At phase boundary: Dynamic equilibrium between two phases
\[ \Delta G = 0 \]
Phase boundaries: Where are they?

Phase 1: \( dG_m(1) = V_m(1)dp - S_m(1)dT \)
Phase 2: \( dG_m(2) = V_m(2)dp - S_m(2)dT \) \{ in equilibrium \}

Along the phase boundary, the molar Gibbs energies stay equal
\( \Rightarrow \) the changes in their molar Gibbs energies must be equal

\[ V_m(1)dp - S_m(1)dT = V_m(2)dp - S_m(2)dT \]
\( \Rightarrow \) \[ [S_m(2) - S_m(1)]dT = [V_m(2) - V_m(1)]dp \]

\( \Delta_{trs} S \)
\( \Delta_{trs} V \)

\[ \frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V} \]
Clapeyron equation
Special case: The liquid-vapor boundary

\[ \frac{dp}{dT} = \frac{\Delta_{vap} S}{\Delta_{vap} V} = \frac{\Delta_{vap} H}{T \Delta_{vap} V} = \frac{\Delta_{vap} H}{T V_m(g)} = \frac{\Delta_{vap} H}{T(RT/p)} = \frac{p \Delta_{vap} H}{RT^2} \]

trs → vap  \[ \Delta_{vap} S = \Delta_{vap} H/T \]

≈ \( V_m(g) \); approximation

\( V_n(l) \) small

Clausius-Clapeyron equation

\[ \int_{p}^{p'} d \ln p = \int_{T}^{T'} \frac{\Delta_{vap} H}{RT^2} dT \]

\[ \Rightarrow \ln \frac{p'}{p} = \frac{\Delta_{vap} H}{R} \left( \frac{1}{T} - \frac{1}{T'} \right) \]
Characteristic points

Same as melting point; “normal” = at 1 atm

Closed vessel:
Pressure increases until critical point is reached ($T_c$, $p_c$); phase boundary is lost

Open vessel:
Vapor pressure equals external pressure ⇒ vapor drives back atmosphere: Boiling

Highest T for liquid

Lowest T for liquid

Only set of conditions where all three phases coexist (water: 273.16 K, 611 Pa)
How many phases can coexist in equilibrium?

Four phases: \( G_m(1) = G_m(2); \ G_m(2) = G_m(3); \ G_m(3) = G_m(4) \)

**BUT:** Only two unknown parameters \((p, T)\) in a phase diagram

\[ \Rightarrow \text{Four phases cannot coexist in equilibrium!} \]

Phase rule: \( F = C - P + 2 \)
- \( F \) = Number of degrees of freedom
- \( C \) = number of components (pure: 1)
- \( P \) = number of phases
Liquid water has a higher density than water ice.

On Mt. Everest "boiling" eggs becomes easier.
Phase diagrams: CO$_2$ and Helium

**CO$_2$: quite typical**

- Sublimes at 1 atm; exists as a liquid only under pressure.
- 5.11 bar at 217 K
- 1 bar at 195 K
- 67 bar at 298 K
- 72.8 bar at 304 K

**He**: solid and gas are never in equilibrium; He-II is superfluid.

- 2.2 K at 2.3 bar
- 5.2 K at 2.3 bar

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