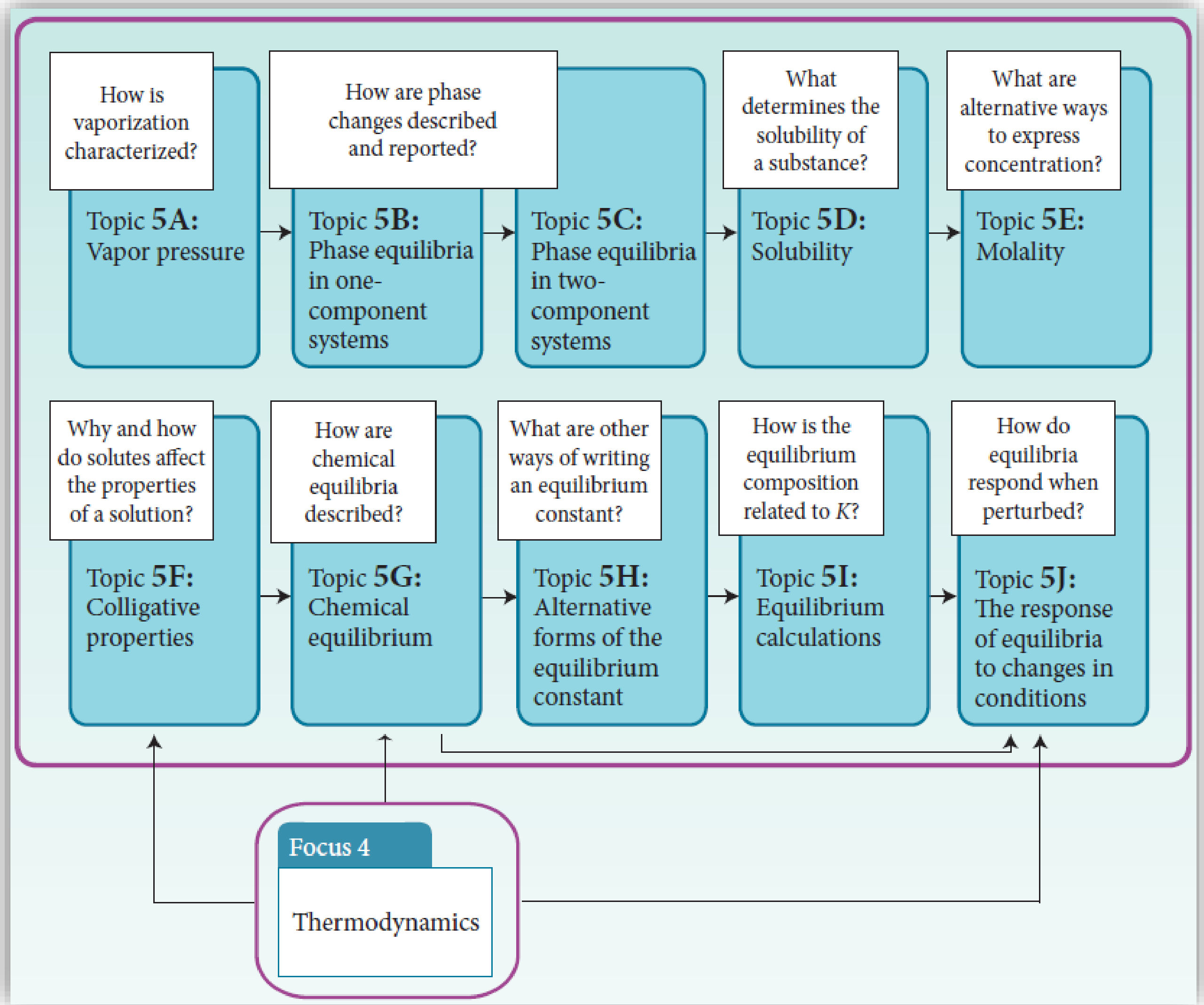
Focus 5. Equilibrium *Overview*



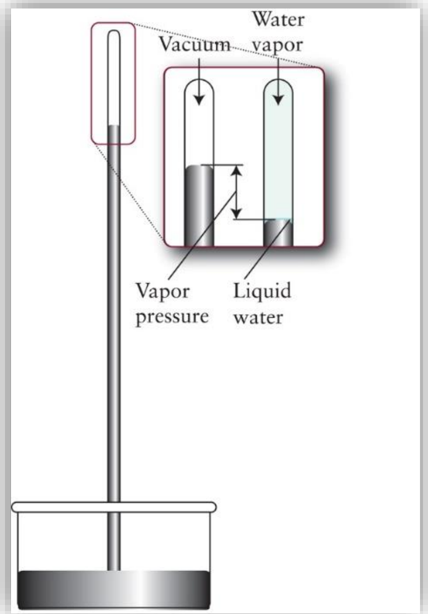
Topic 5A. Vapor Pressure

Phase

- Phase: a specific physical state of matter
  - Solid, liquid, and gas
  - Carbon: diamond and graphite
- Phase transition

Vapor Pressure

- Vapor pressure: the pressure exerted by its vapor when the vapor is in dynamic equilibrium with the condensed phase
  - Dependent on the molecular structure
  - Dependent on temperature, T
  - Independent of the amount of liquids and solids



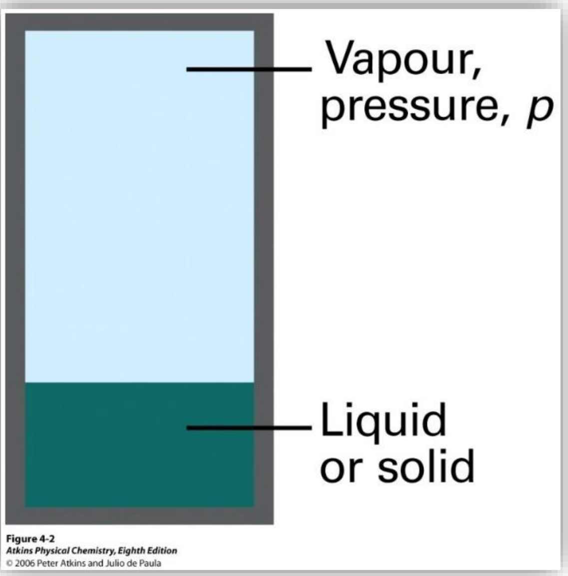


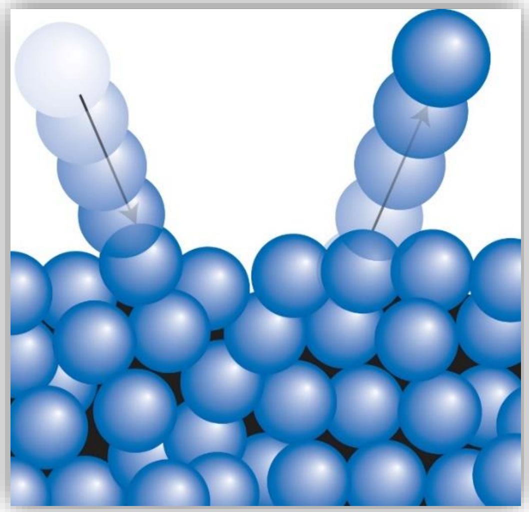
TABLE 5A.1 Vapor Pressures at 25 °C

Substance	Vapor pressure P/Torr
benzene	94.6
ethanol	58.9
mercury	0.0017
methanol	122.7
toluene	29.1
water*	23.8

Equilibrium

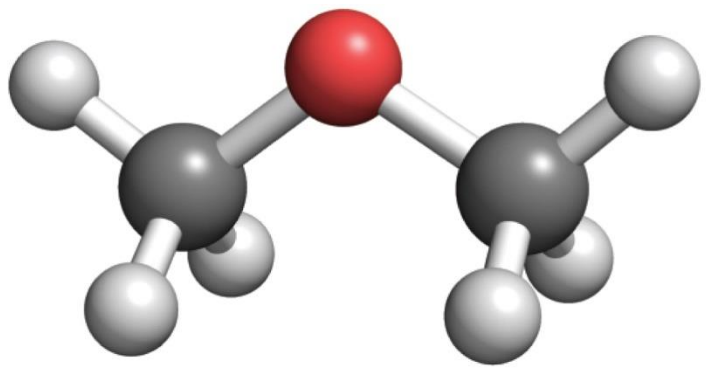
- Thermodynamic (see Topic 4J)
  - Condensed and vapor phases are in equilibrium when there is no Gibbs energy change
- Kinetic (see Topic 7D)
  - The rates of evaporation and condensation are equal
  - Dynamic equilibrium

$$H_2O\ (l)\ \leftrightarrow H_2O\ (g)$$

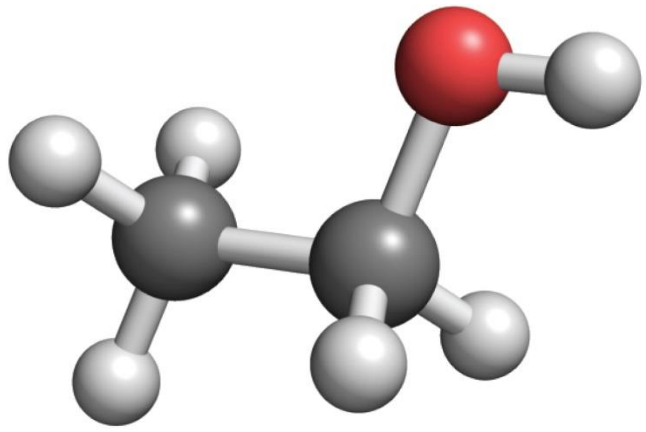


Volatility and Intermolecular Forces

- Higher vapor pressure
  → lower intermolecular forces between the molecules of a liquid
- Dimethyl ether (CH_3–O–CH_3; gas) vs. ethanol (CH_3–CH_2–OH; liquid, *hydrogen bonding*)



1 Dimethyl ether, C_2H_6O



2 Ethanol, C_2H_6O

Vapor Pressure vs. Temperature

- Temperature dependence of vapor pressure

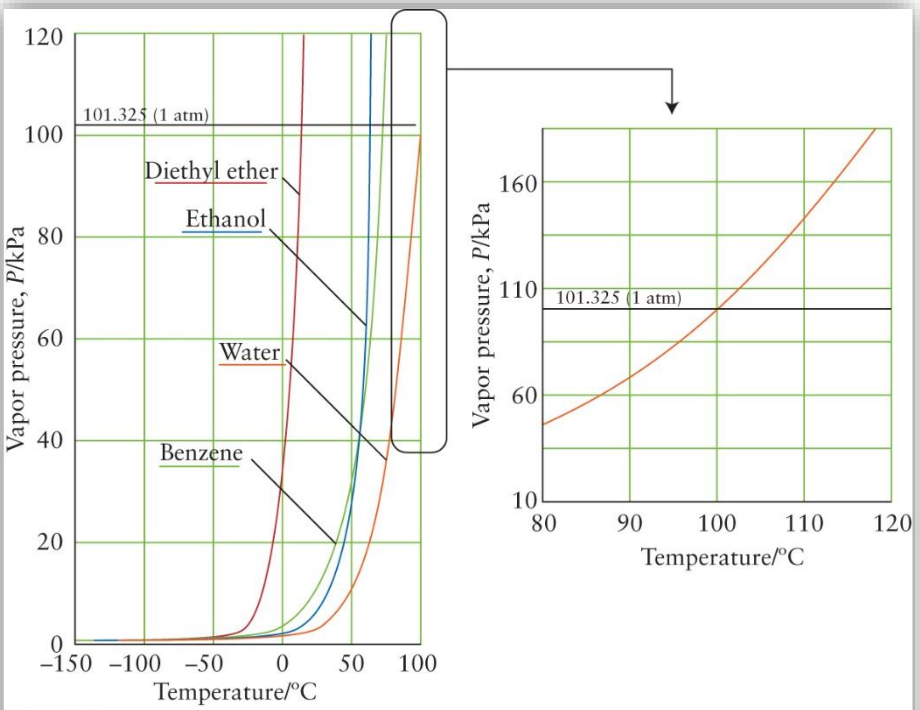


Figure 5A.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

TABLE 5A.2 Vapor Pressure of Water

Temperature/°C	Vapor pressure P/Torr
0	4.58
10	9.21
20	17.54
21	18.65
22	19.83
23	21.07
24	22.38
25	23.76
30	31.83
37*	47.08
40	55.34
60	149.44
80	355.26
100	760.00

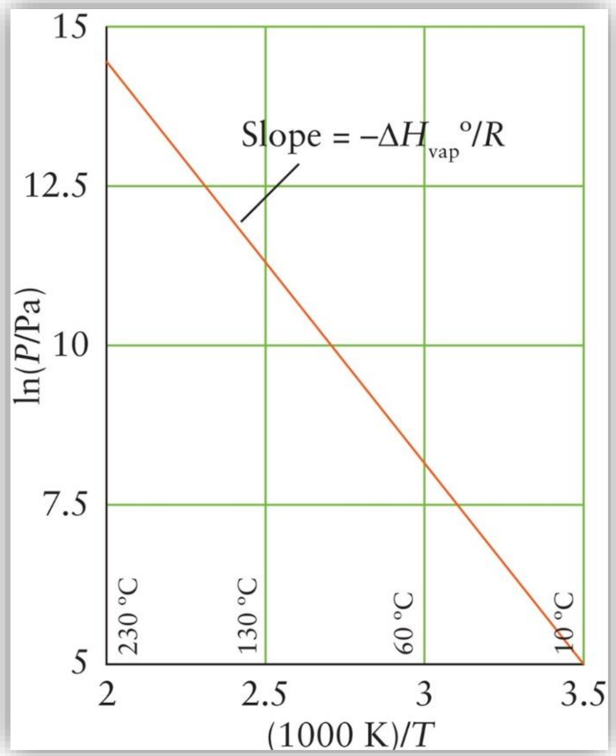
Vapor Pressure vs. Temperature

- Clausius-Clapeyron equation

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

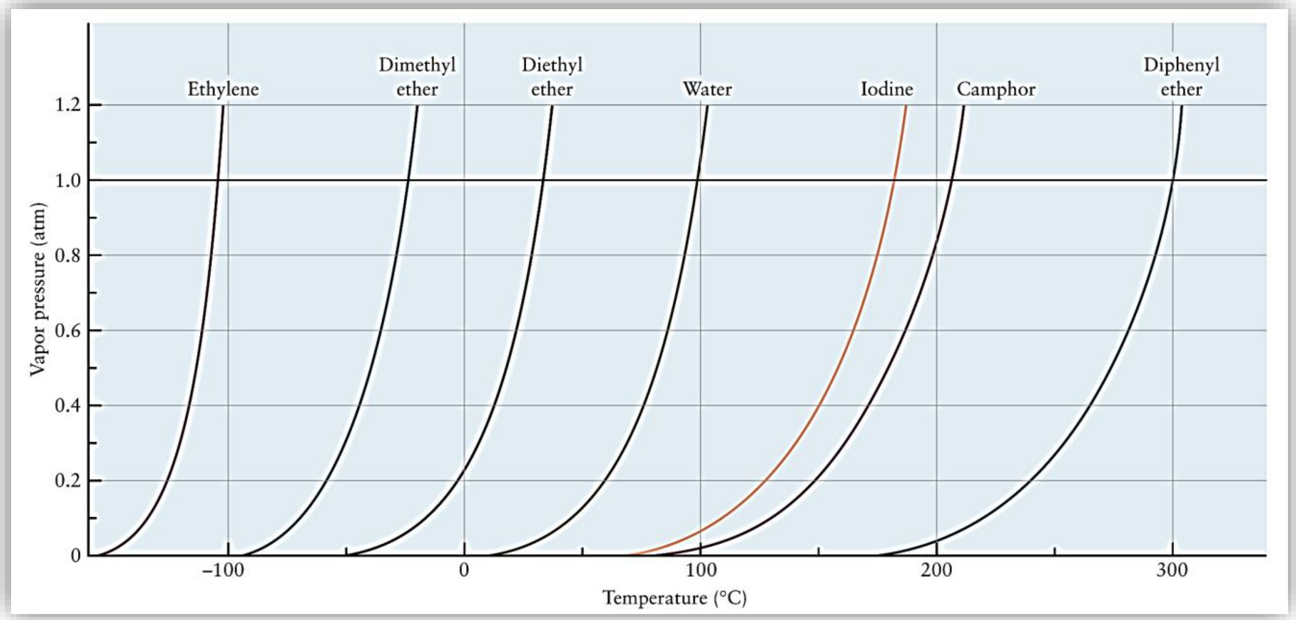
$$\ln P = \underbrace{\ln P_1 + \frac{\Delta H_{vap}°}{RT_1}}_{A} - \underbrace{\frac{\Delta H_{vap}°}{RT}}_{B/T}$$

$$\ln P = A - \frac{B}{T}$$



Boiling

- Boiling: vapor pressure of liquid = external pressure
  → rapid vaporization occurs throughout the entire liquid
- Normal boiling point, T_b: when external pressure is 1 atm
- Higher external pressure → higher T_b



Freezing

- Freezing (melting): solidification of a liquid (liquefaction of a solid)
- Freezing (melting) point, : T at which liquid freeze (solid melts)
- Normal freezing point, T_f : T at which liquid begins to freeze at 1 atm
- T_f increases with pressure for most substances (exception: H_2O)

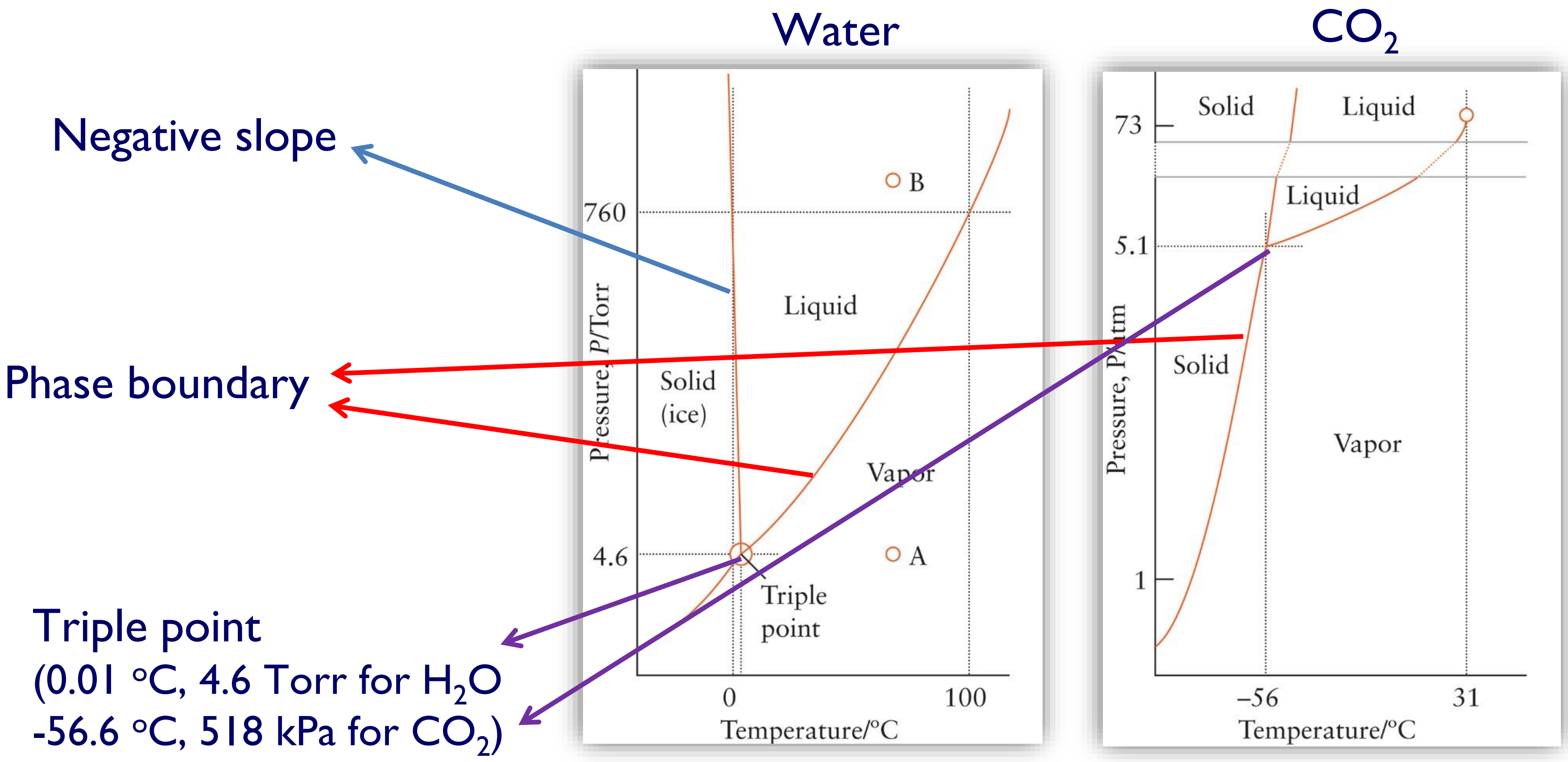
Topic 5B. Phase Equilibria in One-Component Systms

5B.1 One-Component Phase Diagram

5B.2 Critical Properties

Phase Diagram

- Phase diagram: a map that shows which phase is the most stable at certain pressures and temperatures

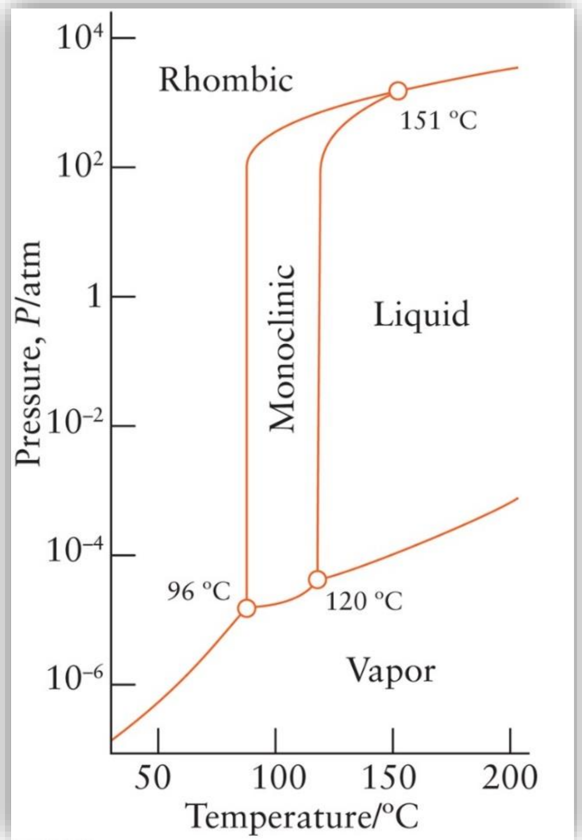


Phase Diagram

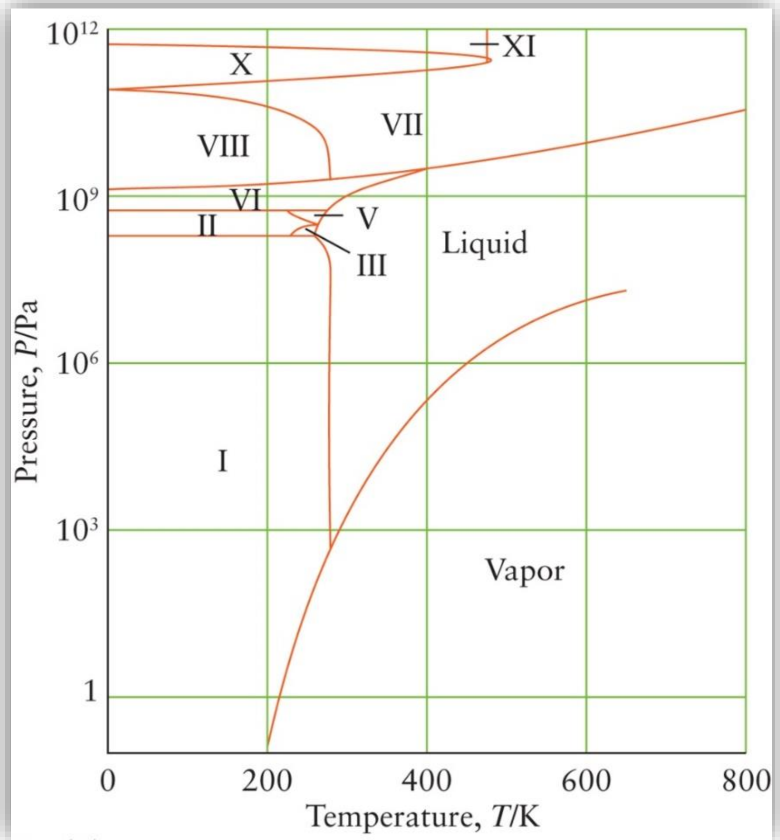
- Phase boundary: curves separating region on a phase diagram
  → Represents a set of P and T values for which 2 phases coexist in dynamic equilibrium
- Triple point: point where three phase boundaries intersect
  → a single value of P and T for which 3 phases coexist in dynamic equilibrium

Phase Diagram

Sulfur



Water



Critical Properties

- Critical point: terminus of liquid-gas phase boundary
- Critical temperature, critical pressure

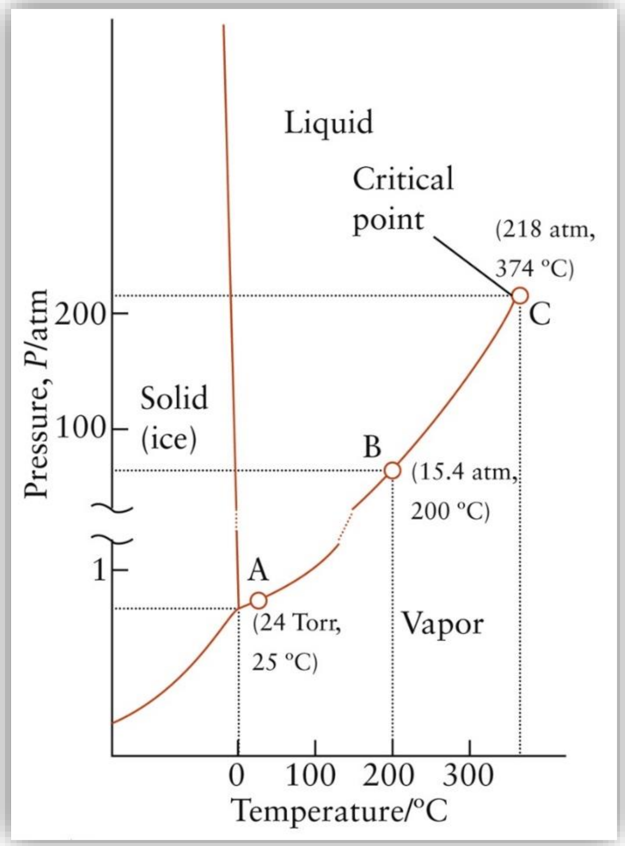


TABLE 5B.1 Critical Temperatures and Pressures of Selected Substances

Substance	Critical temperature/ °C	Critical pressure P_c/atm
He	−268 (5.2 K)	2.3
Ne	−229	27
Ar	−123	48
Kr	−64	54
Xe	17	58
H_2	−240	13
O_2	−118	50
H_2O	374	218
N_2	−147	34
NH_3	132	111
CO_2	31	73
CH_4	−83	46
C_6H_6	289	49

Critical Properties

Critical Properties

- Supercritical fluid