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

\[
\text{average rate} = \frac{\text{change in moles B}}{\text{change in time}} = \frac{\Delta \text{moles B}}{\Delta t} \quad \text{if } A \to B
\]

\[
\Delta \text{moles B} = \text{moles B at final time} - \text{moles B at initial time}
\]

\[
\text{average rate} = -\frac{\Delta \text{moles A}}{\Delta t} \quad \text{if } A \to B
\]

14.2.1 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

14.2.2 Reaction Rates and Stoichiometry

- for the irreversible reaction \( aA + bB \to cC + dD \)

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

14.3: Concentration and Rate

- 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
- \( k = \text{rate constant} \)
14.3.1 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

14.3.2 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$^{-1}$

14.3.3 Using Initial Rates to Determine Rate Laws

- zero order – no change in rate when concentration changed
- first order – change in concentration gives proportional changes in rate
- second order – change in concentration changes rate by the square of the concentration change, such as $2^2$ or $3^2$, 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

14.4.1 First-Order Reactions

\[ \text{rate} = -\frac{\Delta [A]}{\Delta t} = k[A] \]

and in integral form:

\[ \ln[A]_t - \ln[A]_0 = -kt \]

or

\[ \ln\frac{[A]_t}{[A]_0} = -kt \]

\[ \ln[A]_t = -kt + \ln[A]_0 \]

- corresponds to a straight line with $y = mx + b$
- 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
  \[ t_{\frac{1}{2}} = -\frac{\ln\frac{1}{2}}{k} = \frac{0.693}{k} \]
  - **half-life** – time required for concentration of reactant to drop to one-half of initial value
  - \( t_{\frac{1}{2}} \) 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 reactants each raised to first power
  \[ \text{Rate} = k[A]^2 \]
  \[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \]
  \[ \text{half life} = t_{\frac{1}{2}} = \frac{1}{k[A]_0} \]
  - half life dependent on initial concentration of reactant

14.5: Temperature and Rate

- rate constant must increase with increasing temperature, thus increasing the rate of reaction

14.5.1 The Collision Model

- **collision model** – molecules must collide to react
  - greater frequency of collisions the greater the reaction rate
  - for most reactions only a small fraction of collisions leads to a reaction

14.5.2 Activation Energy

- Svante August 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 temperature and $E_a$
• Lower $E_a$ means faster reaction
• Reactions occur when collisions between molecules occur with enough energy and proper orientation

14.5.3 The Arrhenius Equation

• reaction rate data:
  • the Arrhenius Equation:
    \[
    k = A e^{\frac{-E_a}{RT}}
    \]
  • $k$ = 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
    \[
    \ln k = -\frac{E_a}{RT} + \ln A
    \]
  • the $\ln k$ vs. $1/T$ graph (also known as an Arrhenius plot) has a slope $-\frac{E_a}{R}$ and the 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 $(T_1)$

14.6: Reaction Mechanisms

• reaction mechanism – process by which a reaction occurs

14.6.1 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 multi-step mechanism must always add to give chemical equation of overall process
• intermediate – product formed in one step and consumed in a later step

14.6.2 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

### 14.6.3 Rate Laws of Multi-step Mechanisms

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

### 14.6.4 Mechanisms with an Initial Slow Step vs. Mechanisms with an Initial Fast Step

• intermediates are usually unstable, in low concentration, and difficult to isolate
• when 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

#### 14.7.1 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

#### 14.7.2 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

#### 14.7.3 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