# Chapter 15
# Chemical Equilibrium

## Review

- **Chemical equilibrium:** occurs when opposing reactions proceed at equal rates: the rate at which the products form from the reactants equals the rate at which the reactants form from the products.
  1) Only the reversible reaction in closed system which under a constant temperature can establish a chemical equilibrium;
  2) Chemical equilibrium is a dynamic equilibrium, the forward reaction rate equals the reverse reaction rate;
  3) At equilibrium, the concentration of reactants and products no longer change with time;
  4) For equilibrium to occur, neither reactants nor products can escape from the system;
  5) At equilibrium, a particular ratio of concentration terms equals a constant.

- **Equilibrium-constant:**

$$\mathbf{aA + bB \rightleftharpoons dD + eE}$$

$$\boldsymbol{K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}}$$

- $\boldsymbol{K_c}$**: concentration equilibrium constant.**
  1) The equilibrium-constant expression depends only on the stoichiometry of the reaction, not on its mechanism;
  2) The value of $K_c$ depends only on the particular reaction and on the temperature;
- $\boldsymbol{K_p}$**: pressure equilibrium constant.**

$$\boldsymbol{K_p = \frac{[P_D]^d[P_E]^e}{[P_A]^a[P_B]^b}}$$

- **Relationship between $\boldsymbol{K_c}$ and $\boldsymbol{K_p}$:**

$$\boldsymbol{K_p = K_c(RT)^{\Delta n}}$$

$$\boldsymbol{\Delta n = (moles\ of\ gaseous\ product) - (moles\ of\ gaseous\ reactant)}$$

- If K≫1 (large K): equilibrium lies to right, products predominate;
  If K≪1 (small K): equilibrium lies to left, reactants predominate;

1) The equilibrium constant of a reaction in the reverse direction is the inverse of the equilibrium constant of the reaction in the forward direction:

$$\mathrm{A + B \rightleftharpoons C + D} \quad K_1$$

$$\mathrm{C + D \rightleftharpoons A + B} \quad K = 1/K_1$$

2) The equilibrium constant of a reaction that has been multiplied by a number is equal to the original equilibrium constant raised to a power equal to that number:

$$\mathrm{A + B \rightleftharpoons C + D} \quad K_1$$

$$n\mathrm{A} + n\mathrm{B} \rightleftharpoons n\mathrm{C} + n\mathrm{D} \quad K = K_1^n$$

3) The equilibrium constant for a net reaction made up of two or more reactions is the product of the equilibrium constants for the individual reactions:

$$\begin{array}{lll} A + B \rightleftharpoons C + D & K_1 \\ C + F \rightleftharpoons G + A & K_2 \\ \hline B + F \rightleftharpoons D + G & K_3 = (K_1)(K_2) \end{array}$$

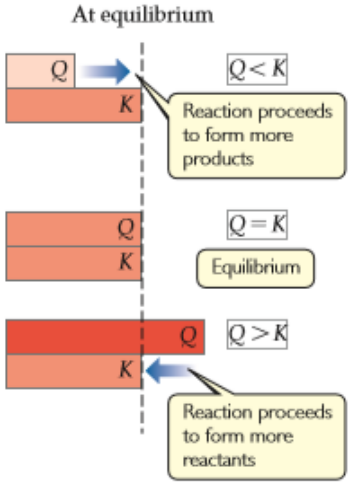
- **Homogeneous equilibria:** equilibria involve substances that are all in the same phase.
- **Heterogeneous equilibria:** equilibria involve substances that are in different phases.
  1) Whenever a solid or pure liquid is involved in a heterogeneous equilibrium, its concentration isn't included in the equilibrium-constant expression;
  2) The concentration of solvent in a dilute solution isn't included in the equilibrium-constant expression;
  3) In a non-aqueous system, the concentration of water should be in the equilibrium constant expression;

- **Reaction quotient (Q):** a number obtained by substituting reactant and product concentrations or partial pressures at any point during a reaction into an equilibrium-constant expression.

$$\mathbf{aA + bB \rightleftharpoons dD + eE}$$

$$Q_c = \frac{[D]^d[E]^e}{[A]^a[B]^b} \qquad Q_p = \frac{[P_D]^d[P_E]^e}{[P_A]^a[P_B]^b}$$

1) Q＜K: The concentration of products is too small and that of reactants too large. The reaction achieves equilibrium by forming more products; it proceeds from left to right.
2) Q=K: The reaction quotient equals the equilibrium constant only if the system is at equilibrium.
3) Q＞K: The concentration of products is too large and that of reactants too small. The reaction achieves equilibrium by forming more reactants; it proceeds from right to left.



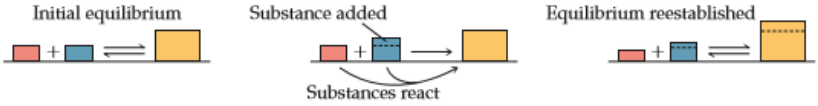

- **Le Chatelier's principle:** If a system at equilibrium is disturbed by a change in temperature, pressure, or a component concentration, the system will shift its equilibrium position so as to counteract the effect of the disturbance.
  ✓ Changing pressure, or concentration　K value keeps constant
  ✓ Endothermic　Increasing T results in higher K value
  ✓ Exothermic　Increasing T results in lower K value

**Le Châtelier's Principle**

If a system at equilibrium is disturbed by a change in **concentration, pressure,** or **temperature,** the system will shift its equilibrium position so as to counter the effect of the disturbance.

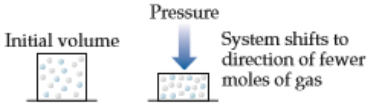
**Concentration:** adding or removing a reactant or product

*If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from a system, the system reacts to produce more of substance.*




**Pressure:** changing the pressure by changing the volume

*At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.*




**Temperature:**

*If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the "excess reactant," namely heat.*

| Endothermic | | Exothermic | |
|---|---|---|---|
| Increasing $T$ | Reaction shifts right | Increasing $T$ | Reaction shifts left |
| Decreasing $T$ | Reaction shifts left | Decreasing $T$ | Reaction shifts right |

- **Catalyst:** a catalyst increases the rate at which equilibrium is achieved but does not change the composition of the equilibrium mixture.