Reactant Order
any	none	0
double	double	1
double	quadruples	2
double	halves	-1

Determining the Rate Law

- *Integrated Rate Laws*
- For the Reaction: $R \rightarrow \text{Products}$
 - If it is zeroth order with respect to R, the rate law is $[R]_t - [R]_0 = -k \cdot t$
 - If reaction is first order with respect to R, the rate law is $\ln[R]_t - \ln[R]_0 = -k \cdot t$
 - If reaction is second order with respect to R, the rate law is $\frac{1}{[R]_t} - \frac{1}{[R]_0} = k \cdot t$
- Note on form of Integrated Rate Laws for following Product Formation

Integrated Rate Laws

- Can be rearranged to a Linear Form in t

	$y = m \cdot x + b$			Units on k
0 th Order	$[R]_t$	$-k \cdot t$	$[R]_0$	$M \cdot s^{-1}$
1 st Order	$\ln[R]_t$	$-k \cdot t$	$\ln[R]_0$	s^{-1}
2 nd Order	$\frac{1}{[R]_t}$	$+k \cdot t$	$\frac{1}{[R]_0}$	$M^{-1} \cdot s^{-1}$

- Prepare different graphs of concentration as a function of time until get a straight line

Integrated Rate Laws

- Integrated Rate Laws can only be used when there is only one Reactant
 - With more than one reactant need to keep other reactant concentrations constant
- *Isolation Method*
 - Make all but one reactant concentration very large (won't change during course of reaction)

$$\text{rate} = \underbrace{k[A]^x[B]^y}_{\substack{\text{Large and} \\ \text{constant}}} [C]^z = k_{obs}[C]^z$$

$$k_{obs} = k[A]^x[B]^y$$

Integrated Rate Laws

- Using the Isolation Method
 - Integrated rate law used to get order of isolated reactant
 - Systematically vary which reactant is isolated
 - Calculate k from k_{obs} at known concentrations once orders are all known
- Sometimes Reactants can't be isolated
 - Rearrange k_{obs} expression to get linear relationship as follows
 - If rate = $k[A]^x[B]^y = k_{obs}[B]^y$ with $k_{obs} = k[A]^x$ then $\log(k_{obs}) = \log k + x \log[A]$

Additional Rate Law Information

- *Half-Life*
 - Form for first-order reaction is important in nuclear processes
- Further Complications
 - *Induction period*
 - Complex reactions can't be treated with any of these methods (must solve full set of differential equations)
 - Rates for all reactions deviate from ideal behavior toward end of the reaction

Meaning of the Rate Law

- *Reaction Mechanism* is proposed Series of *Elementary Steps* by which Reactants are Transformed to Products
 - *Stoichiometric mechanism*: shows which species are present and the order in which they appear/disappear as the reaction proceeds
 - *Intimate mechanism*: concerned with what bonds break, etc. when one species is transformed to another in a chemical reaction

Elementary Steps

- Chemical Equations that represent single Molecular Events
- Each Elementary Step has own Rate Law and Rate Constant
 - Can write rate law for a step from its equation
 - *Molecularity*
 - *Rate determining step*
- Sum of Elementary Steps must be the Overall Balanced Chemical Equation

Mechanism and the Rate Law

- A Multi-step Mechanism will have only one Rate Limiting Step which determines
 - How fast the reaction can go
 - Rate law for the overall reaction
- From Mechanism derive a Rate Law, which must match Experimental Rate Law for Mechanism to be Accepted
 - If mechanism does not give correct rate law, it is rejected

Stoichiometric Mechanisms

- First Step is Slow
 - It determines rate law
 - No information about subsequent step(s) can be gained
- Initial Step is Fast
 - *Intermediate* determines reaction rate
 - *Steady state approximation*
 - Characteristics of first step can be inferred
 - Rate law must be calculated
- Example

Stoichiometric Mechanisms

- If Predicted Rate Law is consistent with Experiment
 - Evidence for mechanism
 - Does not mean it is true mechanism
- Kinetics points to existence of Intermediates, but does not give Structure
 - Structural information (spectroscopic or other) must be obtained separately
 - Structure of intermediate can be further evidence for a mechanism

Intimate Mechanisms

- Attempts to show what Bonds break and form during Reaction based on known
 - Reactions
 - Bonding rules (with accommodation that intermediates are not very stable)
- Formalism used in Intimate Mechanism
 - Electrons (either paired or unpaired) attack
 - Opposite charges try to combine
 - Single electron attack is single-headed arrow
 - Paired electron attack is double-headed arrow

Kinetics and Thermodynamics

- Why don't Reactions with $\Delta G < 0$ just happen?
- Why do Reactions with $\Delta G < 0$ require an Input of Energy to occur?
 - $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
- Reactants must come together in correct Orientation with sufficient Energy for Reaction to occur

Arrhenius Equation

- Experimentally Derived relationship between Rate Constant and
 - Energy required to bring reactants together (*activation energy*, E_a , almost always positive)
 - The *frequency factor*, A , which is a measure of collision frequency and orientation

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

$$E_a = RT^2 \frac{d \ln k}{dT} \quad R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$$

Eyring Equation

- Rate Constant in terms of *Thermodynamic Activation Parameters* (ΔH^\ddagger , and ΔS^\ddagger)

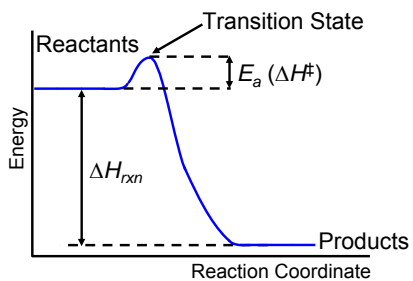
$$k = (\text{constant}) \cdot e^{\frac{\Delta S^\ddagger}{R}} \cdot e^{-\frac{\Delta H^\ddagger}{RT}}$$

- E_a is related to ΔH^\ddagger so is a measure of bonding (*intermolecular or intramolecular*)
- A is related to ΔS^\ddagger so it has to do with organization of transition state
- ΔH^\ddagger is always positive (why?)
- ΔS^\ddagger is always negative (why?)
- How does this affect rate constant?

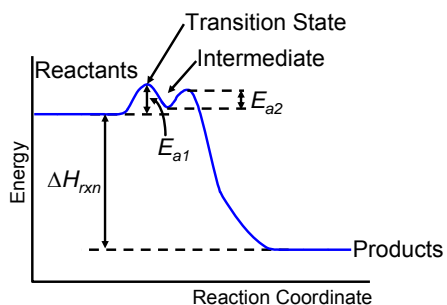
Arrhenius Equation

- Energy must be added to push Reactants to the Point where they can react
 - *Activated complex or transition state*
 - Transition state vs. intermediate
- Reactions occur by deforming Bonds in Reactants to look like Products
 - Multi-dimensional problem for molecules
 - Reaction profiles simplify multi-dimensional problem

Reaction Profile



Reaction Profile

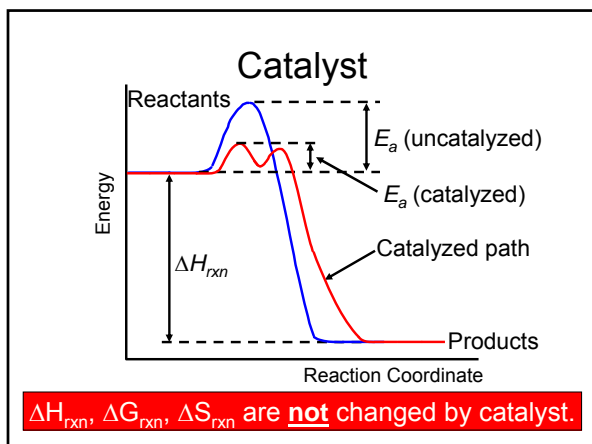


Reaction Profile

- Endothermic Reactions are similar, except Energy of Products higher than Energy of Reactants (ΔH is positive)
 - Endothermic reactions tend to have larger E_a (why?)
- Sometimes Gibbs Energy is on the y-Axis
 - Energy difference between reactants and products is ΔG_{rxn}
 - Energy to achieve transition state is ΔG^\ddagger

Catalyst

- Substance that increases the Rate of Reaction but is not consumed in the Reaction (may occur in Rate Law)
 - *Homogeneous*: catalyst is in same phase as the reaction (enzymes)
 - *Heterogeneous*: catalyst is in a different phase from the reaction (Pt in catalytic converter)
- Catalyst changes Rate by changing Reaction Pathway
 - New pathway has a lower E_a



Kinetics vs. Thermodynamics

- Thermodynamics defines permissible Change and its Spontaneous Direction, while Kinetics defines how Change occurs
 - Kinetics and thermodynamics can either complement each other or fight each other
- Direction of Change with negative ΔG is toward more *thermodynamically stable* State
 - Thermodynamic stability is always relative

Kinetics vs. Thermodynamics

- Substance is kinetically stable (*inert*) if Rates of all possible Reactions are slow
 - Large E_a or small A
 - Kinetically unstable (*labile*) substances have at least one fast pathway to something else
- Achieving a thermodynamically stable State depends on Lability
 - You can't get there from here
 - Trapping thermodynamically unstable species
 - *Metastable*
