CHEM3520 - Spring 2023

Focus 1: Properties of gases

Focus 2: The First Law

Focus 3: The Second and Third Laws

Focus 4: Physical transformation of pure substances

Focus 5: Simple mixtures

Focus 6: Chemical equilibrium

Focus 16: Molecules in motion

Focus 17: Chemical kinetics

Focus 18: Reaction dynamics

Focus 4: Physical transformation of pure substances

Phase diagrams of pure substances

Thermodynamic aspects of phase transitions

Phase

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Phase transitions

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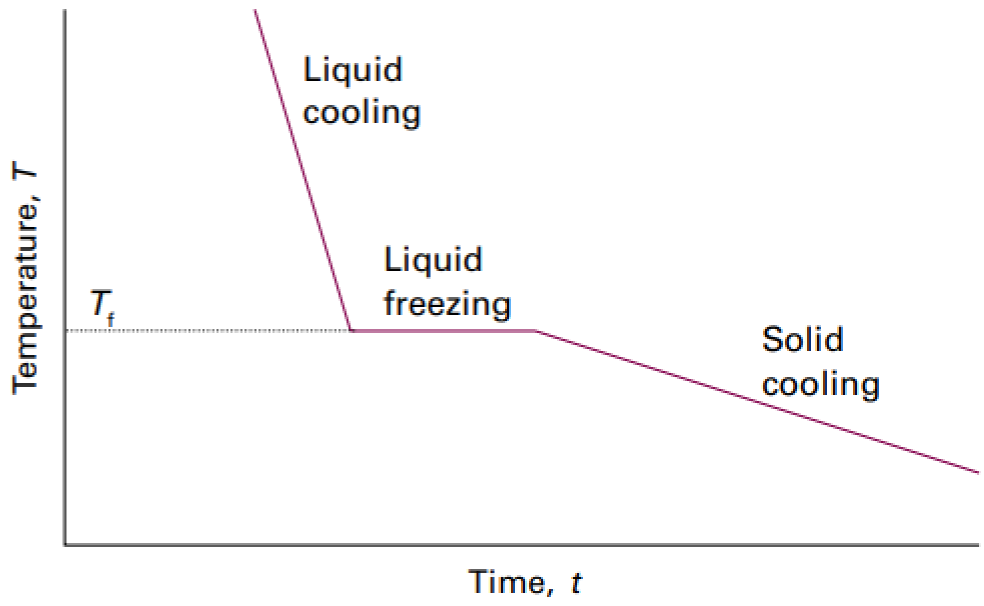

Thermal analysis,

A pause in the temperature increase or decrease can indicate a phase transition during thermal analysis.

Spontaneous phase changes

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Thermodynamics vs kinetics

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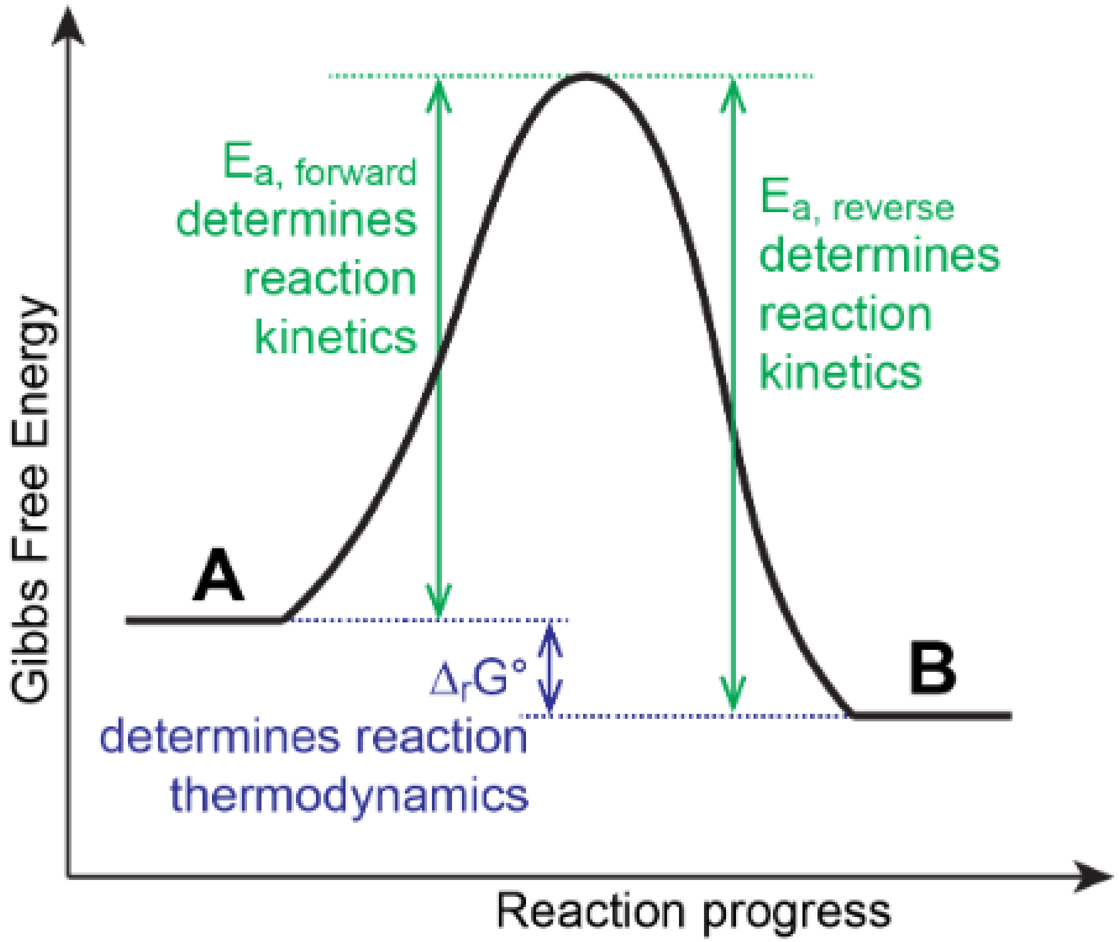

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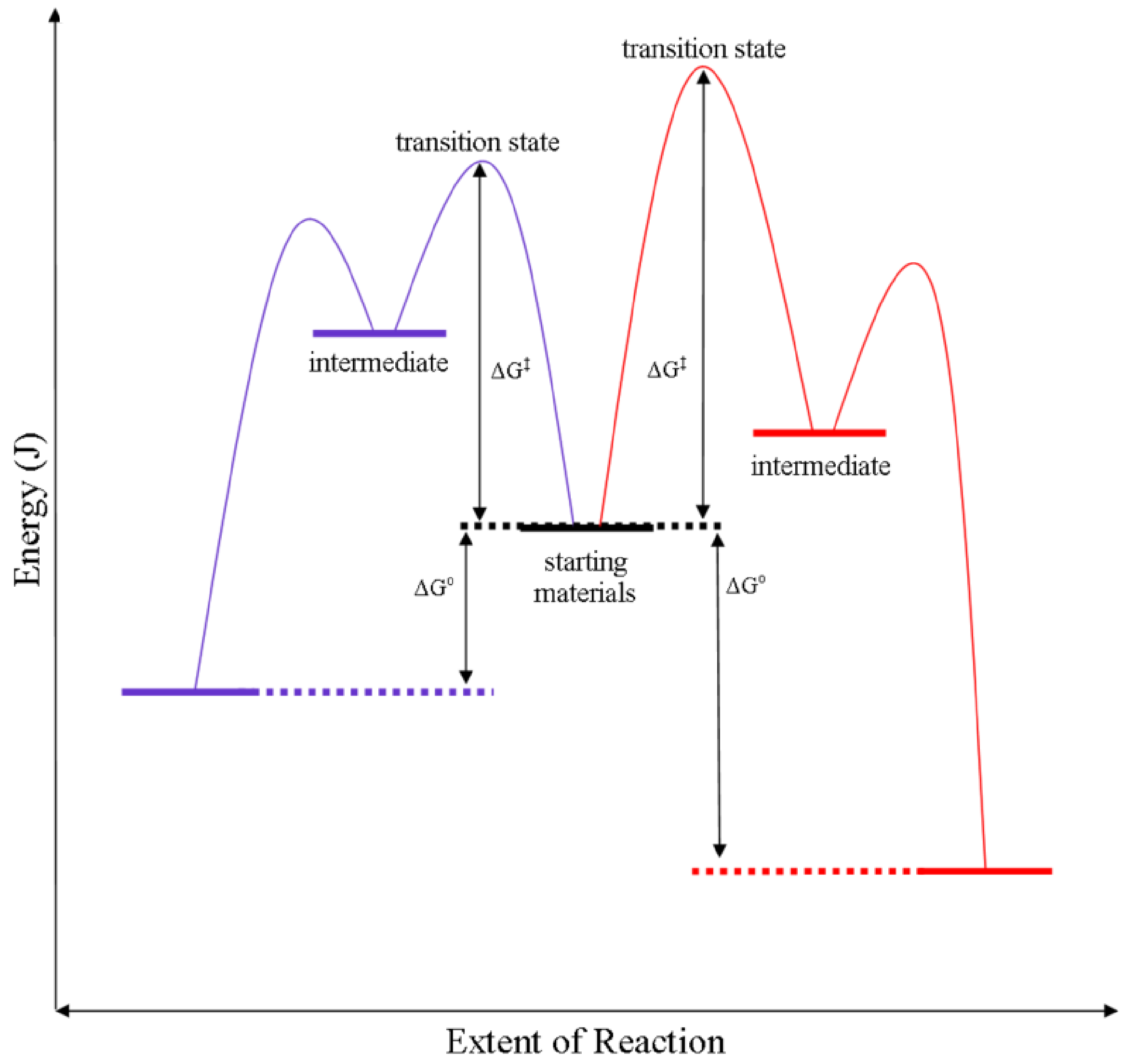
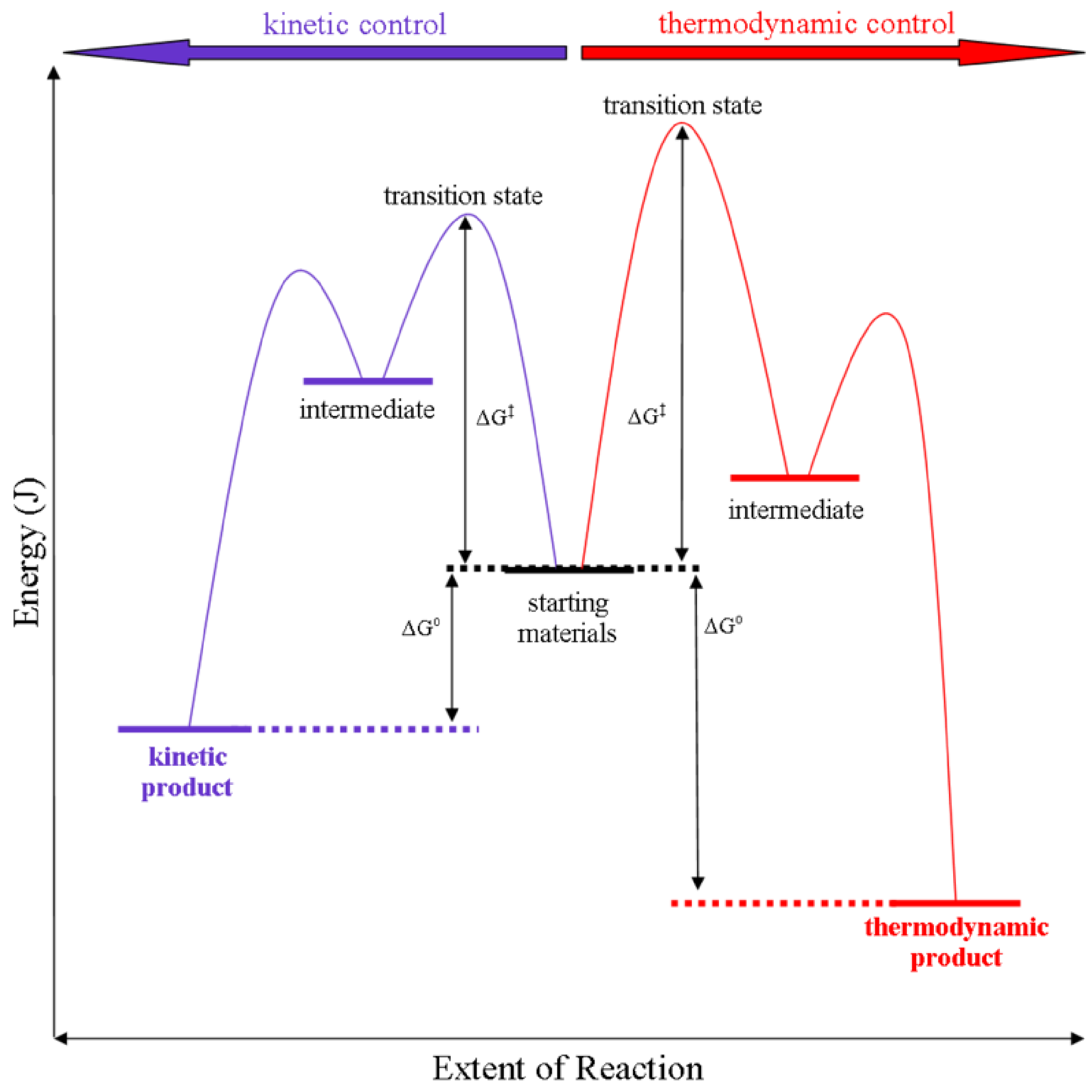
Thermodynamic vs kinetic control



Thermodynamic vs kinetic control

Low temperature,
short reaction time



High temperature,
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Diels-Alder Reaction

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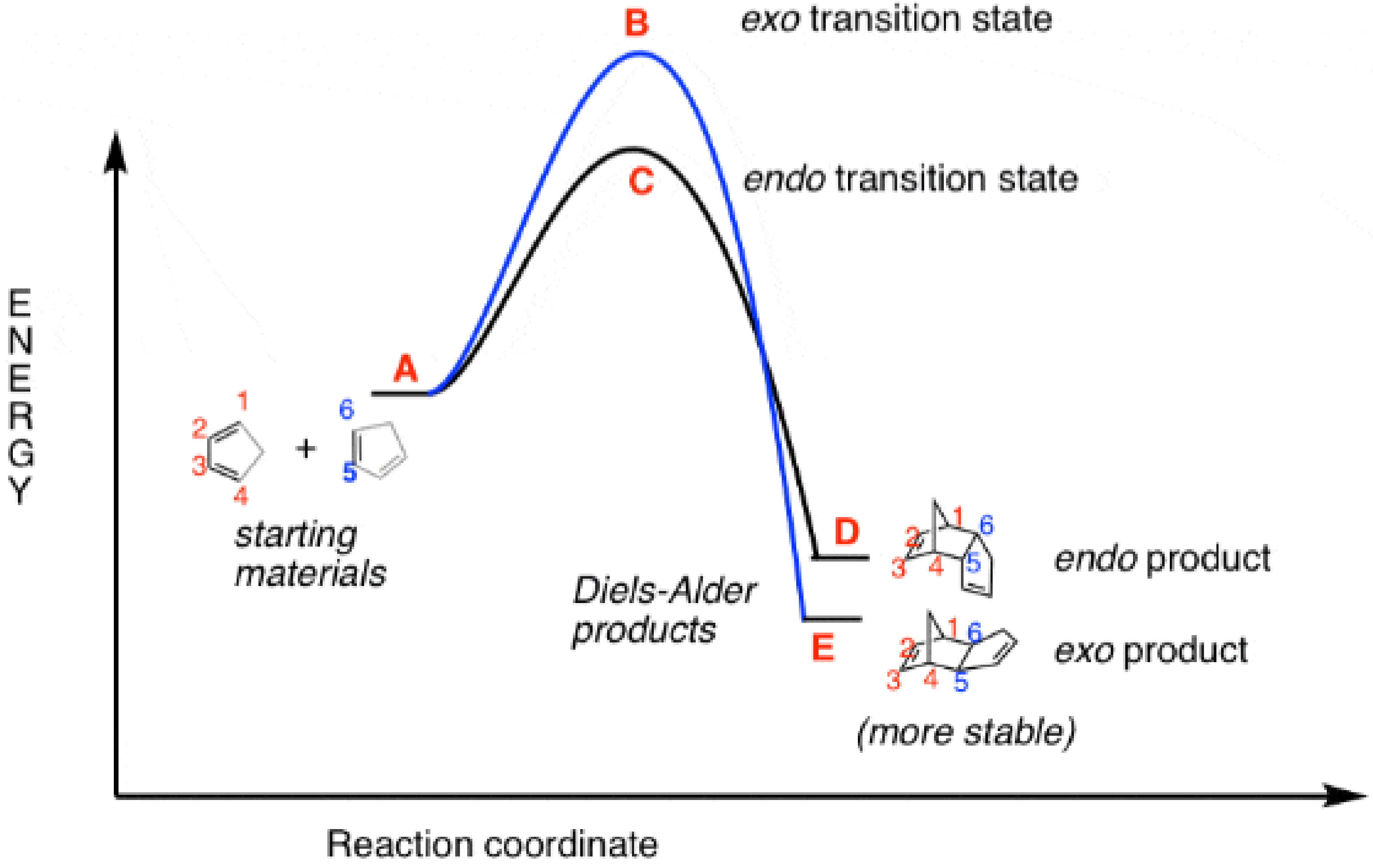

Thermodynamic criteria of phase stability

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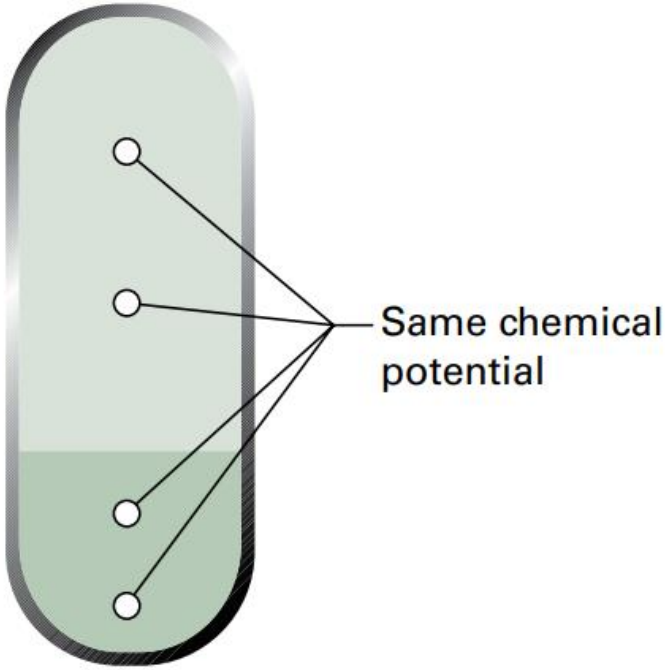
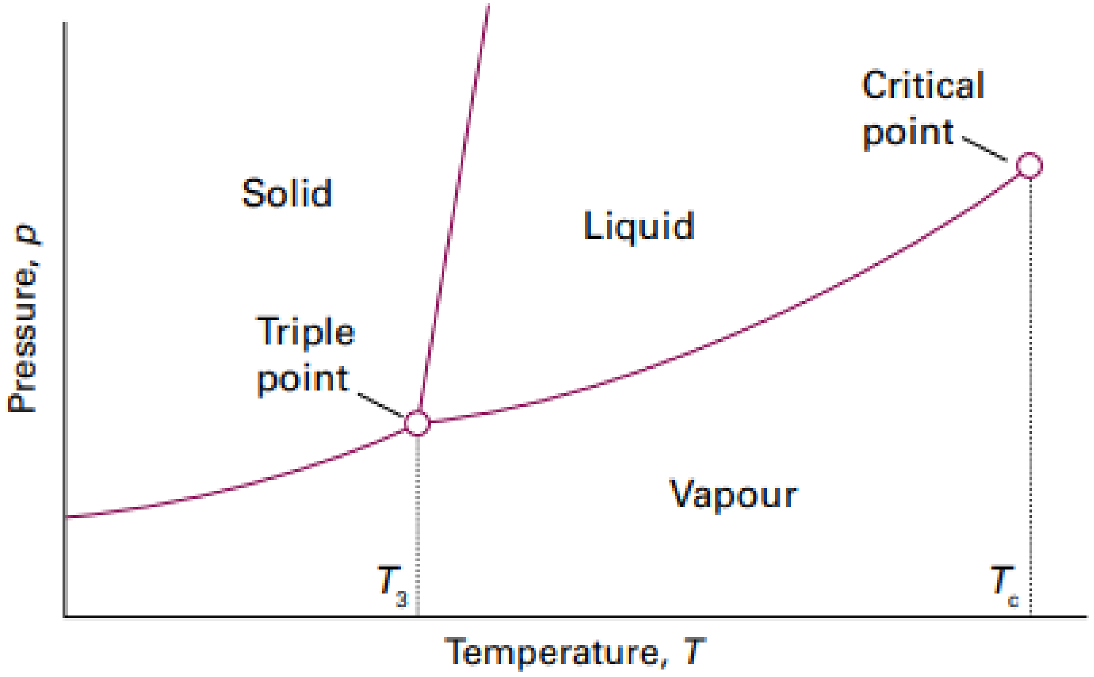
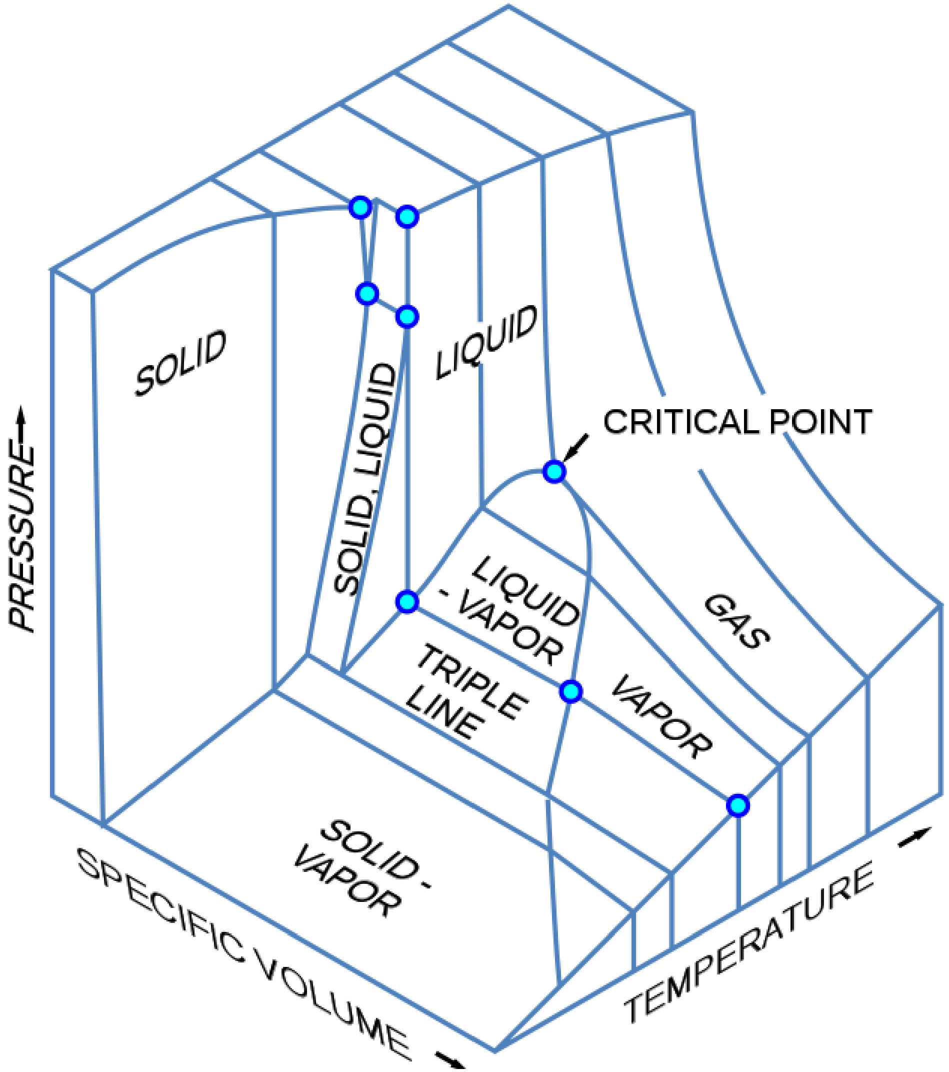


Phase diagram





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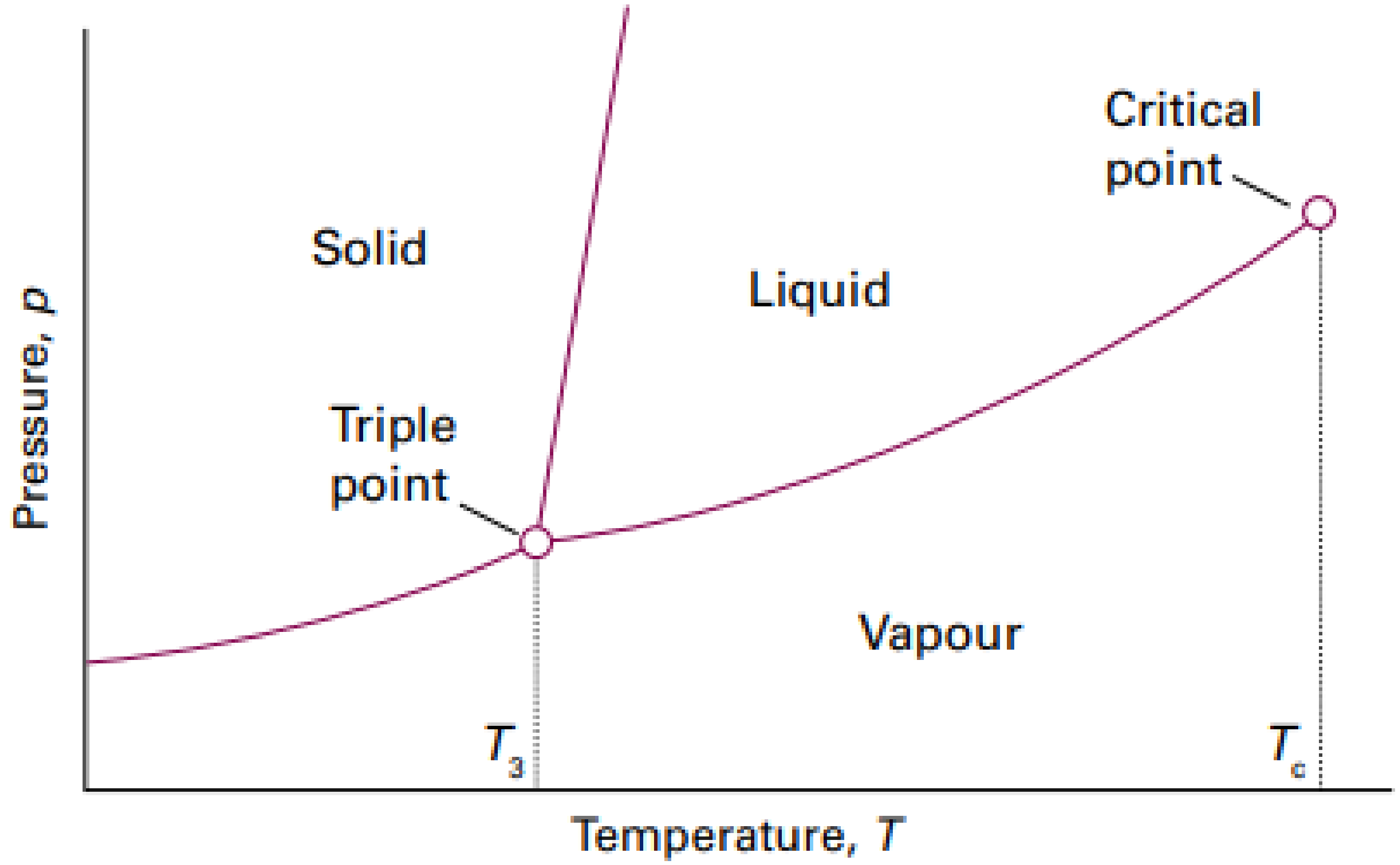
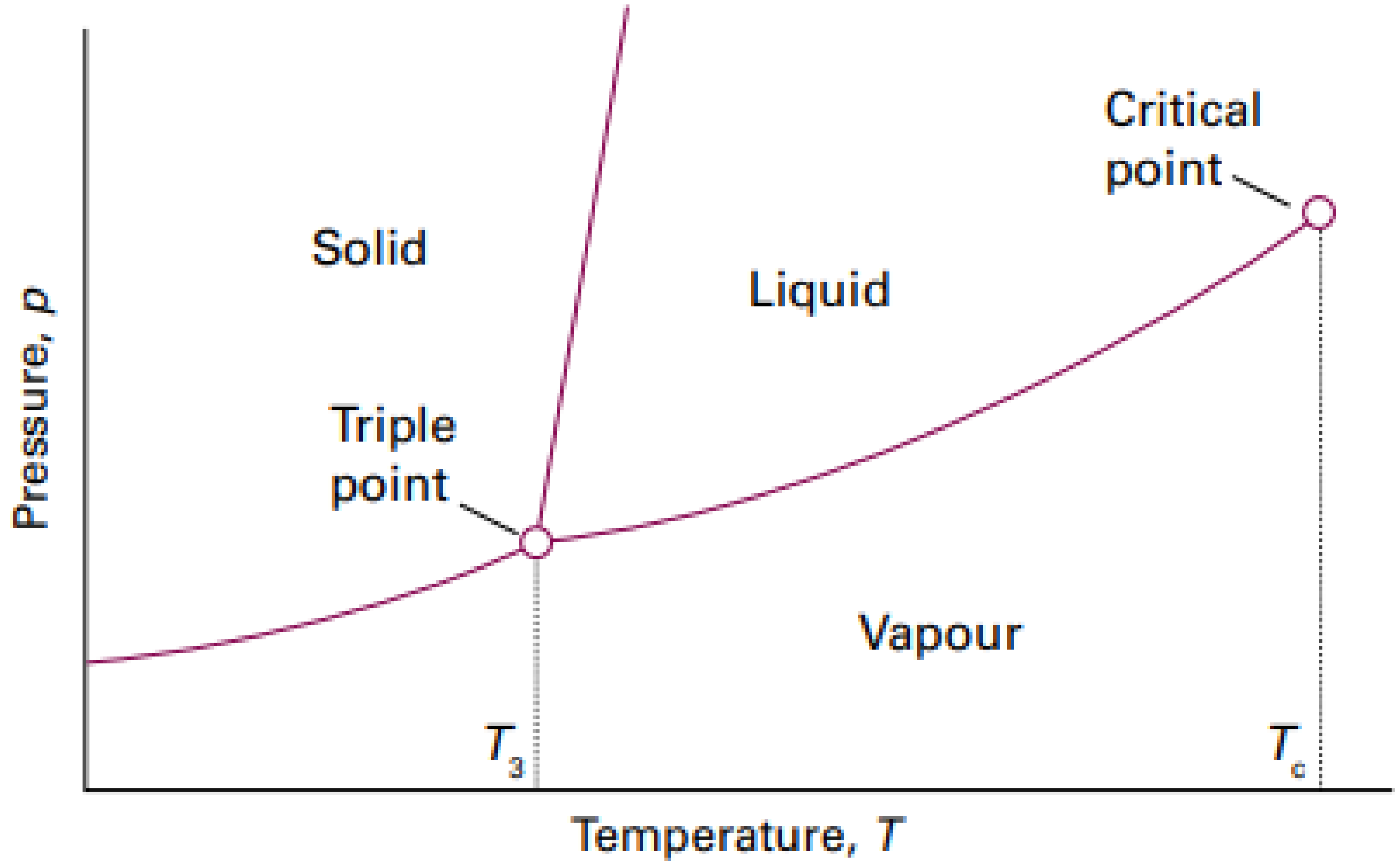


Phase diagram

(1.00 bar = 0.987 atm)



normal boiling point	1 atm
standard boiling point	1 bar

The temperatures at which vapor pressure reaches 1 atm or 1 bar

Phase diagram

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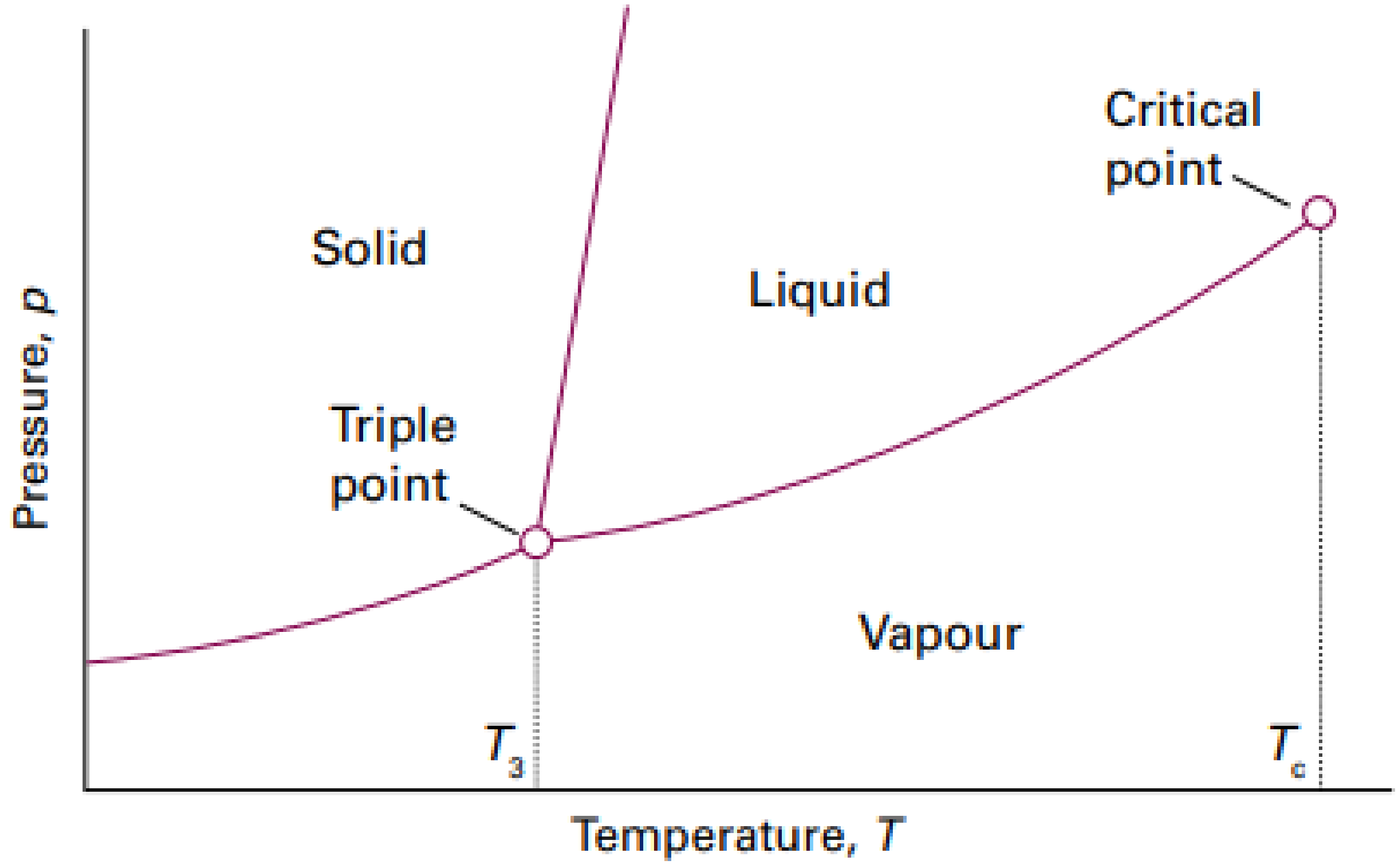
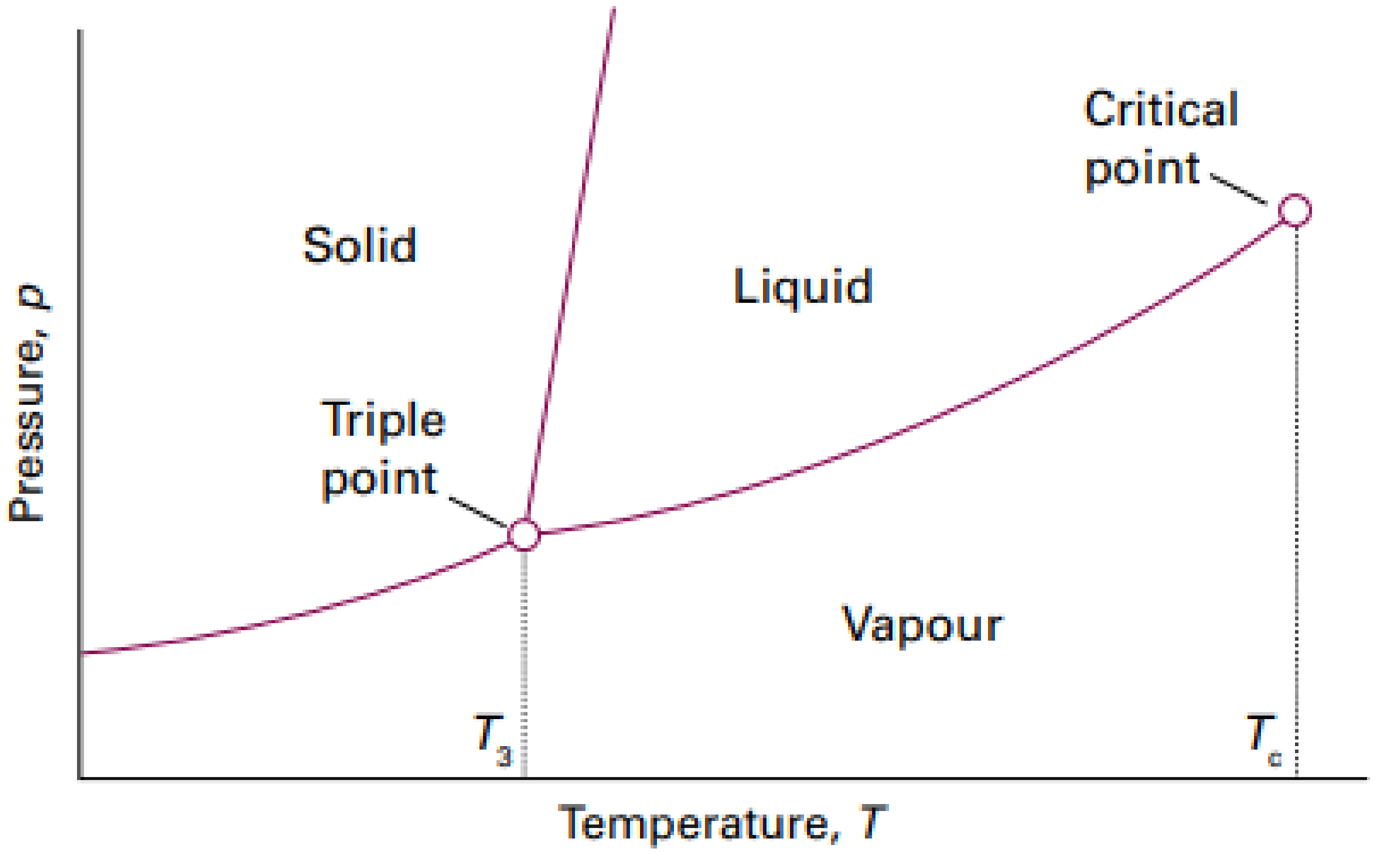
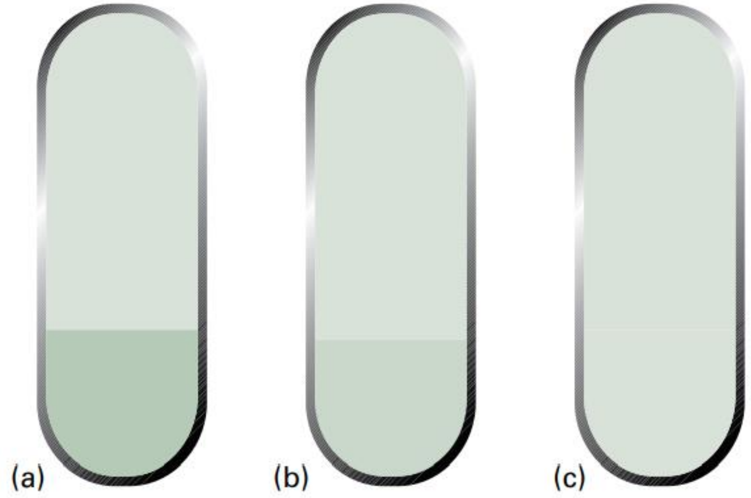


normal boiling point	1 atm	Normal boiling point of water is 100.0 °C
standard boiling point	1 bar	Standard boiling point is 99.6 °C.

Phase diagram





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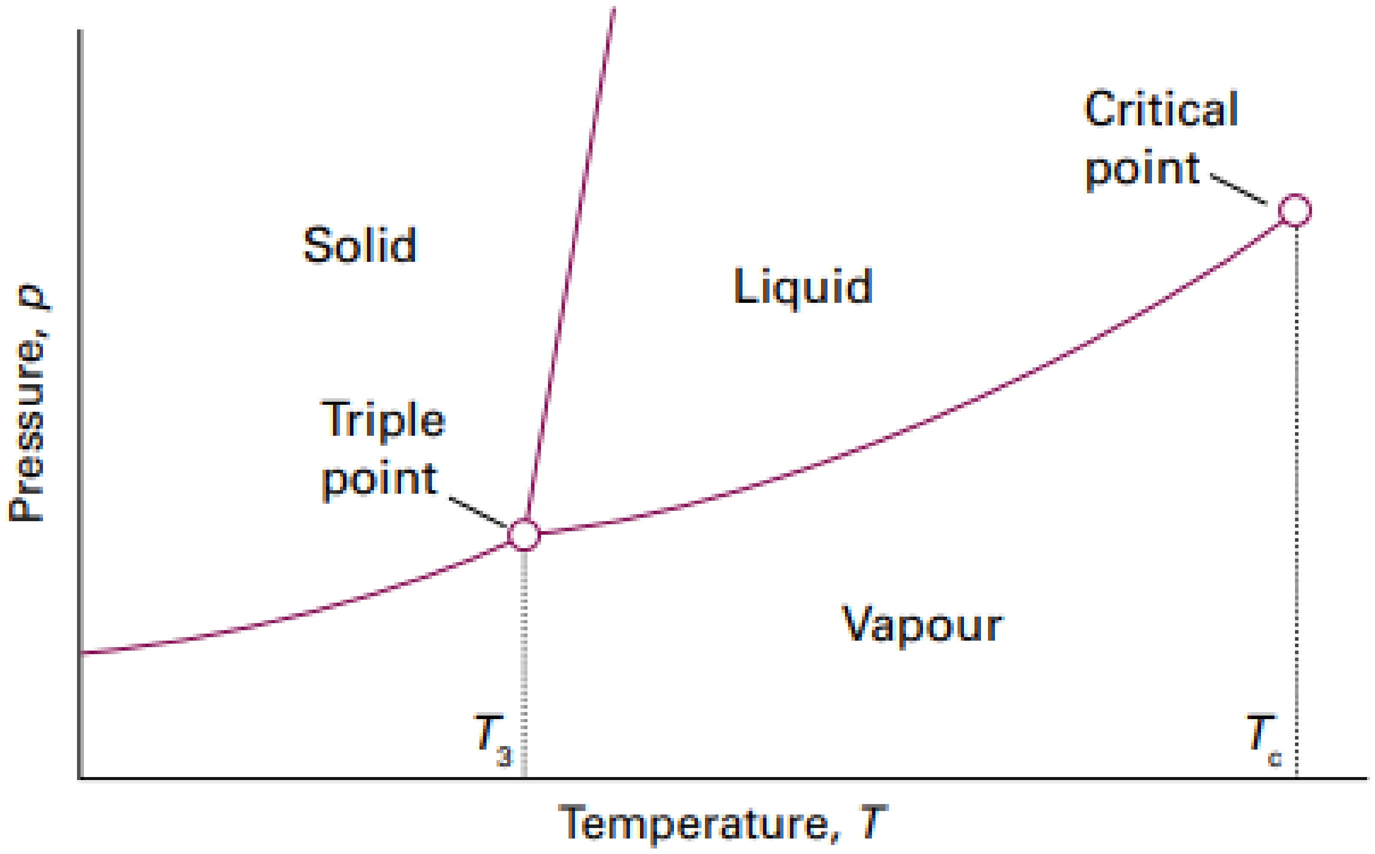
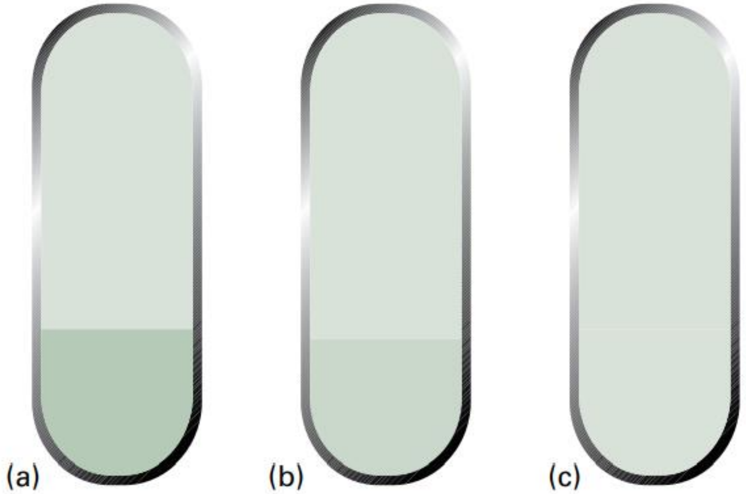


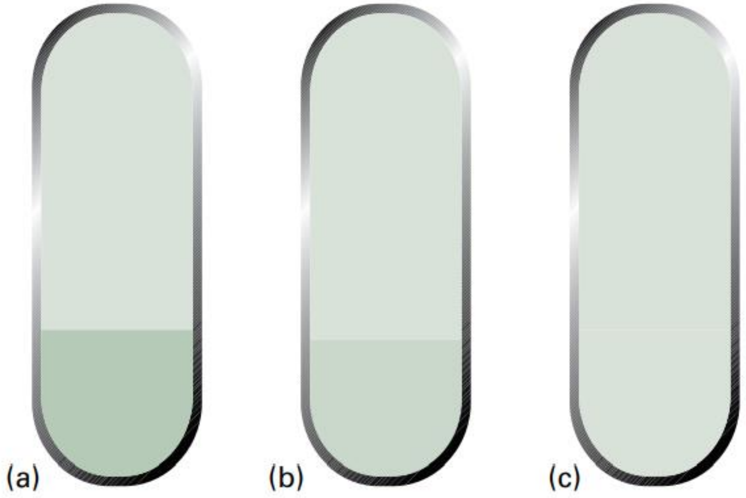


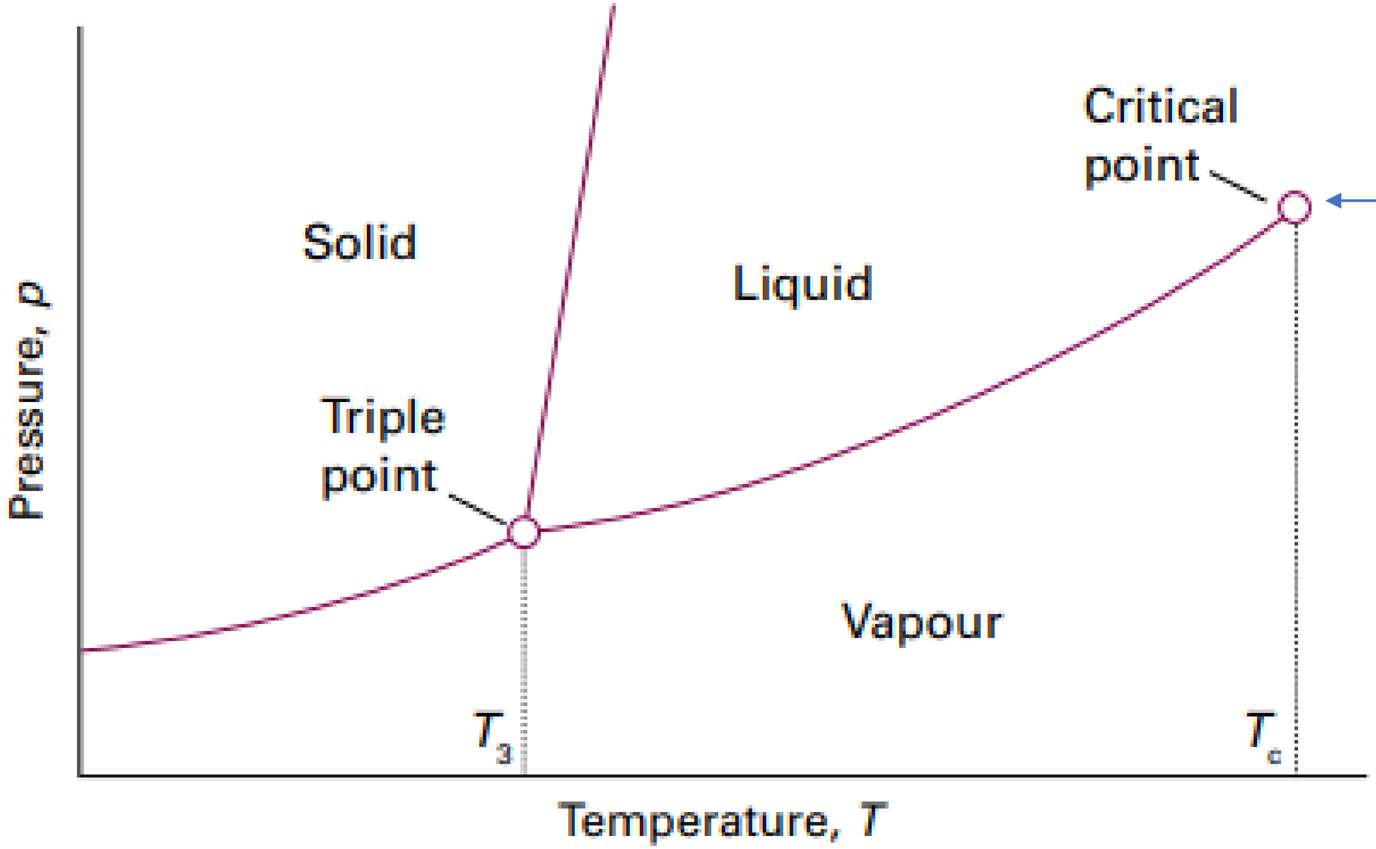
- If the container is sealed and does not allow vapor to escape, the liquid will not boil in the traditional sense.

- In a sealed container, as the temperature rises, the vapor pressure increases, but since the vapor cannot escape, the pressure inside also rises.

- The liquid may transition into a supercritical fluid rather than boiling if the temperature exceeds the critical temperature (T_a), beyond which there is no distinct liquid and gas phase.

Phase diagram

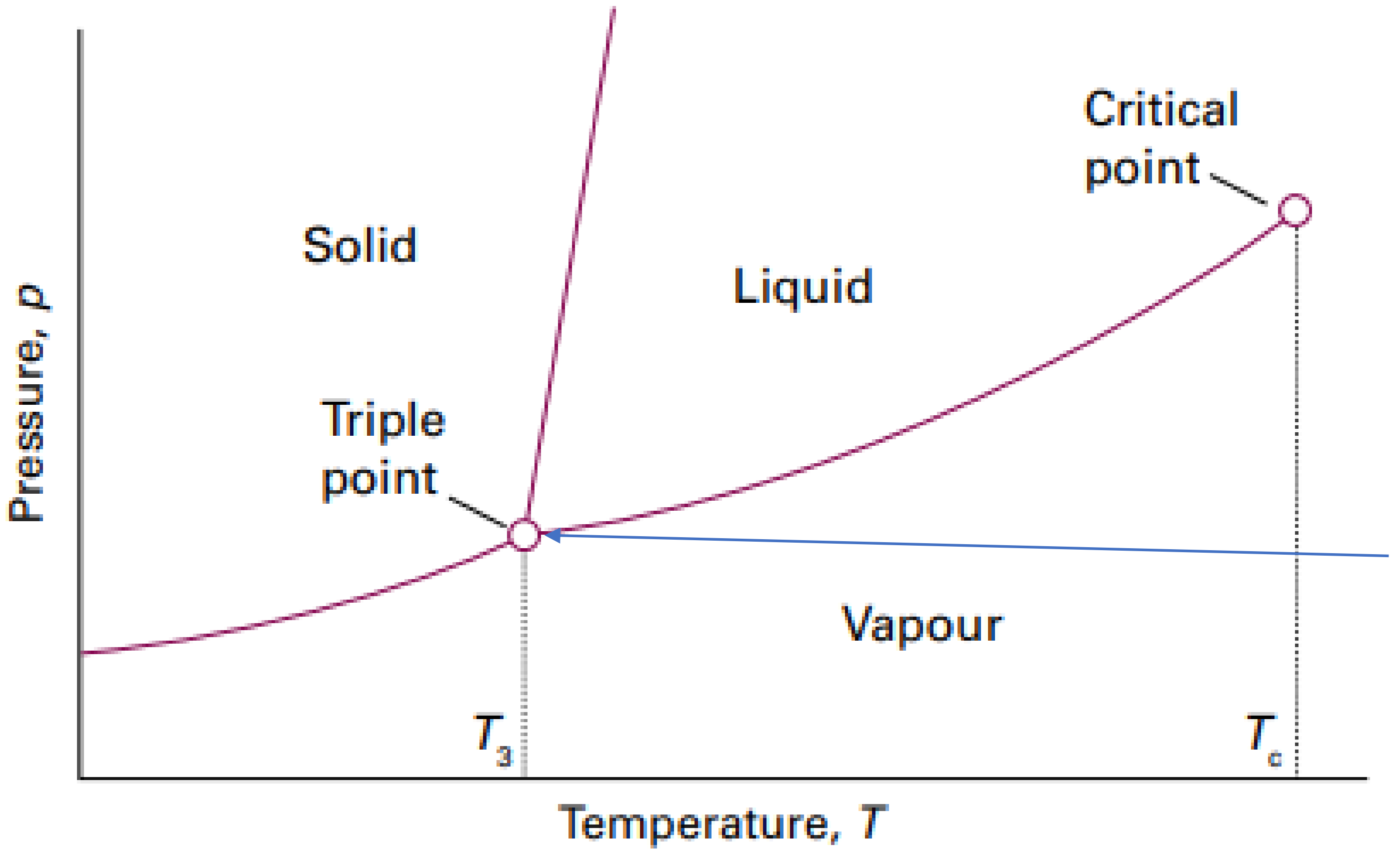




374 °C and 218 atm

Tc for water

Phase diagram

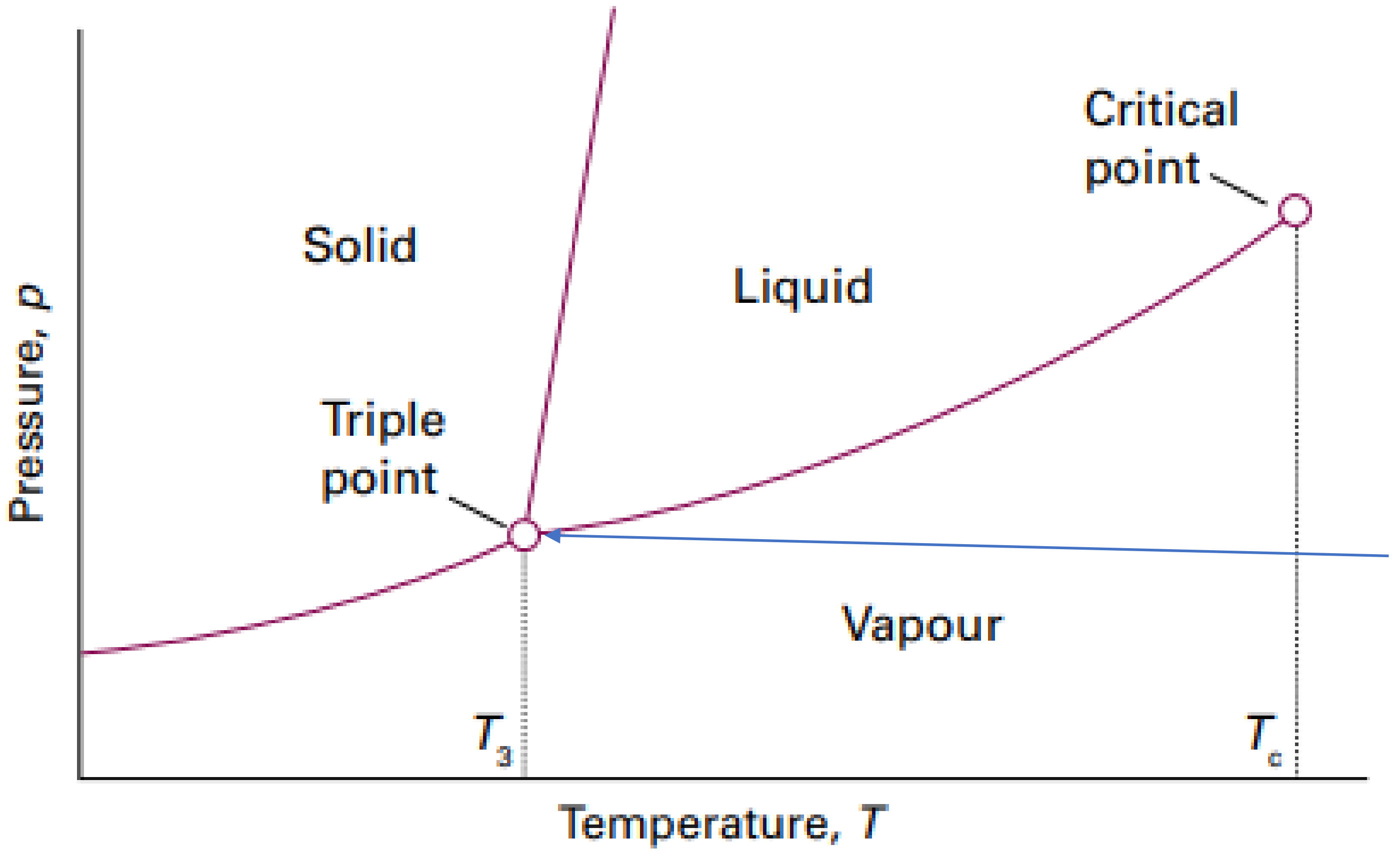


0.01 °C (273.16 K)
and 0.006. atm

T3 for water

Phase diagram

- A substance can have more than one triple point if it has multiple solid phases that can coexist with the liquid and gas phases under different conditions.



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Gibbs Phase rule

$$F = C - P + 2$$

Phase rule

The **variance** (or *number of degrees of freedom*), *F*, of a system is the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium.

Variance

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Number of components (chemically independent species in the system)

Number of components

☐	Example	System	Number of Components (C)	Reason
1	Pure Water	H_2O (ice, liquid, vapor)	1	All phases consist of the same substance (H_2O).

- C counts independent chemical species needed to describe all phases.
- If a species can be expressed as a combination of others (like CaO from $CaCO_3$), it does not count as an additional component.
- If two substances mix but do not react (like ethanol and water), they are separate components.

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4	Water-Ethanol Mixture	$H_2O + C_2H_5OH$	2	H_2O and ethanol mix but do not react, so both are independent.

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Variance

No of phases

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Number of components (chemically independent species in the system)

Phase rule

Single-Phase System (e.g., Liquid Water)

•**C = 1** (Water)

•**P = 1** (Only liquid phase)

•**F = 1 - 1 + 2 = 2**

•This means both temperature and pressure can be varied independently.

$$F = C - P + 2$$

Phase rule

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Two-Phase System (e.g., Water Coexisting as Liquid and Vapor)

- **C = 1** (Water)
- **P = 2** (Liquid and Vapor)
- **F = 1 - 2 + 2 = 1**
- Only one variable (temperature or pressure) can be independently changed, as the other will be fixed by the phase equilibrium.

$$F = C - P + 2$$

Phase rule

Single-Phase System (e.g., Liquid Water)

- **C = 1** (Water)
- **P = 1** (Only liquid phase)
- **F = 1 - 1 + 2 = 2**
- This means both temperature and pressure can be varied independently.

Triple Point (Three Phases: Solid, Liquid, and Gas in Equilibrium)

- **C = 1** (Water)
- **P = 3** (Solid, Liquid, and Vapor)
- **F = 1 - 3 + 2 = 0**
- No degrees of freedom! This means the temperature and pressure are fixed at a single unique value (e.g., 0.01°C and 0.006 atm for water).

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$$F = C - P + 2$$

Phase rule $F = C - P + 2$

P=1, C=1; F=2 => both p and T can be varied independently without changing the number of phases **bivariant**

=> A single phase is represented by an area on a phase diagram

P=2, C=1; F=1 => Only 1 variable can be varied independently without changing the number of phases **Univariant**

=> equilibrium of two phases is represented by a line

P=3, C=1; F=0 => no variable can be varied independently without changing the number of phases **invariant**

=> equilibrium of three phases is therefore represented by a point