A general chemistry Libretexts Textmap organized around the textbook

**Chemistry: The Central Science**
by Brown, LeMay, Busten, Murphy, and Woodward

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These is a summary of key concepts of the chapter in the Textmap created for "Chemistry: The Central Science" by Brown et al.
14.1: Factors that Affect Reaction Rates

**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

14.2: Reaction Rates

- **reaction rate** – speed of a chemical reaction

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

14.3: Concentration and Rate

- equation used only if C and D only substances formed
- \[ \text{Rate} = k[A][B] \]
• **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 \( 2^2 \) or \( 3^3 \), etc...
  - rate constant does not depend on concentration

**14.4: The Change of Concentration with Time**

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

**14.3.1 First-Order Reactions**

- 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

• 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 \( \frac{1}{2} \) 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
• Rate = \( k[A]^2 \)

• half life dependent on initial concentration of reactant

14.5: 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:

• (Arrhenius Equation)
• $k = \text{rate constant, } E_a = \text{activation energy, } R = \text{gas constant (8.314 J/mol K), } T = \text{absolute temperature, } A = \text{frequency factor}$
• $A$ relates to frequency of collisions, favorable orientations

• In $k$ vs 1/t graph has slope $-E_a/R$ and y-intercept $\ln A$
• for two temperatures:

• used to calculate rate constant, $k_1$ and $T_1$

14.6: 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

14.7: 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