

Lecture 3 “Laws of chemical equilibrium and energetics of equilibrium processes”

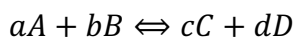
Goal of the lecture: To study the fundamental laws governing chemical equilibrium, understand the relationship between equilibrium constants and thermodynamic functions, and explain how energy changes influence the direction and extent of chemical reactions.

Brief lecture notes: Chemical equilibrium is a fundamental concept in physical chemistry that describes the state of a reversible chemical reaction in which the rates of the forward and reverse reactions are equal. This dynamic balance means that, although molecules continue to react and form products, the overall concentrations of reactants and products remain constant with time. Equilibrium does not imply that the reaction has stopped; rather, it signifies a steady state where microscopic changes occur continuously but without any macroscopic change in the system's composition. In any reversible reaction, the forward process initially dominates as reactants are converted into products. Over time, as the concentration of reactants decreases and that of products increases, the rate of the forward reaction slows down while the rate of the reverse reaction accelerates. Eventually, these two rates become equal, establishing a state of equilibrium. The equilibrium composition depends on the relative energies of the reactants and products, as well as the reaction conditions such as temperature, pressure, and concentration.

1. Law of Mass Action

The **Law of Mass Action**, formulated by Guldberg and Waage (1864), states that at constant temperature, the rate of a chemical reaction is proportional to the product of the concentrations of the reactants, each raised to a power equal to its stoichiometric coefficient.

For a general reversible reaction:



the **equilibrium constant (K_c)** is expressed as:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where square brackets denote molar concentrations at equilibrium.

The equilibrium constant depends only on temperature and is **independent of initial concentrations**.

2. Characteristics of Chemical Equilibrium

- Chemical equilibrium is **dynamic**, meaning that the forward and reverse reactions occur simultaneously at equal rates.
- It can be **homogeneous** (all substances in the same phase) or **heterogeneous** (reactants and products in different phases).
- It depends on external factors such as **temperature, pressure, and concentration**.

3. Le Chatelier's Principle

Le Chatelier's Principle states that if a system at equilibrium is subjected to a change in temperature, pressure, or concentration, the system will shift its equilibrium position to counteract the applied change.

- **Change in concentration:** Increasing reactant concentration shifts equilibrium toward products.
- **Change in temperature:** For exothermic reactions, increasing temperature shifts equilibrium to the left; for endothermic reactions, to the right.
- **Change in pressure:** Affects only gaseous systems; equilibrium shifts toward the side with fewer gas moles when pressure increases.

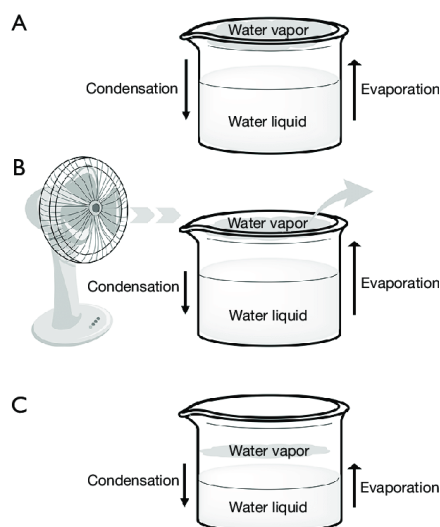


Figure – 1. The implementation of the Le Chatelier principle for the evaporation of water. (A) Liquid water and water vapor are in equilibrium, with the condensation and evaporation rates being equal; (B) when water vapor is exposed to a stress, such as an air fan, the vapor is moved away from the surface and the vapor concentration is reduced; at this point the evaporation process is accelerated to counteract the stress; (C) the stress is removed and the equilibrium is restored.

4. Relationship Between Thermodynamics and Equilibrium

The position of chemical equilibrium is determined by the **Gibbs free energy change (ΔG)** of the reaction.

At equilibrium:

$$\Delta G = 0$$

and the relationship between the standard Gibbs energy change (ΔG°) and the equilibrium constant (K_{eq}) is given by:

$$\Delta G = -RT \ln K_{eq}$$

where

- R = universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$),
- T = temperature in Kelvin.

This equation shows that **when $K_{eq} > 1$** , ΔG° is negative, meaning the reaction is spontaneous in the forward direction; **when $K_{eq} < 1$** , ΔG° is positive, meaning the reverse process is favored.

5. Energetics of Equilibrium Processes

The energy changes associated with a chemical equilibrium are described by thermodynamic quantities such as **enthalpy (ΔH)**, **entropy (ΔS)**, and **Gibbs free energy (ΔG)**.

The relationship among these is given by:

$$\Delta G = \Delta H - T\Delta S$$

- **ΔH (enthalpy)** represents the heat absorbed or released.
- **ΔS (entropy)** measures the degree of disorder.
- **ΔG (free energy)** determines whether a reaction is spontaneous.

At equilibrium, $\Delta G = 0$, which means that the energy of the system is minimized and the forward and reverse reactions are balanced.

6. Temperature Dependence of the Equilibrium Constant

According to the **van't Hoff equation**, the equilibrium constant changes with temperature:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

- For **endothermic reactions ($\Delta H^\circ > 0$)**, K increases with temperature.
- For **exothermic reactions ($\Delta H^\circ < 0$)**, K decreases with temperature.

This relationship provides a thermodynamic link between **heat effects** and **equilibrium composition**.

Questions for self-control

1. State the Law of Mass Action and derive the expression for the equilibrium constant.
2. How does Le Chatelier's Principle explain the effect of temperature on equilibrium?
3. Explain the relationship between ΔG° and K_{eq} .
4. What is the significance of the van't Hoff equation?
5. Why is chemical equilibrium considered a dynamic process?

Literature:

1. Atkins, P., de Paula, J. *Atkins' Physical Chemistry*, 11th Edition, Oxford University Press, 2018.
2. Moran, M.J. *Fundamentals of Engineering Thermodynamics*, 9th Edition, Wiley, p.156.

3. House, J.E. *Fundamentals of Quantum Chemistry*, 2nd Edition, Academic Press, 2004.
4. Hammes-Schiffer, S. et al. *Physical Chemistry for the Biological Sciences*, University Science Books, 2009.
5. Zhdanov, V.P. *Elementary Physicochemical Processes on Solid Surfaces*, Springer, 1991.