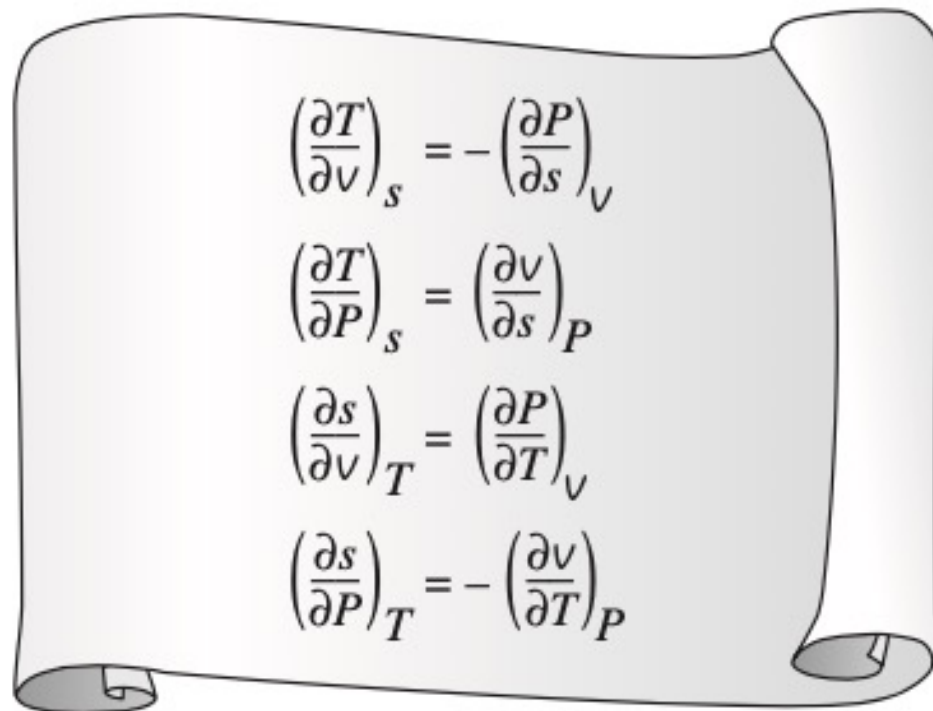


Chemical Engineering Thermodynamics

Lecture 4 Thermodynamic Properties

Xiaofei Xu



A scroll with a light gray background and a darker gray border, featuring four thermodynamic equations written in black. The scroll is slightly curved, with the top and bottom edges rolled up.

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$
$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$
$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

Internal Energy and Free Energy

- $U = U(S, V, N)$
- Free energy: useful work

Fundamental Equation

$$U = U(S, V, N)$$

$$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial N} dN$$

$$\frac{\partial U}{\partial S} \equiv T$$

Temperature

$$-\frac{\partial U}{\partial V} \equiv P$$

Pressure

$$\frac{\partial U}{\partial N} \equiv \mu$$

Chemical Potential

Fundamental Equation

$$U = U(S, V, N)$$

$$dU = TdS - PdV + \mu dN$$

This fundamental equation is not popular for experimenters. WHY???

S, V, N are extensive parameters.

T, P, μ are intensive parameters.

Could we use intensive parameters, rather than extensive ones, as the independent variables?

Legendre Transformation

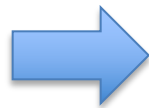
$$L : C[x] \rightarrow C[p]$$

$$f(x) \mapsto f^*(p)$$

$$p = \frac{df}{dx}$$

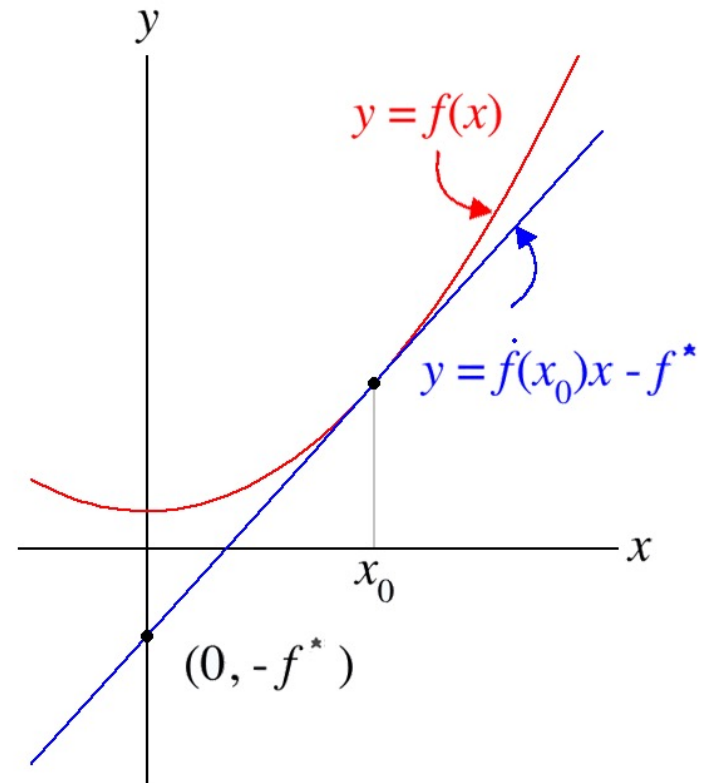
$$y = f(x)$$

$$p = \frac{df}{dx}$$



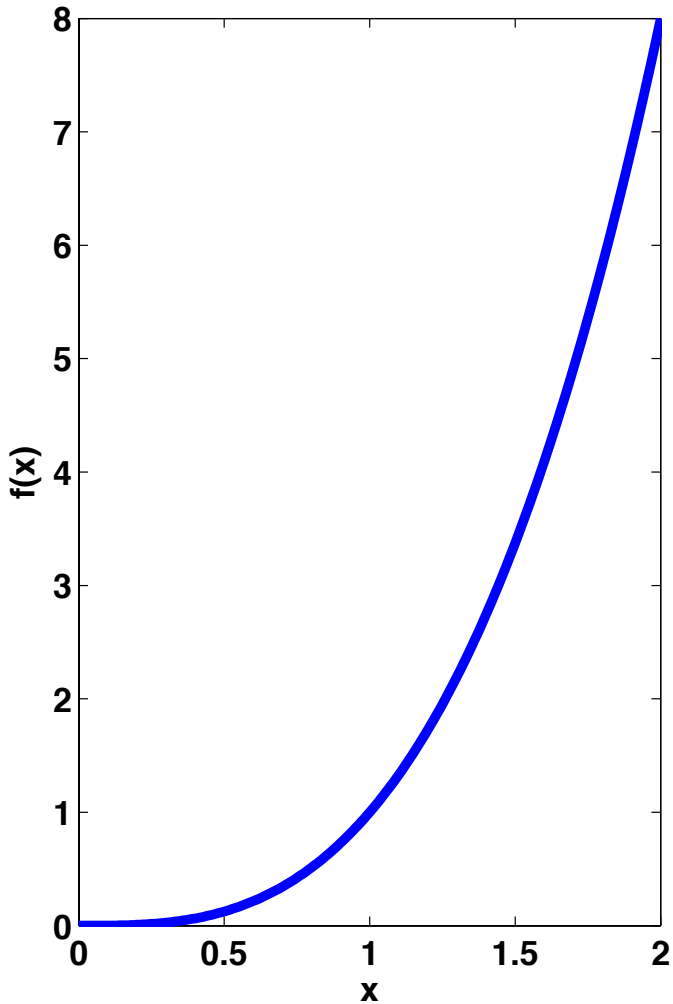
$$y = f^*(p)$$

$$f^* = -px + y$$

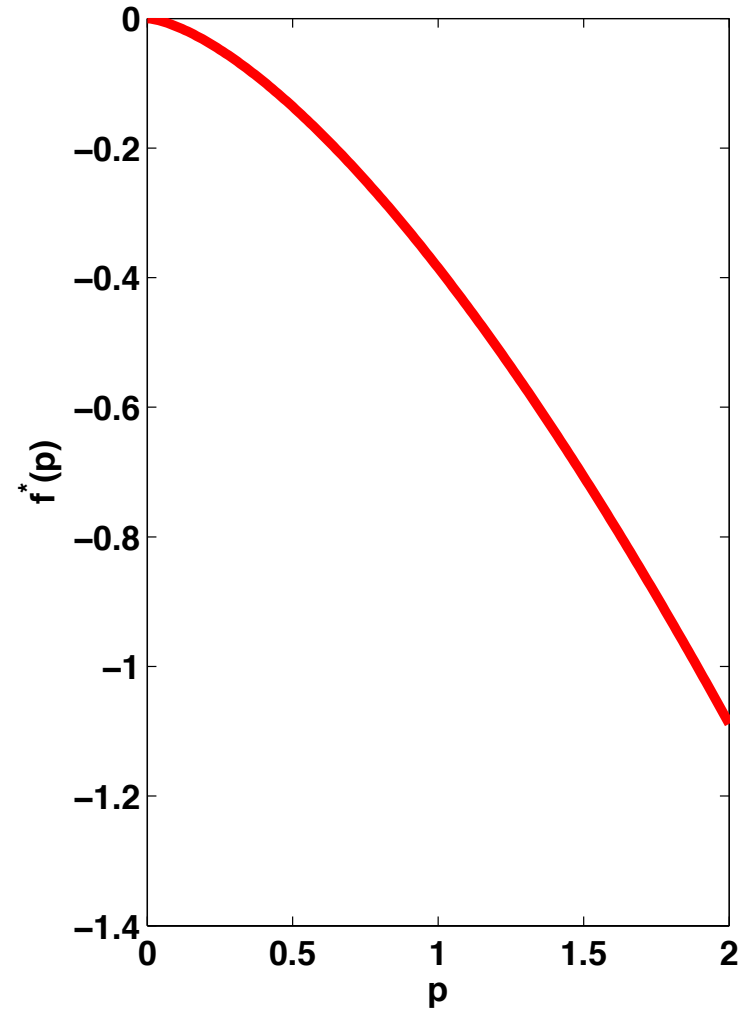


Example

$$y = f(x)$$



$$y = f^*(p)$$



Thermodynamic Potential

- The Legendre transformation of the internal energy.

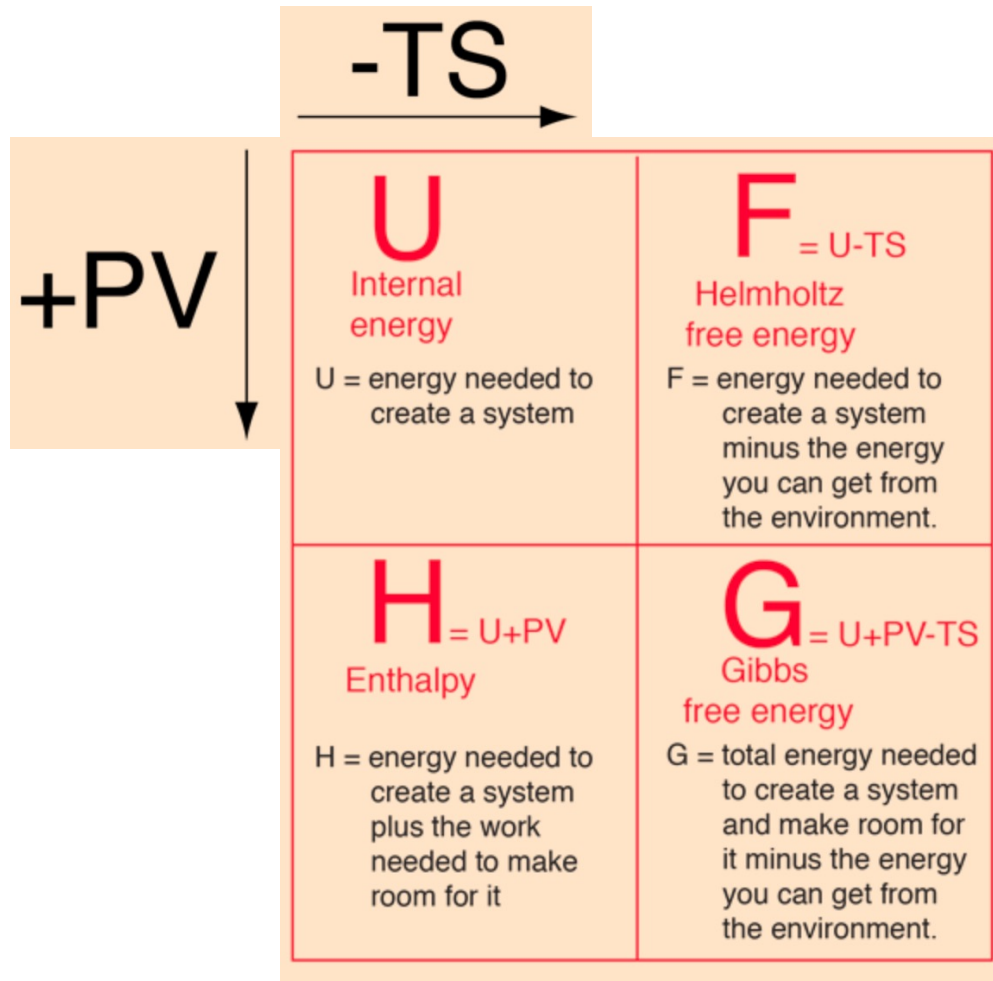


A.M. Legendre
(1752-1833)



L. Legendre
(1752-1797)

Thermodynamic Potential



Helmholtz Free Energy

$$U = U(S, V, N)$$

$$T = \frac{\partial U}{\partial S}$$

$$F = U - TS$$

$$F = F(T, V, N)$$

It measures the useful work obtainable from a closed system at a constant temperature.

$$dF = -SdT - PdV + \mu dN$$

Enthalpy

$$U = U(S, V, N)$$

$$-P = \frac{\partial U}{\partial V}$$

$$H = U + PV$$

$$H = H(S, P, N)$$

Enthalpy change is a measure of heat transfer during phase transition or chemical reaction.

$$dH = TdS + VdP + \mu dN$$

Gibbs Free Energy

$$U = U(S, V, N)$$

$$T = \frac{\partial U}{\partial S}, \quad -P = \frac{\partial U}{\partial V}$$

$$G = U - TS + PV$$

$$G = G(T, P, N)$$

It measures the useful work obtainable from a closed system at a constant temperature and pressure.

$$dG = -SdT + VdP + \mu dN$$

Grand Canonical Potential

$$U = U(S, V, N)$$

$$T = \frac{\partial U}{\partial S}, \quad \mu = \frac{\partial U}{\partial N}$$

$$\Omega = U - TS - \mu N$$

$$\Omega = \Omega(T, V, \mu)$$

$$d\Omega = -SdT - PdV - Nd\mu$$

Maxwell's Relation

$$\begin{aligned}dF &\equiv \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \\ &\equiv Mdx + Ndy\end{aligned}$$

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 F}{\partial x \partial y}}$$

Maxwell's Relation

$$\begin{aligned}dU &= TdS - PdV \\dH &= TdS + VdP \\dA &= -SdT - PdV \\dG &= -SdT + VdP\end{aligned}$$

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P\end{aligned}$$

Calculation of Entropy and Enthalpy

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T} \right)_P dP$$

Ideal gas state

$$dH^{id} = C_P^{id} dT$$

$$dS^{id} = C_P^{id} \frac{dT}{T} - nR \frac{dP}{P}$$

Calculation of Internal Energy

- As a function of pressure:

$$\left(\frac{\partial U}{\partial P}\right)_T = (-\beta T + \kappa P)V$$

- As a function of temperature and volume

$$dU = C_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

Gibbs Free Energy as a Generating Function

- $G(T, P)$
- Volume: $\frac{V}{RT} = \left[\frac{\partial(G/RT)}{\partial P} \right]_T$
- Enthalpy: $\frac{H}{RT} = -T \left[\frac{\partial(G/RT)}{\partial T} \right]_P$
- Entropy: $\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$
- Internal Energy: $\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$
- Helmholtz free energy: $F = U - TS$

Residual Properties

$$M^R(T, P) \equiv M(T, P) - M^{id}(T, P)$$

- Gibbs free energy

$$\frac{G_n^R}{RT} = \int_0^P (Z - 1) \frac{dP}{P}$$

- Enthalpy:

$$\frac{H_n^R}{RT} = -T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

- Entropy:

$$\frac{S_n^R}{R} = -T \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P (Z - 1) \frac{dP}{P}$$

Residual Properties for Virial EOS

- Viral equation: $Z - 1 = BP/RT$
- Gibbs free energy: $\frac{G_n^R}{RT} = \frac{BP}{RT}$
- Enthalpy: $\frac{H_n^R}{RT} = \frac{P}{R} \left(\frac{B}{T} - \frac{dB}{dT} \right)$
- Entropy: $\frac{S_n^R}{R} = - \frac{P}{R} \frac{dB}{dT}$

Residual Properties for Pressure-Explicit EOS

- Pressure-explicit EOS: $P = Z\rho_n RT$
- Gibbs free energy: $\frac{G_n^R}{RT} = \int_0^{\rho_n} (Z - 1) \frac{d\rho_n}{\rho_n} + Z - 1 - \ln Z$
- Enthalpy: $\frac{H_n^R}{RT} = -T \int_0^{\rho_n} \left(\frac{\partial Z}{\partial T} \right)_{\rho_n} \frac{d\rho_n}{\rho_n} + Z - 1$
- Entropy: $\frac{S_n^R}{R} = \ln Z - T \int_0^{\rho_n} \left(\frac{\partial Z}{\partial T} \right)_{\rho_n} \frac{d\rho_n}{\rho_n} - \int_0^{\rho_n} (Z - 1) \frac{d\rho_n}{\rho_n}$

Residual Properties in the Zero-Pressure Limit

- Volume: $\lim_{P \rightarrow 0} V_n^R = RT \lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P} \right)_T$
- Internal energy: $\lim_{P \rightarrow 0} U_n^R = 0$
- Enthalpy: $\lim_{P \rightarrow 0} H_n^R = 0$

Evaluation of Entropy and Enthalpy for Gases

- **Step 1** $\rightarrow 1^{ig}$: A hypothetical process that transforms a real gas into an ideal gas at T_1 and P_1 . The enthalpy and entropy changes for this process are:

$$H_1^{ig} - H_1 = -H_1^R \quad S_1^{ig} - S_1 = -S_1^R$$

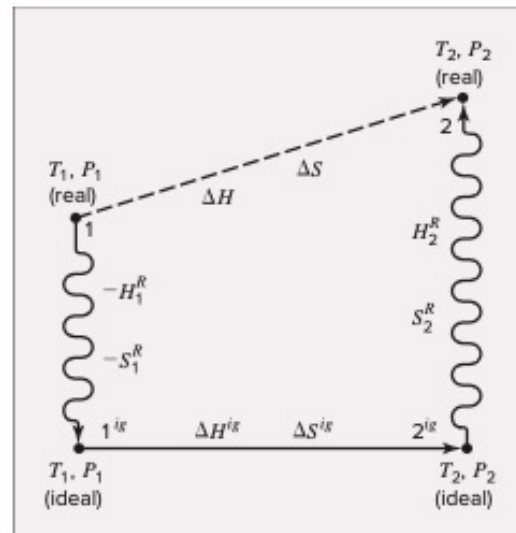
- **Step 1^{ig}** $\rightarrow 2^{ig}$: Changes in the ideal-gas state from (T_1, P_1) to (T_2, P_2) . For this process,

$$\Delta H^{ig} = H_2^{ig} - H_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} dT \quad (6.76)$$

$$\Delta S^{ig} = S_2^{ig} - S_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} \quad (6.77)$$

- **Step 2^{ig}** $\rightarrow 2$: Another hypothetical process that transforms the ideal gas back into a real gas at T_2 and P_2 . Here,

$$H_2 - H_2^{ig} = H_2^R \quad S_2 - S_2^{ig} = S_2^R$$



Example

Supercritical CO_2 is increasingly used as an environmentally friendly solvent for cleaning applications, ranging from dry cleaning clothing to degreasing machine parts to photoresist stripping. A key advantage of CO_2 is the ease with which it is separated from “dirt” and detergents. When its temperature and pressure are reduced below the critical temperature and vapor pressure respectively, it vaporizes, leaving dissolved substances behind. For a change in state of CO_2 from 70°C and 150 bar to 20°C and 15 bar, estimate the changes in its molar enthalpy and entropy.

The Claperyron Equation

At saturation

$$\left(\frac{dP}{dT}\right) = \frac{h_2 - h_1}{T(v_2 - v_1)}$$

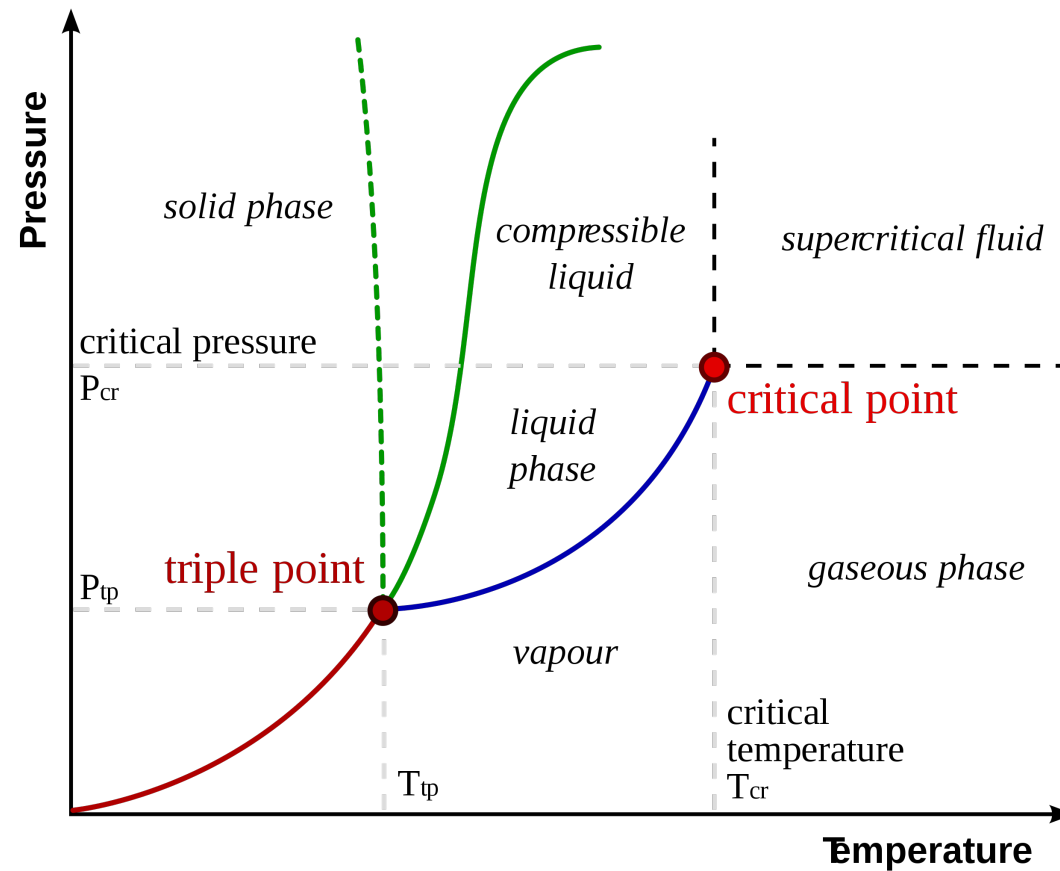
At low saturated pressure

$$\ln\left(\frac{P_2}{P_1}\right) \approx \frac{h_2 - h_1}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The Clapeyron-Clausius Equation

P-T relation at first-order phase transition

P-T Phase Diagram



Summary Points

- Thermodynamic potential
- Maxwell's relation
- Residual's properties
- The Claperyron equations