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

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

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

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

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 \((aA+bB \to cC+dD)\)

\[
\text{rate} = -\frac{\Delta \text{moles A}}{\Delta t} = -\frac{\Delta \text{moles B}}{\Delta t}
\]
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[reactant 1]^m[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

\[ \text{half life} = t_{\frac{1}{2}} = \frac{0.693}{k} \]

- 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:

\[
\text{\( k = A e^{\frac{-E_a}{RT}} \)}
\]

\( k \) = 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. \( \frac{1}{T} \) 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

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### 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