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

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

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

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

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)
- 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 ($8.314 \text{ J/(mol K)}$), $(T)$ = 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 = $k[A][B]$)
• 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