Chemical equilibrium is a fundamental concept in chemistry, describing the state achieved by a reversible chemical reaction when the rate of the forward reaction equals the rate of the reverse reaction. This condition is reached when the composition of the reaction mixture corresponds to the minimum Gibbs free energy.

1. Nature of Chemical Equilibrium

A chemical equilibrium is a **dynamic equilibrium**. This means that while the concentrations of all species remain constant, the forward and reverse reactions continue to take place simultaneously at equal rates. Because there is no tendency for spontaneous change in either direction, the total Gibbs free energy change (ΔG) of the reaction is zero at equilibrium, provided the process is occurring at constant temperature and pressure.

Chemical reactions tend spontaneously toward equilibrium. Equilibria are classified based on the phases of the substances involved:

- **Homogeneous Equilibria:** All reactants and products are in the same phase.
- **Heterogeneous Equilibria:** The system involves more than one phase, such as the equilibrium between a solid salt and its dissolved ions in a saturated solution.

2. The Equilibrium Constant (K)

The composition of a reaction mixture at equilibrium is characterized by a single quantity called the **equilibrium constant (K)**. The mathematical relation that summarizes the equilibrium composition is known as the **law of mass action**.

For a general reversible reaction: $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

The equilibrium constant K is expressed as the ratio of the activities of products raised to their stoichiometric coefficients divided by the activities of reactants similarly raised:

$$K = \frac{\text{(activities of products)}}{\text{(activities of reactants)}}$$

Key rules for calculating K:

- **Activities:** For practical calculations involving low-pressure gases and dilute solutions, activities are often approximated by numerical values of partial pressure (in bar) or molar concentration (in moles per liter).
- **Pure Solids and Liquids:** The activity of a pure solid or liquid is defined as 1 and is consequently omitted from the expression for K.
- **Temperature Dependence:** K is a fixed value for a specific reaction at any given temperature.
- **Stoichiometry:** If a chemical equation is reversed, the new equilibrium constant is $1/K$; if the equation is multiplied by a factor n, the new constant is K^n.

The Extent of Reaction

The magnitude of K indicates the relative amounts of products and reactants present at equilibrium:

- **Large** K **($> 10^3$):** The equilibrium favors the products, meaning the reaction essentially goes to completion.
- **Small** K **($< 10^{-3}$):** The equilibrium favors the reactants.
- **Intermediate** K**:** Neither reactants nor products are strongly favored.

3. Thermodynamic Basis

The thermodynamic condition for equilibrium is $\Delta G = 0$. The standard Gibbs free energy of reaction (ΔG_r°) is linked to the equilibrium constant by the fundamental equation: $\Delta G_r^\circ = -RT \ln K$

This relation confirms that if ΔG_r° is negative, then K must be greater than 1 (products are favored), and if ΔG_r° is positive, K must be less than 1 (reactants are favored).

Predicting the Direction of Reaction

The **reaction quotient (Q)** expresses the ratio of activities (or concentrations/pressures) at any arbitrary stage of a reaction. By comparing Q to K, the spontaneous direction of change can be predicted:

- $Q < K$: The reaction proceeds toward products (forward reaction is spontaneous).
- $Q = K$: The mixture is at equilibrium.
- $Q > K$: The reverse reaction is spontaneous (products tend to decompose into reactants).

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4. Response of Equilibria to Changes in Conditions

Since chemical equilibria are dynamic, they respond to external changes according to **Le Chatelier's principle**: when a stress is applied to a system in dynamic equilibrium, the equilibrium tends to adjust to minimize the effect of the stress.

Change (Stress Applied)	Response (Equilibrium Shift)	Effect on K
Concentration/Activity (Adding reactant or removing product)	Shifts toward products to restore Q to K.	No change (K is a constant).
Pressure (Volume) (Compression/Volume reduction, for gaseous reactions)	Shifts toward the side containing the fewest moles of gas, thereby minimizing the pressure increase.	No change.
Temperature	Shifts in the direction of the **endothermic** reaction (the one that absorbs heat).	**Changes** K (quantified by the van 't Hoff equation).
Adding a Catalyst	Increases the rates of both the forward and reverse reactions equally.	**No change** in the equilibrium composition or the value of K.

5. Mathematical Tools

Calculating the equilibrium composition of a reaction mixture, given initial concentrations, typically involves setting up an **equilibrium table**. This table systematically tracks the initial composition, the changes needed to reach equilibrium (represented by an unknown variable x), and the final equilibrium composition.

6. Application to Aqueous Equilibria

The principles of chemical equilibrium extend extensively to solutions, particularly aqueous systems which are critical in chemistry and biology.

- **Acids and Bases:** Weak acid and weak base equilibria are quantified using the acidity constant (K_a) and basicity constant (K_b), respectively. The pH of the solution fundamentally determines the speciation of these molecules in solution.

- **Solubility:** For sparingly soluble salts in saturated solutions, the dissolution equilibrium is governed by the **solubility product constant (K_{sp})**.

- **Buffers:** Buffer solutions, mixtures of a weak acid and its conjugate base (or vice versa), stabilize the pH by using the conjugate pair equilibrium to absorb small amounts of added acid or base.