A general chemistry Libretexts Textmap organized around the textbook

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

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• Homework

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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

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

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

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

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 = 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 ½ 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 \( -(E_a/R) \) 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 = \( k[A][B] \))
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