

Lecture 14 Thermodynamics of phase transitions and multi-component systems

Goal of the lecture: To understand the thermodynamic principles governing phase transitions and equilibrium in multi-component systems, and to analyze the relationships between pressure, temperature, and composition during phase changes.

Brief lecture notes: This lecture examines the fundamental thermodynamic mechanisms behind phase transitions—such as melting, vaporization, and sublimation—and extends these concepts to systems containing multiple components. Students will explore the Gibbs phase rule, the conditions for phase equilibrium, and the behavior of binary mixtures and solutions. The discussion will also include the Clapeyron and Clausius–Clapeyron equations, partial molar properties, chemical potentials, and phase diagrams that describe multi-component equilibria. Practical examples will illustrate how these principles are applied in distillation, metallurgy, materials science, and chemical engineering.

Main part

A phase transition occurs when a substance changes from one physical state to another, such as solid to liquid (melting), liquid to vapor (boiling), or solid to vapor (sublimation). These transformations involve changes in molecular arrangement and energy, particularly enthalpy and entropy. During a phase transition at constant pressure and temperature, both phases coexist in equilibrium. At equilibrium, the chemical potential of the substance is identical in both phases:

$$\mu_{\alpha} = \mu_{\beta}$$

where μ_{α} and μ_{β} are the chemical potentials of the two coexisting phases (e.g., liquid and vapor).

The energy associated with phase transitions includes:

- Latent heat of fusion (melting): energy required to convert solid to liquid,
- Latent heat of vaporization: energy required to convert liquid to vapor,
- Latent heat of sublimation: energy required to convert solid directly to vapor.

Thermodynamic Description of Phase Transitions

The Clapeyron equation relates the slope of a phase boundary on a pressure–temperature (P–T) diagram to the latent heat and volume change of the transition:

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

This relation describes how equilibrium pressure varies with temperature for a given phase transition. For liquid–vapor transitions, since the vapor phase volume is much greater than the liquid phase, this can be simplified to the Clausius–Clapeyron equation:

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

These relations form the foundation for understanding vapor–liquid equilibrium and are essential for calculating boiling points, vapor pressures, and sublimation temperatures.

Phase Equilibrium in Multi-Component Systems

In systems with more than one chemical species, the equilibrium condition requires that the chemical potential of each component be the same in all coexisting phases:

$$\mu_i^{(1)} = \mu_i^{(2)} = \mu_i^{(3)} = \dots$$

For multi-component mixtures, the composition of each phase differs, leading to phase separation based on thermodynamic stability.

The Gibbs phase rule defines the number of degrees of freedom (independent variables) in a system:

$$F = C - P + 2$$

where

- F = degrees of freedom,
- C = number of components,
- P = number of phases present.

This rule provides insight into how temperature, pressure, and composition affect the equilibrium state. For example, a single-component system with two phases (liquid and vapor) has one degree of freedom, meaning pressure and temperature are interdependent (i.e., at a given temperature, there is a unique vapor pressure).

Binary and Multi-Component Phase Diagrams

For two-component systems (binary mixtures), phase behavior can be represented on T–x (temperature–composition) or P–x (pressure–composition) diagrams.

A typical example is a binary mixture of ethanol and water. At equilibrium:

- The liquid phase and vapor phase have different compositions.
- The boiling point curve (liquidus line) and dew point curve (vaporus line) define the two-phase region.

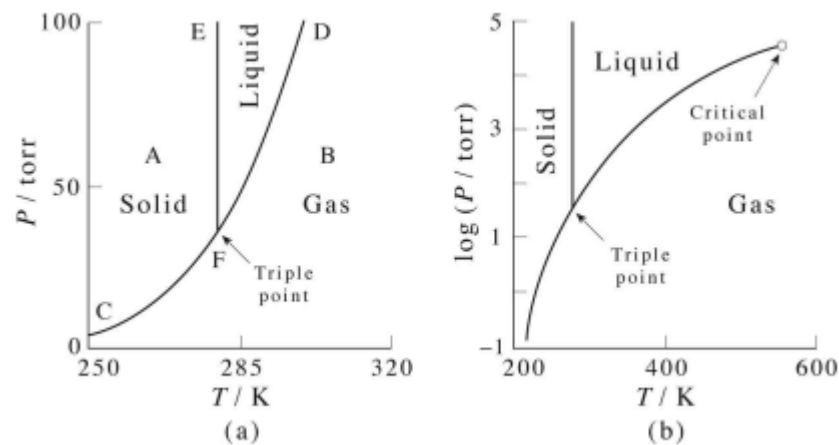
These diagrams are essential for understanding distillation, liquid–liquid extraction, and crystallization processes.

The intersection of curves corresponds to azeotropic points, where the vapor and liquid have the same composition and cannot be separated by simple distillation.

Table 1 : Comparison of Single- and Multi-Component Systems

Aspect	Single-Component System	Multi-Component System
Number of Components (C)	1	≥ 2
Example	Water (H ₂ O)	Water–Ethanol, Air
Variable Composition	No	Yes
Equilibrium Condition	$\mu_\alpha = \mu_\beta$	$\mu_i^{(1)} = \mu_i^{(2)}$ for all i
Phase Rule	$F = 3 - P$	$F = C - P + 2$
Applications	Pure substance vaporization, melting	Distillation, extraction, alloy formation

Figure 1. Typical binary phase diagram (Temperature–Composition)



Questions for Self-Control

1. What are the main types of phase transitions and how are they classified thermodynamically?
2. How does the Clausius–Clapeyron equation describe the relationship between pressure and temperature during a phase change?
3. What information does the Gibbs phase rule provide about multi-component systems?
4. How do binary phase diagrams help in the design of distillation and separation processes?
5. What is an azeotrope, and why is it important in practical applications?

Literature

1. Çengel, Y. A., & Boles, M. A. Thermodynamics: An Engineering Approach. McGraw-Hill, 2020.
2. Moran, M. J., & Shapiro, H. N. Fundamentals of Engineering Thermodynamics. Wiley, 2018.
3. Smith, J. M., Van Ness, H. C., & Abbott, M. M. Introduction to Chemical Engineering Thermodynamics. McGraw-Hill, 2017.
4. Callen, H. B. Thermodynamics and an Introduction to Thermostatistics. Wiley, 1985.
5. Atkins, P., & de Paula, J. Atkins' Physical Chemistry. Oxford University Press, 2022.