21: Chemiscal Kinetics II – Reaction Mechanisms

Key Chemistry Terms

- **Reaction Mechanism:** Series of elementary steps that add up to the overall reaction.
- **Elementary Reactions:** The reaction step that involves only one or two molecules.
- **Intermediate:** Species produced in an elementary step and then consumed in another step—does not appear in the overall equation.
- **Rate Determining Step:** Slowest step in a reaction mechanism.
- **Chain Reaction** – A sequence of reactions that one or more of products from the previous step that are active species and trigger subsequent reactions.
- **Chain Carriers** – The active and unstable products are sometimes called intermediates. The intermediates that cause another reaction are called chain carriers.
- **Photolysis** – A dissociation reaction initiated by photons. The molecules are stimulated by the absorption of electromagnetic energy.
- **Thermolysis** – A dissociation reaction initiated by heat. The molecules are stimulated by the absorption of kinetic energy through intermolecular collisions.
- **Pyrolysis** – A thermolysis in the absence of air.
- **Photochemical Reaction** – The reactions initiated by the absorption of light. Most important photochemical reactions occur in the atmosphere that absorb ultraviolet light and lead to the temperature increase.
- **Photosensitization** - If a molecule obtained kinetic energy from another molecule which is stimulated by photons, this process is called photosensitization.
- **Quenching** - The molecules stimulated by absorption of photons can lose part of its energy by collisions with other molecules. The process is called quenching.

Steps of Chain Reactions

- **Initiation Step** – The step that the chain carriers are initially formed. They include: photolysis, thermolysis, pyrolysis, etc.
- **Propagation Step** – The chain carriers formed in the initiation step attack other reactant molecules, and yield new carriers.
- **Termination Step** – The carriers combine to form stable species.
- **Inhibition Step** – The carriers are removed by reaction with walls or with foreign molecules, other than chain termination.

Example of Chain Reaction:
The pyrolysis of acetaldehyde

Initiation:	$CH_3CHO \rightarrow CH_3 + CHO$
Propagation:	$CH_3CHO + CH_3 \rightarrow CH_4 + CH_3CO$
Propagation:	$CH_3CO \rightarrow CH_3 + CO$
Termination:	$CH_3 + CH_3 \rightarrow CH_3CH_3$

Explosions

- **Thermal Explosion** is due to the fast increase of reaction rates with increasing temperature.
- **Chain-Branching Explosion** is caused by the chain-branching steps which create more than one chain carriers in each step. Therefore, the number of chain centers grows exponentially and the rate of reaction may cascade into an explosion.

Quantum Yields

- **Energy of photon -** The energy of each photon is determined by the frequency.

  $E=h\nu$, ν is the frequency in s^{-1},
  h is Planck constant, $h = 6\times10^{-34}$ Js.
- **Number of photons :** $N = \dfrac{E}{h\nu}$
- **Quantum Yield Φ** - The number of product molecules generated per photon absorbed.

$$\Phi = \frac{\text{Number Of Product Molecules Generated}}{\text{Number Of Photons Absorbed}}$$

Polymerization

Polymerization – Polymerization is a process of monomer molecules form polymer chains in a chemical reaction. Polymer molecules consist of a large number of atoms.

There are two major types of polymerization:

1. **Chain polymerization** – An activated monomer (usually a free radical) attacks another monomer, links to it, and then the unit attacks another monomer. In chain polymerization, the monomer is used up slowly through the reaction by linking to growing chains.
2. **Step polymerization** – Any two monomers present in the reaction mixture can link together at any time. Step polymerization commonly proceeds by a condensation reaction. The monomer is used up early in the reaction.

Catalysis

- **Catalysis** – Acceleration of chemical reactions due to a catalyst.
- **Catalyst** – A substance that increases the rate of a chemical reaction, but itself is not consumed by the overall reaction.
- **Homogeneous Catalysis** – A catalyst in the same phase as the reaction mixture.
- **Heterogeneous Catalyst** – A catalyst in the different phase as the reaction mixture.
- **Autocatalysis** – the reaction product itself is the catalyst for that reaction.
- **Oscillating Reactions** – In an oscillating reaction, some species are created and then consumed. This is usually an consequence of autocatalysis.

Michaelis-Menten Mehcanism

Michaelis-Menten is the mechanism of enzyme reaction in which an intermediate of substrate-enzyme is formed.

$$E + S \underset{k_a}{\longleftrightarrow} ES \xrightarrow{k_b} PE + P$$

$$\frac{dP}{dt} = k_b[ES]$$

$$\frac{d[ES]}{dt} = k_a[E][S] - k_a^{'}[ES] - k_b[ES]$$

Using the assumption of steady-state, the rate law of product P formation can be approximated by the equation:

$\dfrac{d[P]}{dt} = k_b[E]_0$, where $[E]_0$ is the initial concentration of the enzyme.

How to Use This Cheat Sheet: These are the keys related this topic. Try to read through it carefully twice then recite it out on a blank sheet of paper. Review it again before the exams.