# 20: Kinetics & Equilibrium

## Key Chemistry Terms

- **Kinetics:** 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: $\underline{\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2}$
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**. Is 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

 