20: Kinetics & Equilibrium

Key Chemistry Terms

- **Kinetics:** The study of reaction rates.
- **Reaction Rate:** Rate at which reactants produce products.
- **Activation Energy (E_A):** Minimum energy a collision must have in order to produce a reaction.
- **Reaction Coordinate Diagram:** Shows energy of reactants, products, activated complex.
- **Activated Complex (or Transition State):** In-between stage—reactants have not yet broken apart and products have not yet formed.
- **Endothermic:** Energy is absorbed from the surroundings—the products have more energy than the reactants.
- **Exothermic:** Energy is released into the surroundings—the products have less energy than the reactants.
- **Catalyst:** Speeds up the reaction without being used up.
- **Elementary Step:** Chemical equation showing reactants in one collision and the products formed.
- **Reaction Mechanism:** Series of elementary steps that add up to the overall reaction.
- **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.
- **Differential Rate Law:** relates concentration and rate.
- **Rate Order:** The number of times that species must collide in the rate determining elementary step.
- **Reversible Reaction:** Reaction that can proceed in both directions.
- **Equilibrium:** When the rate of the forward and reverse of a reversible process are equal.
- **Dynamic Equilibrium:** The number of reactants and products do not change, but the reaction continues to occur in both directions.
- **Equilibrium Constant Expression:** Equation showing the ratio of the concentration of products to reactants with the balanced equation coefficients as powers.
- **Equilibrium Constant (*K*):** The value found when equilibrium concentrations are plugged into the equilibrium constant expression.
- **Homogeneous Equilibrium:** When all species are the same state of matter.
- **Heterogeneous Equilibrium:** When there are at least 2 different states of matter present.
- **Reaction Quotient (*Q*):** When concentrations at any time are plugged into the equilibrium constant expression. Used to determine if a system is at equilibrium.
- **Solubility Product (K_{sp}):** Equilibrium constant for a dissolution reaction.
- **Dissolution Reaction:** The process of a solid dissolving and forming ions.
- **Saturated Solution:** A solution that is at equilibrium.
- **Solubility:** The amount of a solid that will completely dissolve to form a saturated solution.
- **Le Chatelier's Principle:** A system at equilibrium will re-adjust to reach equilibrium again when disturbed.
- **Exothermic Reaction:** System gives off energy to the surroundings. Energy can be thought of as a product.
- **Endothermic Reaction:** System gains energy from the surroundings. Energy can be thought of as a reactant.

Collision Theory

In order for a reaction to occur, the molecules must:

√ Collide
√ Collide with the correct orientation
√ Collide with the at least the Activation Energy

Factors Affecting Rate

Factors will increase rate by increasing the change that a successful collisions will occur:

√ **Surface area**—as surface area increases, rate increases
√ **Concentration**—as concentration increases, rate increases.
√ **Temperature**—as temperature increases, rate increases.
√ **Catalyst**—presence of a catalyst increases rate.

Reaction Mechanisms

Example:

Step 1: $\cancel{NO_2} + NO_2 \rightarrow NO + \cancel{NO_3}$
Step 2: $\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2$
Overall: $NO_2 + CO_2 \rightarrow NO + CO_2$
NO_3 is **intermediate**
The reaction mechanism must match the experimentally determined rate law.

Rate Laws

- k = **rate law constant**. It's different for each reaction at each temperature.
- [A] = concentration of reactant.
- $[A]_0$ = initial concentration of reactant.
- t = time

Rate Laws:

Order	Differential Law
0	Rate = k
1	Rate = k[A]
2	Rate = $k[A]^2$

Establishing Equilibrium

Equilibrium is not established instantly. The forward reaction must produce products, which can then reform reactants. As the forward rate slows and the reverse rate increases, equilibrium will be established.

Equilibrium Constants

Writing equilibrium constant expressions

- Write the concentration of the products over the concentration of the reactants except pure liquids & solids.
- Use the coefficients of the balanced equations as powers for each species.

Le Chatelier's Principle

The system will try to un-do what you did

Change made	Reaction will shift towards
Add reactant	Products
Remove reactant	Reactants
Add a product	Reactants
Remove a product	Products
Decrease volume	Side with least gas particles
Increase volume	Side with most gas particles

- For endothermic reactions, energy is reactant.
- For exothermic reactions, energy is a product.

Changes that do not affect equilibrium:

- Adding/removing a pure solid or liquid.
- Adding/removing a non-reactive gas.
- Changing the volume of a reaction with equal number of gas particles on each side.
- Adding a catalyst.

Equilibrium & Free Energy

ΔG = 0 at equilibrium

$$\Delta G^\circ = -RT \ln K \quad \text{and} \quad \Delta G = \Delta G^\circ + RT \ln Q$$

ΔG° = free energy change at standard state (1 atm and 25°C)
R = 8.31 J/mole×K T = temperature (in Kelvin)
K = equilibrium constant Q = Reaction Quotient