

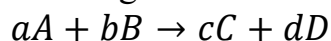
Lecture 4 Stoichiometric Analysis, Influence of Concentrations, Pressure, and Phase State

Goal of the lecture: To study the principles of stoichiometric relationships in chemical reactions and analyze how variations in concentration, pressure, and phase state affect reaction extent, equilibrium position, and process efficiency.

Brief lecture notes: This lecture explores the fundamental concept of stoichiometry as a quantitative framework for chemical reactions, linking reactants and products through balanced equations and mole relationships. Attention is given to how concentration, pressure, and phase state influence chemical equilibria and reaction rates, based on the principles of thermodynamics and kinetics. The discussion also includes Le Chatelier's principle, reaction extent, and stoichiometric coefficients, providing the foundation for analyzing both homogeneous and heterogeneous systems in industrial and laboratory settings

Main part

Stoichiometry forms the basis of quantitative chemical analysis and process calculations, describing the fixed proportional relationships among reactants and products in a chemical reaction. For a general chemical equation:



the stoichiometric coefficients a , b , c , and d define the molar ratios in which substances participate. These ratios allow the determination of limiting reactants, conversion, and product yields.

The extent of reaction (ξ) is a quantitative measure of how far a reaction proceeds and is defined as:

$$dn_i = \nu_i d\xi$$

where dn_i is the change in the number of moles of component i and ν_i is its stoichiometric coefficient (positive for products, negative for reactants). This concept is crucial for mass balance calculations and for establishing the relationship between thermodynamic and kinetic data.

Influence of Concentration

The rate of most reactions depends on the concentration of reactants, as described by the law of mass action. Increasing concentration enhances the probability of molecular collisions, thus accelerating reaction rates. In reversible reactions, however, increasing the concentration of one reactant shifts the equilibrium toward product formation to counterbalance the disturbance — a direct consequence of Le Chatelier's principle.

Influence of Pressure

Pressure primarily affects reactions involving gases. When the total number of gaseous moles decreases during reaction (e.g., synthesis reactions like ammonia formation), increasing pressure shifts equilibrium toward the products, favoring the direction with fewer moles of gas. Conversely, for reactions that produce more gaseous molecules, pressure reduction enhances product formation. The quantitative relationship between pressure and equilibrium is expressed by the equilibrium constant in terms of partial pressures (K_p):

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

where Δn is the difference in the number of moles of gaseous products and reactants.

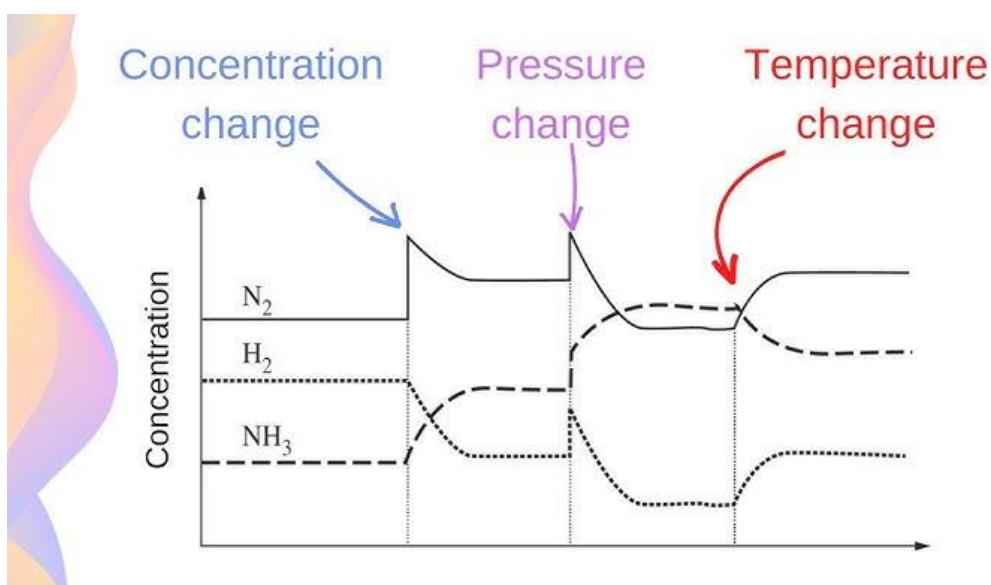
Influence of Phase State

The phase state of reactants and products strongly affects both the rate and equilibrium of reactions. Homogeneous reactions, occurring in a single phase (e.g., gas-phase combustion), are typically governed by molecular collisions and temperature. Heterogeneous reactions, involving multiple phases (solid–gas, liquid–solid), depend additionally on surface area, diffusion, and adsorption processes. For example, in catalytic reactions, reactants must adsorb onto the catalyst surface before reaction occurs, making the physical state of the system a determining factor in the overall kinetics.

Table 1 — Influence of Physical Parameters on Chemical Equilibrium

Parameter	Type of Change	Direction of Equilibrium Shift	Example
Concentration	Increase of reactant	Toward products	$\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$
Pressure	Increase ($\Delta n < 0$)	Toward fewer gas moles	Ammonia synthesis
Pressure	Decrease ($\Delta n > 0$)	Toward more gas moles	Thermal dissociation of CaCO_3
Temperature	Increase (endothermic)	Toward products	$\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$
Phase state	Increased surface area	Increases rate	Heterogeneous catalysis

Figure 1 — Effect of Pressure on Chemical Equilibrium



Stoichiometric and thermodynamic analysis together provide powerful tools for understanding and optimizing chemical processes. By considering how pressure,

concentration, and phase state influence the equilibrium position, chemical engineers can design systems that achieve high yields with minimal energy input. In practical terms, this understanding is applied in industrial processes such as ammonia synthesis (Haber–Bosch process), sulfuric acid production, and catalytic oxidation, where control of process conditions directly impacts economic and environmental efficiency.

Questions for Self-Control

1. What is the role of stoichiometric coefficients in chemical reaction analysis?
2. How is the extent of reaction defined, and what does it represent physically?
3. Explain how pressure affects equilibrium in reactions involving gases.
4. What are the key differences between homogeneous and heterogeneous reactions?
5. How does Le Chatelier's principle predict the direction of equilibrium shift when concentration or pressure changes?

Literature

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