Lecture 13 Thermodynamics of phase and chemical equilibrium

Goal of the lecture: To study the thermodynamic principles governing phase and chemical equilibria in pure substances and mixtures, and to understand the criteria for equilibrium based on Gibbs free energy.

Brief lecture notes: This lecture introduces the fundamental concepts of phase and chemical equilibrium as governed by the laws of thermodynamics. Students will explore the conditions under which systems reach equilibrium, the role of Gibbs energy as a potential function, and how temperature, pressure, and composition influence equilibrium states. The lecture will also discuss the Clapeyron and Clausius–Clapeyron equations for phase transitions, chemical equilibrium constants, and graphical representations such as phase diagrams. Emphasis will be placed on practical applications in separation processes, metallurgy, combustion, and chemical reactor design.

Main part

In thermodynamics, equilibrium represents a state in which macroscopic properties of a system—such as pressure, temperature, and composition—remain constant over time. For a system to be in complete equilibrium, three conditions must be satisfied:

- Thermal equilibrium: no temperature gradients within the system;
- Mechanical equilibrium: uniform pressure throughout the system;
- Chemical equilibrium: no net chemical reactions or mass transfer between phases.

At equilibrium, there are no driving forces for spontaneous change, meaning that the Gibbs free energy (G) of the system has reached its minimum value for the given temperature and pressure.

Criteria for Thermodynamic Equilibrium

For a closed system at constant temperature and pressure, the equilibrium condition is expressed as:

$$dG = 0$$

where $G = H - TS$is the Gibbs free energy, $H$is enthalpy, $T$is temperature, and $S$is entropy. If $dG < 0$, the process proceeds spontaneously; if $dG > 0$, it is nonspontaneous.

Thus, the equilibrium corresponds to the point where the total Gibbs energy of all phases or reacting components is minimized.

Phase Equilibrium

Phase equilibrium occurs when two or more phases coexist in equilibrium at specific temperature and pressure.

The Clapeyron equation describes the slope of the coexistence curve between two phases:

$$\frac{dP}{dT} = \frac{\Delta H_{trans}}{T\,\Delta V_{trans}}$$

where $\Delta H_{trans}$and $\Delta V_{trans}$are the enthalpy and volume changes during the phase transition (e.g., liquid–vapor).

For vaporization processes, an approximate form known as the Clausius–Clapeyron equation is often used:

$$\ln\frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation enables calculation of vapor pressures and boiling points, which are crucial in distillation, drying, and evaporation.

Chemical Equilibrium and the Equilibrium Constant

In a general chemical reaction:

$$aA + bB \rightleftharpoons cC + dD$$

At equilibrium, the chemical potentials (μ_i) of each species are related through:

$$\sum \nu_i \mu_i = 0$$

where ν_i are stoichiometric coefficients (positive for products, negative for reactants). The equilibrium composition can be expressed using the equilibrium constant (K):

$$K = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

where a_i are activities (or partial pressures/concentrations). The equilibrium constant depends on temperature, as given by the van't Hoff relation:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0}{RT^2}$$

Factors Influencing Equilibrium

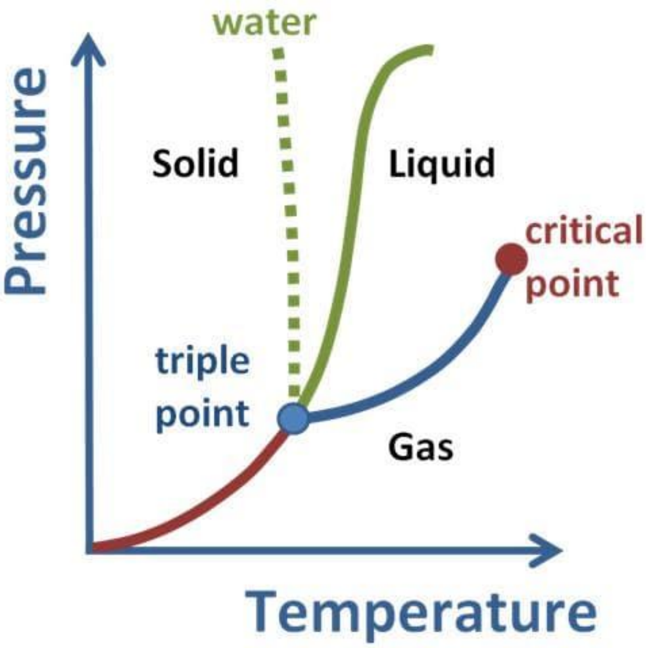
The position of equilibrium depends on temperature, pressure, and composition. According to Le Chatelier's Principle, when a system at equilibrium is subjected to a disturbance, it adjusts to minimize the effect of that disturbance. For example:

- Increasing temperature shifts equilibrium in the direction of the endothermic reaction.
- Increasing pressure shifts equilibrium toward the side with fewer gas moles.
- Removing a product drives the reaction toward product formation.

Table 1 : Comparison of Phase and Chemical Equilibrium

Aspect	Phase Equilibrium	Chemical Equilibrium
Nature	Physical process (e.g., liquid–vapor transition)	Chemical reaction (e.g., A + B ⇌ C + D)
Criterion	Equal chemical potential of each component in all phases	Zero net change in Gibbs free energy ($\sum \nu_i \mu_i = 0$)
Example	Water ↔ Steam at 100 °C, 1 atm	$N_2 + 3H_2 \rightleftharpoons 2NH_3$
Equation	Clapeyron or Clausius–Clapeyron	Equilibrium constant K
Dependence	Temperature and pressure	Temperature, pressure, and concentration

Figure 1. Schematic phase diagram of a pure substance. The diagram shows the solid, liquid, and vapor regions separated by phase boundaries. The lines represent equilibrium conditions between two phases (solid–liquid, liquid–vapor, solid–vapor), all meeting at the triple point, where three phases coexist in equilibrium.



Questions for Self-Control

1. What is the thermodynamic condition for equilibrium in a closed system?
2. How is the Clausius–Clapeyron equation derived and applied?
3. What factors affect the chemical equilibrium constant?
4. Explain how Le Chatelier's Principle predicts the direction of equilibrium shift.
5. What is the difference between phase and chemical equilibrium?

Literature

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