

Chapter 14: Chemical Kinetics

- **chemical kinetics** – area of chemistry dealing with speeds/rates of reactions
- rates of reactions affected by four factors
- 1) concentrations of reactants
- 2) temperature at which reaction occurs
- 3) presence of a catalyst
- 4) surface area of solid or liquid reactants and/or catalysts

14.1 Reaction Rates

- **reaction rate** – speed of a chemical reaction
- average rate = $\frac{\text{change \# moles B}}{\text{change in time}} = \frac{\Delta \text{moles of B}}{\Delta t}$ if $A \rightarrow B$
- $\Delta \text{moles B} = \text{moles B at final time} - \text{moles B at initial time}$
- average rate = $-\frac{\Delta \text{moles A}}{\Delta t}$ if $A \rightarrow B$

14.1.1 Rates in Terms of Concentrations

- rate calculated in units of M/s
- brackets around a substance indicate the concentration
- **instantaneous rate** – rate at a particular time
- instantaneous rate obtained from the straight line tangent that touches the curve at a specific point
- slopes give instantaneous rates
- instantaneous rate also referred to as the rate

14.1.2 Reaction Rates and Stoichiometry

- for the reaction $aA + bB \rightarrow cC + dD$
- rate = $-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = -\frac{1}{c} \frac{\Delta[C]}{\Delta t} = -\frac{1}{d} \frac{\Delta[D]}{\Delta t}$

14.2 The Dependence of Rate on Concentration

- equation used only if C and D only substances formed
- Rate = $k[A][B]$
- **Rate law** – expression that shows that rate depends on concentrations of reactants
 - K = rate constant

14.2.1 Reaction Order

- Rate = $k[\text{reactant 1}]^m[\text{reactant 2}]^n$
- m, n are called reaction orders
- $m+n$, overall reaction order
- reaction orders do not have to correspond with coefficients in balanced equation
- values of reaction order determined experimentally
 - reaction order can be fractional or negative

14.2.2 Units of Rates Constants

- units of rate constant depend on overall reaction order of rate law
- for reaction of second order overall
 - units of rate = (units of rate constant)(units of concentration)²
 - units of rate constant = $M^{-1}s^{-1}$

14.2.3 Using Initial Rates to Determine Rate Laws

- **zero order** – no change in rate when concentration changed

- **first order** – proportional changes in rate
- **second order** – increase rate by 2² or 3³, etc...
- rate constant does not depend on concentration

14.3 The Changes of Concentration with Time

- rate laws can be converted into equations that give concentrations of reactants or products

14.3.1 First-Order Reactions

- $\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$
- $\ln[A]_t = \ln[A]_0 = -kt$ or $\ln \frac{[A]_t}{[A]_0} = -kt$
- $\ln[A]_t = -kt + \ln[A]_0$
- corresponds to $y = mx + b$
- equations used to determine:
 - 1) concentration of reactant remaining at any time
 - 2) time required for given fraction of sample to react
 - 3) time required for reactant concentration to reach a certain level

14.3.2 Half-Life

- half-life of first order reaction
- $t_{1/2} = -\frac{\ln \frac{1}{2}}{k} = \frac{0.693}{k}$
- **half-life** – time required for concentration of reactant to drop by one half initial value
- $t_{1/2}$ of first order independent of initial concentrations
- half-life same at any given time of reaction
- in first order reaction – concentrations of reactant decreases by 1/2 in each series of regularly spaced time intervals

14.3.3 Second-Order Reactions

- rate depends on reactant concentration raised to second power or concentrations of two different reactant each raised to first power
- $\text{Rate} = k[A]^2$
- $\frac{1}{[A]_t} = kt + \frac{1}{k[A]_0}$
- $\text{half life} = t_{1/2} = \frac{1}{k[A]_0}$
- half life dependent on initial concentration of reactant

14.4 Temperature and Rate

- **chemiluminescent reaction** – reaction that produces light
- rate constant must increase with increasing temperature

14.4.1 The Collision Model

- **collision model** – molecules must collide to react
- greater number of collisions the greater the reaction rate
- for most reactions only small amount of collisions lead to a reaction

14.4.2 Activation Energy

- Svante Arrhenius

- Molecules must have a minimum amount of energy to react
- Energy comes from kinetic energy of collisions
- Kinetic energy used to break bonds
- Activation energy, E_a – minimum energy required to initiate a chemical reaction
- Activated complex or transition state – atoms at the top of the energy barrier
- Rate depends on E_a
- Lower E_a means faster reaction
- Reactions occur with collisions and orientation of molecules

14.4.3 The Arrhenius Equation

- reaction rate data:
 - $k = Ae^{-E_a/RT}$ (Arrhenius Equation)
 - k = rate constant, E_a = activation energy, R = gas constant (8.314 J/mol K), T = absolute temperature, A = frequency factor
 - A relates to frequency of collisions, favorable orientations
 - $\ln k = -\frac{E_a}{RT} + \ln A$
 - $\ln k$ vs $1/T$ graph has slope $-E_a/R$ and y-intercept $\ln A$
 - for two temperatures:
 - $\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$
 - used to calculate rate constant, k_1 and T_1

14.5 Reaction Mechanisms

- **reaction mechanism** – process by which a reaction occurs

14.5.1 Elementary Steps

- **elementary steps** – each step in a reaction
- **molecularity** – if only one molecule involved in step
- **unimolecular** – if only one molecule involved in step
- **bimolecular** – elementary step involving collision of two reactant molecules
- **termolecular** – elementary step involving simultaneous collision of three molecules
- elementary steps in multistep mechanism must always add to give chemical equation of overall process
- **intermediate** – product formed in one step and consumed in a later step

14.5.2 Rate Laws of Elementary Steps

- if reaction is known to be an elementary step then the rate law is known
- rate of unimolecular step is first order (Rate = $k[A]$)
- rate of bimolecular steps is second order (Rate = $k[A][B]$)
 - first order in $[A]$ and $[B]$
 - if double $[A]$ than number of collisions of A and B will double

14.5.3 Rate laws of multistep mechanisms

- **rate-determining step** – slowest elementary step
 - determines rate law of overall reaction

14.5.4 Mechanisms with an Initial First Step

- intermediates usually unstable, low and unknown concentrations
- whenever a fast step precedes a slow one, solve for concentration of intermediate by assuming that equilibrium is established in fast step

14.6 Catalysis

- **catalyst** – substance that changes speed of chemical reaction without undergoing a permanent chemical change

14.6.1 Homogeneous Catalysis

- **homogeneous catalyst** – catalyst that is present in same phase as reacting molecule
- catalysts alter E_a or A
- generally catalysts lowers overall E_a for chemical reaction
- catalysts provides a different mechanism for reaction

14.6.2 Heterogeneous Catalysis

- exists in different phase from reactants
- initial step in heterogeneous catalyst is adsorption
- **adsorption** – binding of molecules to surface
- adsorption occurs because ions/atoms at surface of solid extremely reactive

14.6.3 Enzymes

- biological catalysts
- large protein molecules with molecular weights 10,000 – 1 million amu
- **catalase** – enzyme in blood and liver that decomposes hydrogen peroxide into water and oxygen
- **substrates** – substances that undergo reaction at the active site
- **lock-and-key model** – substrate molecules bind specifically to the active site
- **enzyme-substrate complex** – combination of enzyme and substrate
- binding between enzyme and substrate involves intermolecular forces (dipole-dipole, hydrogen bonding, and London dispersion forces)
- product from reaction leaves enzyme allowing for another substrate to enter enzyme
- **enzyme inhibitors** – molecules that bind strongly to enzymes
- **turnover number** – number of catalyzed reactions occurring at a particular active site
- large turnover numbers = low activation energies