

Phase Equilibrium

Introduction

Phase Equilibrium is the study of the coexistence and transformation of different phases (solid, liquid, gas) of matter, often influenced by external variables like temperature and pressure. Understanding phase diagrams is critical for materials science and many industrial processes, such as distillation and alloy production.

This module focuses on quantifying phase stability and predicting phase behavior:

- We will define the concept of phase and component and establish Gibbs Phase Rule to relate them to degrees of freedom.
- We will analyze and interpret phase diagrams for one-component (pure substance) and multi-component (solution) systems.

Learning Objectives

By the end of this module, you will be able to:

- **State and apply** the mathematical expressions for phase equilibrium involving pure substances.
- **Discuss and apply** the thermodynamics to phase equilibria occurring in solutions.
- **Apply** the phase rule to two- and three-component systems.
- **Construct, analyze, and interpret** phase diagrams for two- and three-component systems.

Key Concepts and Definitions

Term	Definition
Phase	A distinct form of matter that is uniform throughout in chemical composition and physical state.
Component (C)	The minimum number of chemically independent species necessary to define the composition of all phases in the system.
Degrees of Freedom (F)	The number of independent intensive variables (e.g., T, P, concentration) that must be specified to define the state of the system.
Gibbs Phase Rule	A relationship that relates the number of phases, components, and degrees of freedom: $F = C - P + 2$.
Triple Point	A specific temperature and pressure at which all three phases (solid, liquid, gas) of a substance coexist in equilibrium.
Eutectic Point	The specific composition and temperature in a two-component system where the liquid phase is in equilibrium with two solid phases.

Detailed Discussion

1. Gibbs Phase Rule

The **Gibbs Phase Rule** is the governing law of phase equilibrium, determining the maximum number of intensive variables (like temperature and pressure) that can be simultaneously changed without changing the number of phases present.

Gibbs Phase Rule Equation:

$$F = C - P + 2$$

Where:

- F = Degrees of Freedom (The number of variables you can change)
- C = Number of Components
- P = Number of Phases in equilibrium

Example (Pure Water): For pure water, C = 1.

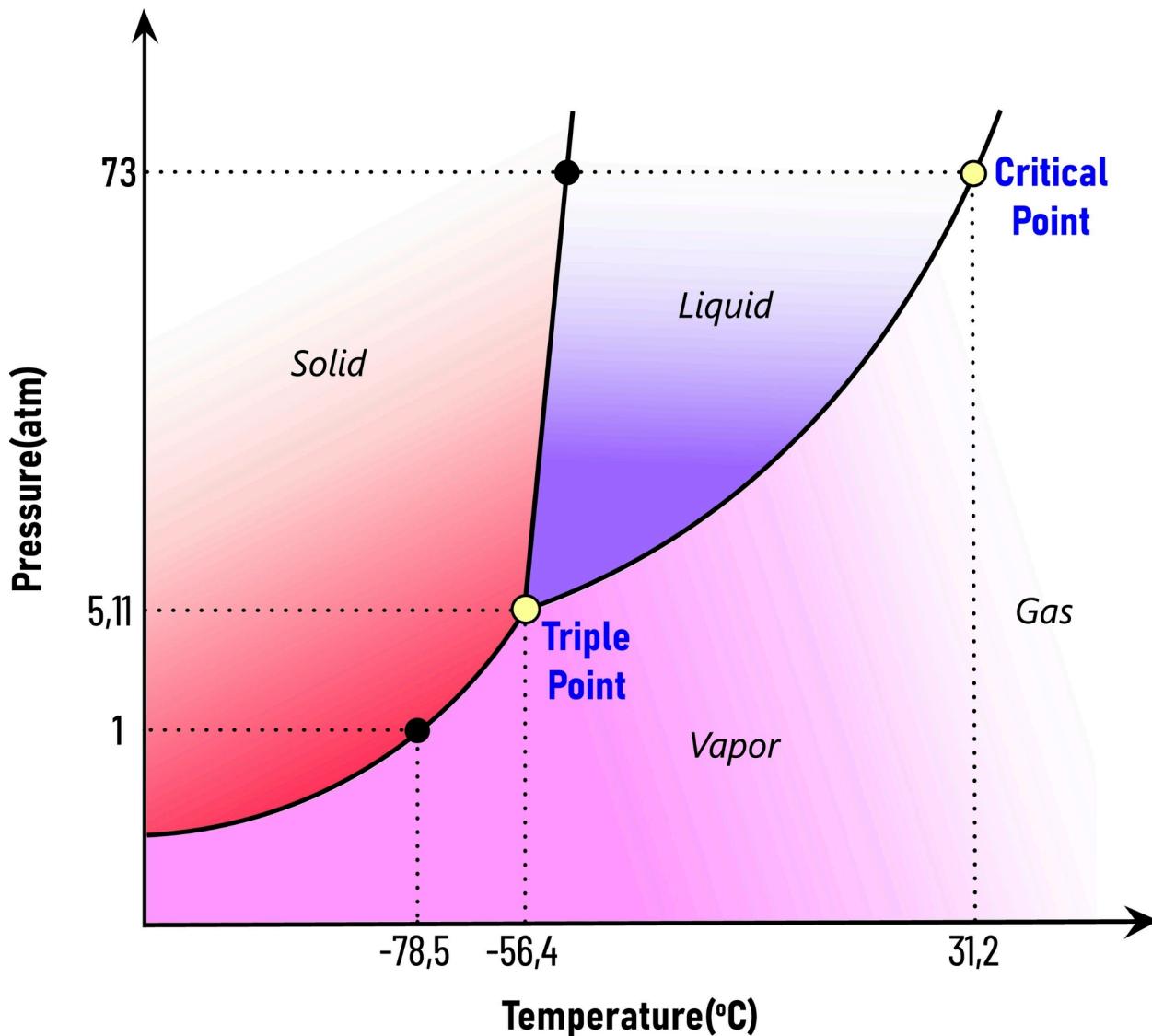
- If P = 1 (e.g., only liquid water exists), F = 1 - 1 + 2 = 2. You can independently change both temperature and pressure.
- If P = 3 (at the triple point), F = 1 - 3 + 2 = 0. You cannot change either temperature or pressure; the state is fixed.

2. One-Component Phase Diagrams (Pure Substances)

The phase diagram for a one-component system (like water) plots pressure (P) versus temperature (T).

- **Regions:** Areas represent single phases (P=1), giving F=2 degrees of freedom (you can move P or T freely within the region).
- **Lines:** Curves represent two phases in equilibrium (P=2), giving F=1 degree of freedom (if you fix T, P is also fixed).

- **Triple Point:** The single point where the three lines intersect, representing three phases in equilibrium ($P=3$), giving $F=0$ (the state is invariant).
- **Critical Point:** The endpoint of the liquid-gas coexistence curve. Above this temperature, no amount of pressure can liquefy the substance.



3. Two-Component Phase Diagrams (Solutions and Alloys)

When $C = 2$ (binary system), the Gibbs Phase Rule becomes $F = 2 - P + 2 = 4 - P$. To keep the diagram visualizable in 2D, we typically fix one variable (usually pressure, $P=1$ atm).

- **Condensed Phase Rule:** When pressure is fixed (P_{ext} is constant), the degrees of freedom become $F' = C - P + 1$. For a binary system, $F' = 3 - P$.
- **Isopleths:** Lines of constant composition.
- **Eutectic Point:** A key feature for many binary systems (like alloys). At this specific point, the liquid phase coexists with two solid phases ($P=3$), meaning $F' = 3 - 3 = 0$. This mixture has the lowest possible melting point.
- **Lever Rule:** Used to determine the relative amounts of the two phases (liquid and solid) present at any point within a two-phase region of the diagram.

4. Thermodynamics of Phase Transitions

Phase changes are governed by the relationship between the chemical potentials (μ) of the phases. At equilibrium, the chemical potential of a substance must be equal in all coexisting phases:

$$\mu_{\text{Phase } A} = \mu_{\text{Phase } B}$$

Clapeyron Equation : Describes the slope of the phase coexistence curves on a P-T diagram:

$$dP/dT = \Delta H / (T * \Delta V)$$

Where ΔH is the enthalpy change and ΔV is the volume change for the phase transition. This equation demonstrates that the slope is determined by the heat required (ΔH) and the change in volume (ΔV) during the transition.

REFERENCES:

Atkins, P. W., de Paula, J., & Keeler, J. (2018). *Atkins' Physical Chemistry* (11th ed.). Oxford University Press.

Engel, T., & Reid, P. (2020). *Physical Chemistry* (4th ed.). Pearson.

LibreTexts. (2024). *Physical and Theoretical Chemistry: Thermodynamics*.

International Union of Pure and Applied Chemistry (IUPAC). (2019). *The Gold Book (Compendium of Chemical Terminology)*.