What is Chemical Equilibrium?

Dynamic equilibrium is the condition in which the rate of the forward reaction equals the rate of the reverse reaction. The concentrations of reactants and products are NOT equal to each other at equilibrium.

Equilibrium Constant (K)

Once equilibrium is reached, the concentrations become constant, so long as the temperature remains constant. The equilibrium constant (K) is used to quantify the relative concentrations of reactants and products at equilibrium. It is defined as the ratio (at equilibrium) of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients. The relationship between the balanced chemical equation and the expression of the equilibrium constant is the law of mass action.

Law of Mass Action

\[ \text{aA} + \text{bB} \leftrightarrow \text{cC} + \text{dD} \]

K = \( \frac{[C]^c[D]^d}{[A]^a[B]^b} \)

Do not include pure solids or pure liquids in the equilibrium expression.

This ratio equals the same number at equilibrium, regardless of the initial concentrations.

Summarizing the Significance of the Equilibrium Constant

- K << 1 Reverse reaction is favored; forward reaction does not proceed very far
- K ≈ 1 Neither direction is favored; forward reaction proceeds about halfway
- K >> 1 Forward reaction is favored; forward reaction proceeds essentially to completion
Relationships between the Equilibrium Constant and Chemical Equilibrium

If a chemical equation is modified, the equilibrium constant will change as a result. There are three common modifications.

1. If we reverse the equation, we invert the equilibrium constant.
   \[ K_{\text{reverse}} = \frac{1}{K_{\text{forward}}} \]

2. If we multiply the coefficients in the equation by a factor, we raise the equilibrium constant to the same factor.
   \[ n \, A + 2n \, B \leftrightarrow 3n \, C \]
   \[ K' = \frac{[C]^{3n}}{[A]^n[B]^{2n}} = \left( \frac{[C]^3}{[A][B]^2} \right)^n = K^n \]

3. If we add two or more individual chemical equations to obtain an overall equation, we multiply the corresponding equilibrium constants by each other to obtain the overall equilibrium constant.
   \[ K_{\text{overall}} = K_1 \times K_2 \]

Expressing the Equilibrium Constant in Terms of Pressure

\[ K_p = K_c (RT)^{\Delta n} \]

\[ \Delta n = \text{moles of gaseous products} - \text{moles of gaseous reactants} \]

The Reaction Quotient: Predicting the Direction of Change

The reaction quotient \((Q_c)\) is defined as the ratio (at any point in the reaction) of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients. For gases, partial pressures (in atm) replace concentrations \((Q_p)\). The reaction quotient is different from the equilibrium constant because the reaction quotient depends on the current state of the reaction. Therefore, its value changes as the reaction proceeds.
Summarizing Direction of Change Predictions

The reaction quotient (Q) relative to the equilibrium constant (K) is a measure of the progress of a reaction toward equilibrium.

- $Q < K$ Reaction goes to the right (toward products).
- $Q > K$ Reaction goes to the left (toward reactants).
- $Q = K$ Reaction is at equilibrium.

Solving Equilibrium Problems

1. Write the balanced equation for the reaction.
2. Write the equilibrium expression using the law of mass action.
3. List the initial concentrations.
4. Calculate $Q$, and determine the direction of the shift of the equilibrium.
5. Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.
6. Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.
7. Check your calculated equilibrium concentrations by making sure they give the correct value of K.

Le Châtelier’s Principle: How a System at Equilibrium Responds to Disturbances

When a chemical system that is already at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.

Summarizing the Effect of a Concentration Change on Equilibrium

If a chemical system is at equilibrium:

- **Increasing** the concentration of one or more of the reactants (which makes $Q < K$) causes the reaction to **shift to the right** (in the direction of the products).
- **Increasing** the concentration of one or more of the products (which makes $Q > K$) causes the reaction to **shift to the left** (in the direction of the reactants).
- **Decreasing** the concentration of one or more of the reactants (which makes $Q > K$) causes the reaction to **shift to the left** (in the direction of the reactants).
- **Decreasing** the concentration of one or more of the products (which makes $Q < K$) causes the reaction to **shift to the right** (in the direction of the products).
Summarizing the Effect of Volume Change on Equilibrium

If a chemical system is at equilibrium:

- **Decreasing** the volume causes the reaction to shift in the direction that has the fewer moles of gas particles.
- **Increasing** the volume causes the reaction to shift in the direction that has the greater number of moles of gas particles.
- Adding an inert gas to the mixture at a fixed volume has no effect on the equilibrium.
- When a reaction has an equal number of moles of gas on both sides of the chemical equation, a change in volume produces no effect on the equilibrium.

Summarizing the Effect of a Temperature Change on Equilibrium

In an **exothermic** reaction, heat is a product.

- **Increasing** the temperature causes an exothermic reaction to shift left (in the direction of the reactants); the value of the equilibrium constant decreases.
- **Decreasing** the temperature causes an exothermic reaction to shift right (in the direction of the products); the value of the equilibrium constant increases.

In an **endothermic** reaction, heat is a reactant.

- **Increasing** the temperature causes an endothermic reaction to shift right (in the direction of the products); the equilibrium constant increases.
- **Decreasing** the temperature causes an endothermic reaction to shift left (in the direction of the reactants); the equilibrium constant decreases.

Summarizing the Effect of a pH Change on Equilibrium

For an acid-base equilibrium (see diagram below) decreasing the pH correlates to increasing the H$^+$ concentration. This causes the equilibrium to shift to the left.
The opposite is true if a base is added. The pH is increased and the H⁺ concentration is lowered. Keep in mind that the H⁺ ions aren’t “removed” from solution. Rather, the OH⁻ ions in the base react with the H⁺ ions to form water. Essentially, this takes them out of the acid-base equilibrium reaction and lowers the concentration of the H⁺ ions.

Lesson 7: Equilibria & Le Chatelier's Principle