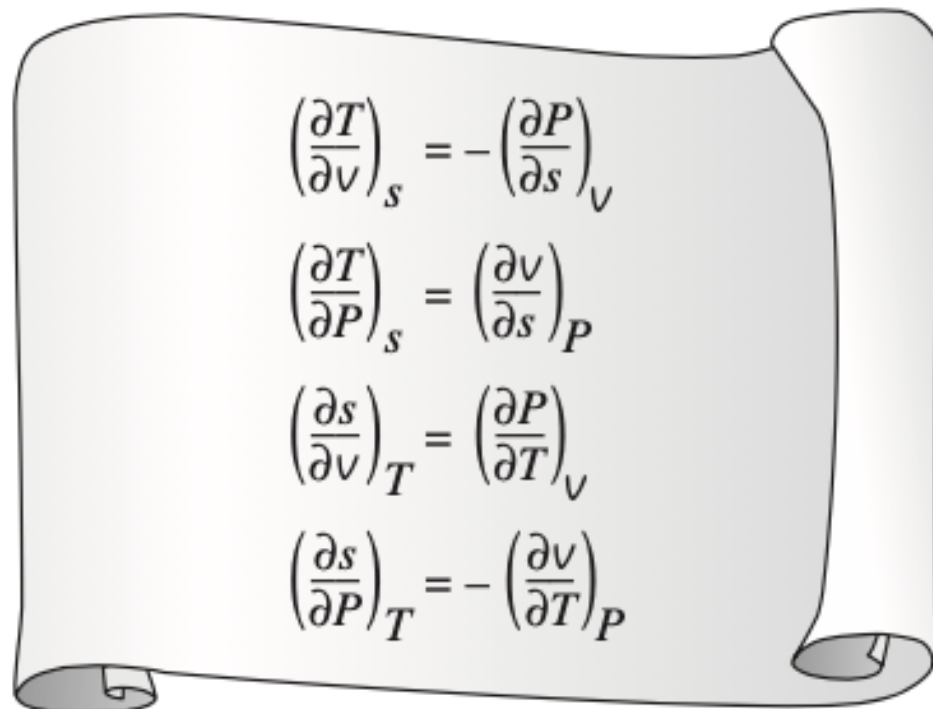


# Chemical Engineering Thermodynamics

## Lecture 4 Thermodynamic Properties

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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 right edge 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

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

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

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

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

$S, V, N$  are extensive parameters.

$T, P, \mu$  are intensive parameters.

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

# Legendre Transformation

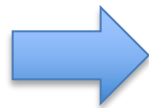
$$L : C[x] \rightarrow C[p]$$

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

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

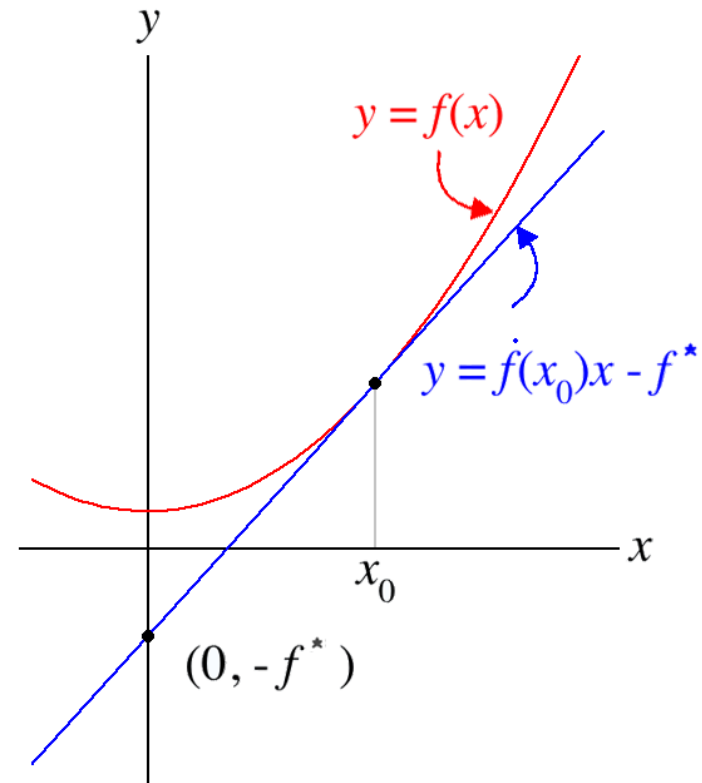
$$y = f(x)$$

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



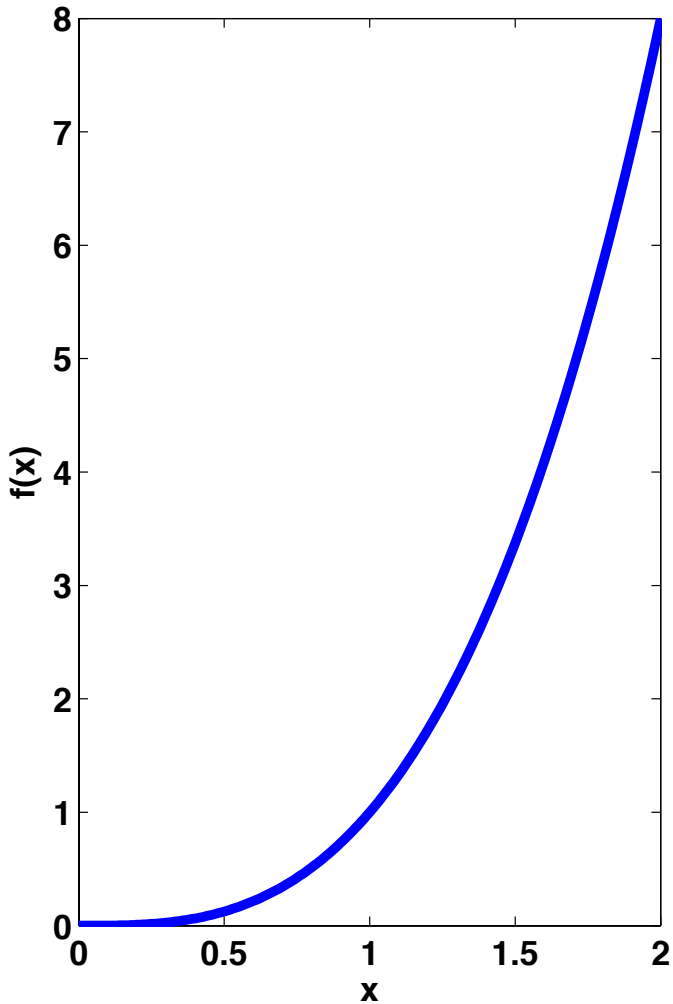
$$y = f^*(p)$$

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

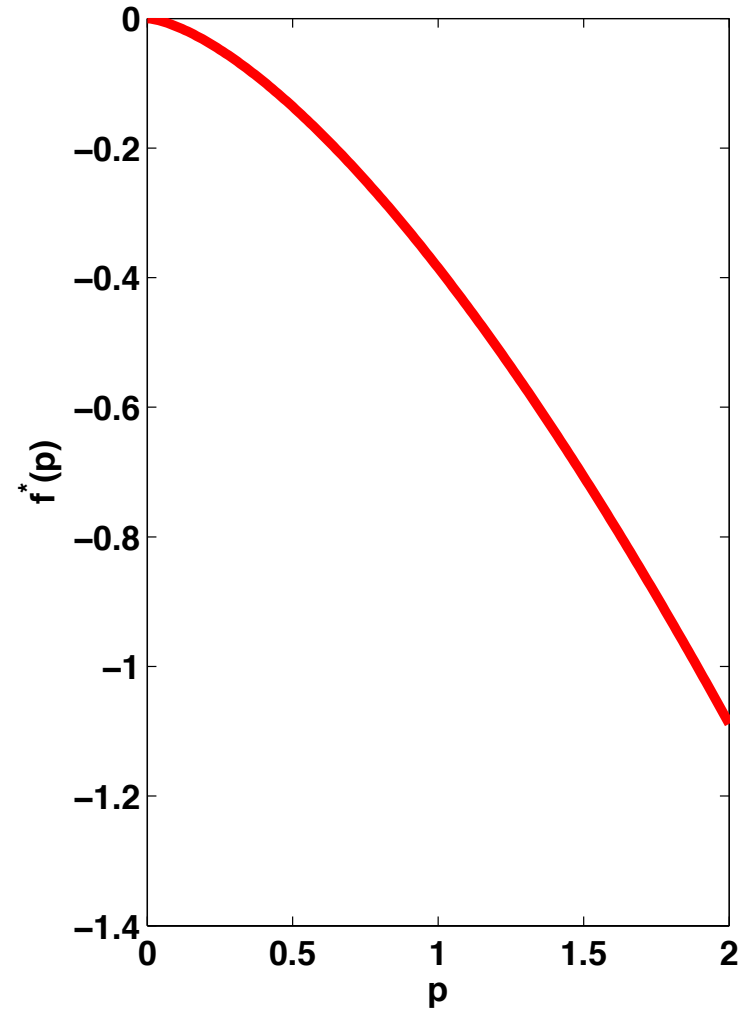


# Example

$$y = f(x)$$



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



# Thermodynamic Potential

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- The Legendre transformation of the internal energy.

# 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

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

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

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

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

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

# Some Formulas

For homogeneous system:  $G = \mu N$

For homogeneous system:  $\Omega = -PV$

$$\Omega = F - \mu N$$

$$\omega = f - \mu \rho$$

$$\mu = \frac{\partial F}{\partial N} = \frac{\partial f}{\partial \rho}$$

$$\text{At fixed } T, N: P = -\frac{\partial F}{\partial V} \Rightarrow F = -\int P dV$$

# Ideal Gas

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$$P = \rho kT$$

$$f = kT \rho \ln \rho$$

$$\mu = kT \ln \rho$$

# van der Waals Fluid

$$P = \frac{\rho kT}{1 - \rho b} - a\rho^2$$

$$f = kT\rho \ln \frac{\rho}{1 - b\rho} - a\rho^2$$

$$\mu = kT \left[ \ln \frac{\rho}{1 - b\rho} - \frac{1}{1 - b\rho} \right] - 2a\rho$$

# 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

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

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



# Evaluation 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

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

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

# Evaluation 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

- 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

- 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:  $\frac{S_n^R}{R} = \ln Z - T \int_0^{\rho_n} \left( \frac{\partial Z}{\partial T} \right)_{\rho_n} \frac{d\rho_n}{\rho_n} - \int_0^{\rho_n} (Z - 1) \frac{d\rho_n}{\rho_n}$

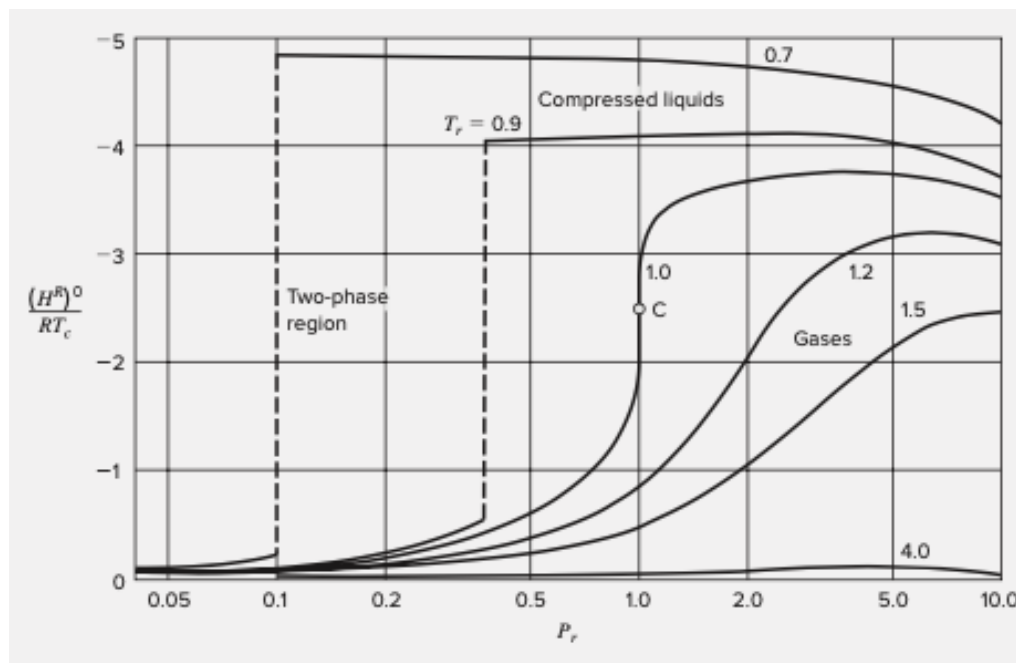
# Residual Properties in the Zero-Pressure Limit

- 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:  $\lim_{P \rightarrow 0} H_n^R = 0$

# Generalized Property Correlations for Gases

$$Z = Z^0 + \omega Z^1$$

- $H_n^R = (H_n^R)^0 + \omega(H_n^R)^1$
- $S_n^R = (S_n^R)^0 + \omega(S_n^R)^1$



$$P_r = \frac{P}{P_c}$$
$$T_r = \frac{T}{T_c}$$



# 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:

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

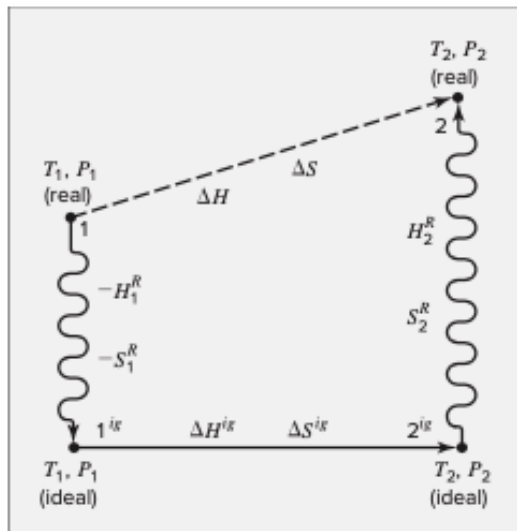
- **Step 1<sup>ig</sup>**  $\rightarrow 2^{ig}$ : Changes in the ideal-gas state from  $(T_1, P_1)$  to  $(T_2, P_2)$ . For this process,

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

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

- **Step 2<sup>ig</sup>**  $\rightarrow 2$ : 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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  from  $70^\circ\text{C}$  and 150 bar to  $20^\circ\text{C}$  and 15 bar, estimate the changes in its molar enthalpy and entropy.

# The Claperyron Equation

At saturation

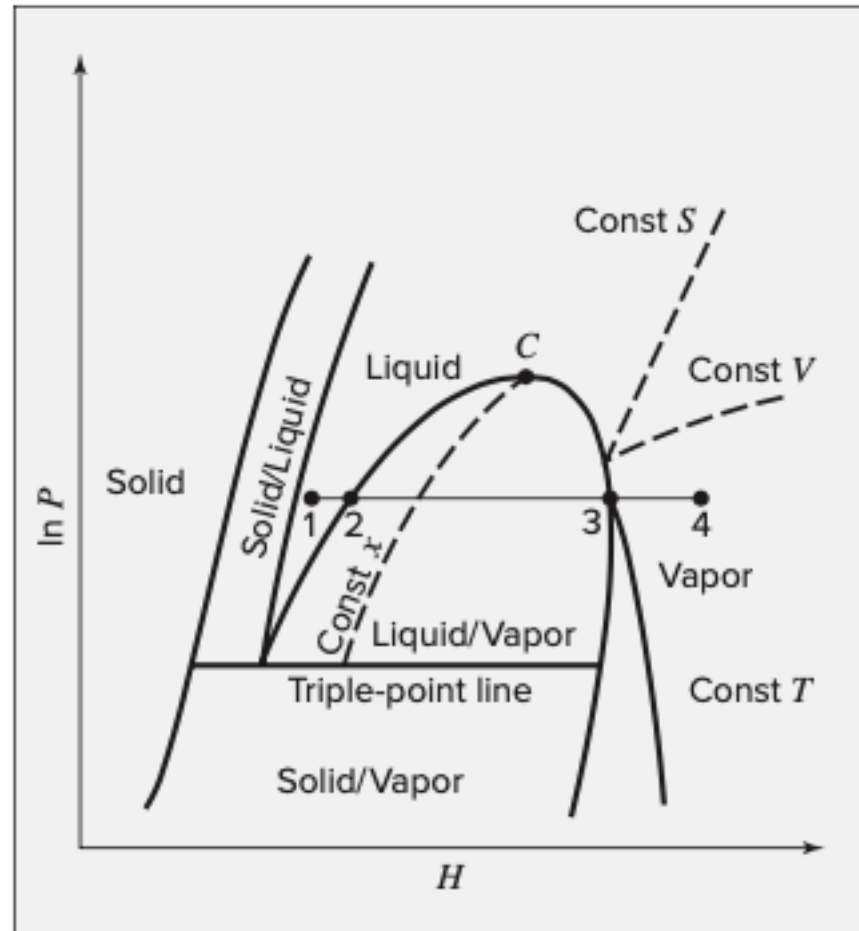
$$\left(\frac{dP}{dT}\right) = \frac{h_2 - h_1}{T(v_2 - v_1)}$$

At low saturated pressure

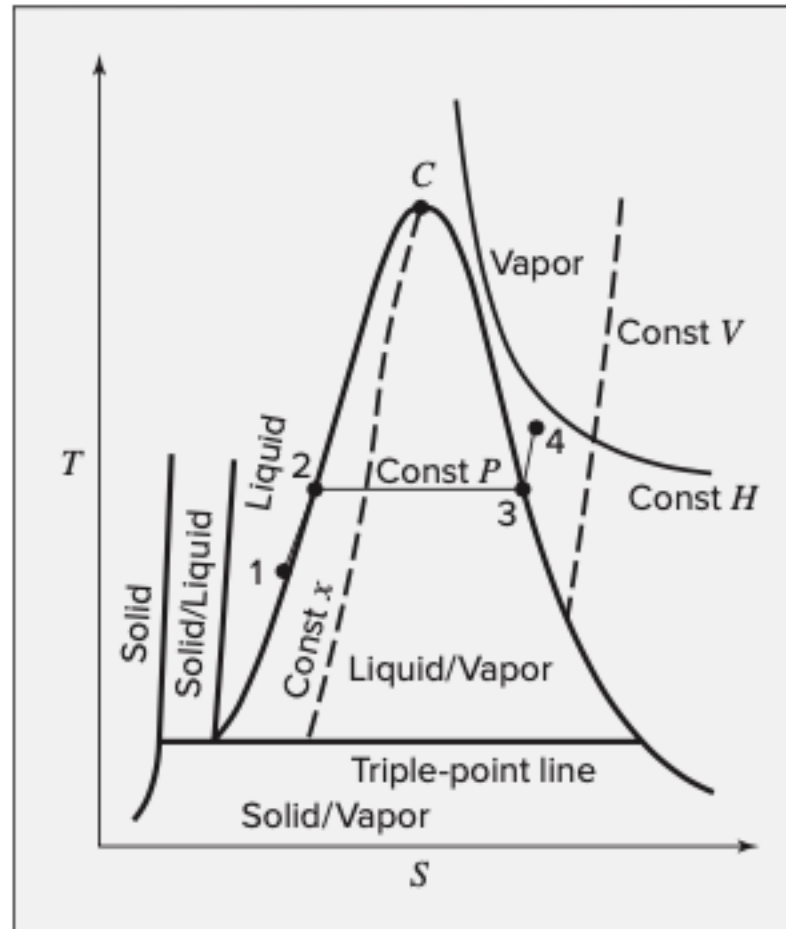
$$\ln\left(\frac{P_2}{P_1}\right) \approx \frac{h_2 - h_1}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The Clapeyron-Clausius Equation

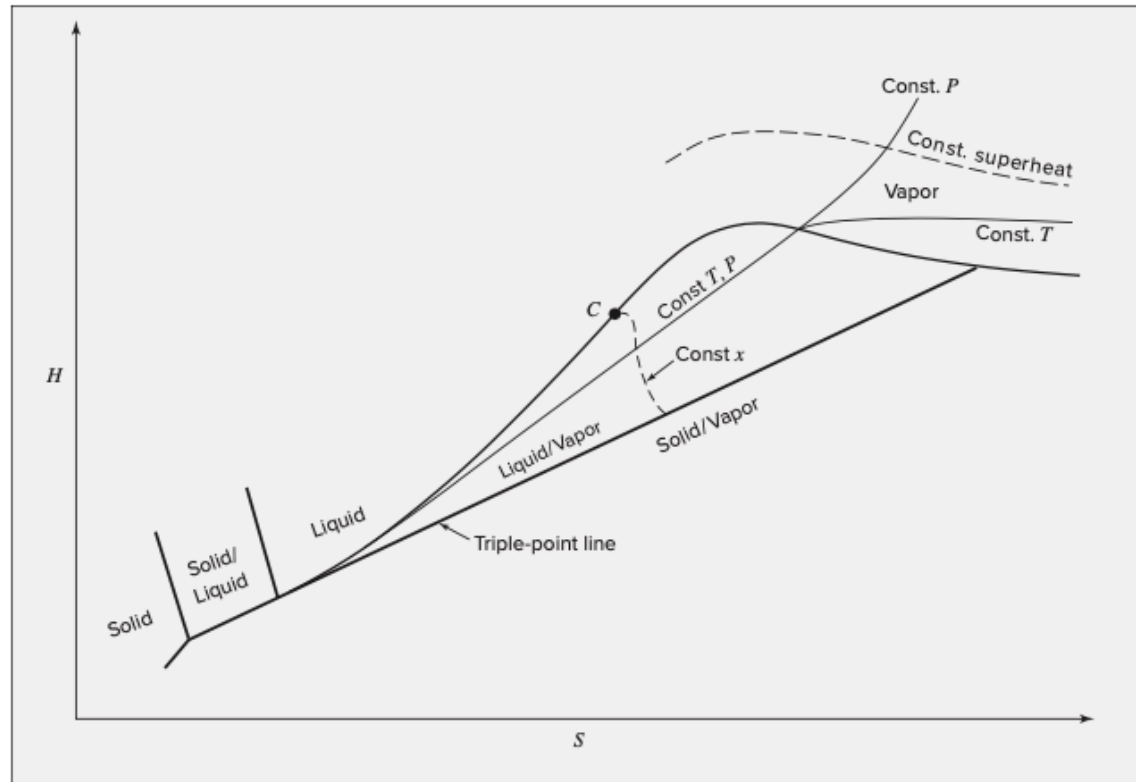
# PH Diagram



# TS Diagram



# HS Diagram



# Tables of Thermodynamic Properties

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- The interpolation is required to evaluate thermodynamic properties.

Superheated steam originally at  $P_1$  and  $T_1$  expands through a nozzle to an exhaust pressure  $P_2$ . Assuming the process is reversible and adiabatic, determine the downstream state of the steam and  $\Delta H$  for  $P_1 = 1000$  kPa,  $t_1 = 250^\circ\text{C}$ , and  $P_2 = 200$  kPa.