Sharif University of Technology

School of Mechanical Engineering

Center of Excellence in Energy Conversion

Advanced Thermodynamics

Lecture 22

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Generalized Properties

- Generalized Equations of State
  - Generalized compressibility factor chart
  - Generalized enthalpy chart
  - Generalized entropy chart
  - Generalized fugacity (pseudo pressure) chart
- Objectives: Real gas calculation
  - Pure real gas
  - Real gas mixtures
- Thermodynamics relations:

$$dU = T\,dS - P\,dV$$

$$dH = T\,dS + V\,dP$$

- If Z is a function of two independent parameters x and y:

$$Z = f(x,y) \rightarrow dZ = \underbrace{\left.\frac{\partial Z}{\partial x}\right|_y}_{M} dx + \underbrace{\left.\frac{\partial Z}{\partial y}\right|_x}_{N} dy \rightarrow dZ = M dx + N dy$$

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

Cyclic Relation: $\left(\frac{\partial Z}{\partial x}\right)_y \left(\frac{\partial y}{\partial Z}\right)_x \left(\frac{\partial x}{\partial y}\right)_Z = -1$

Reciprocal Relation: $\left(\frac{\partial y}{\partial x}\right)_Z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_Z}$

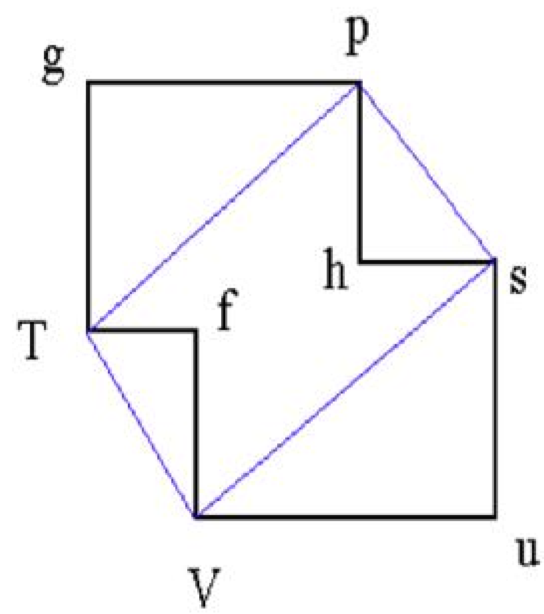
- The Maxwell relations may be represented as:

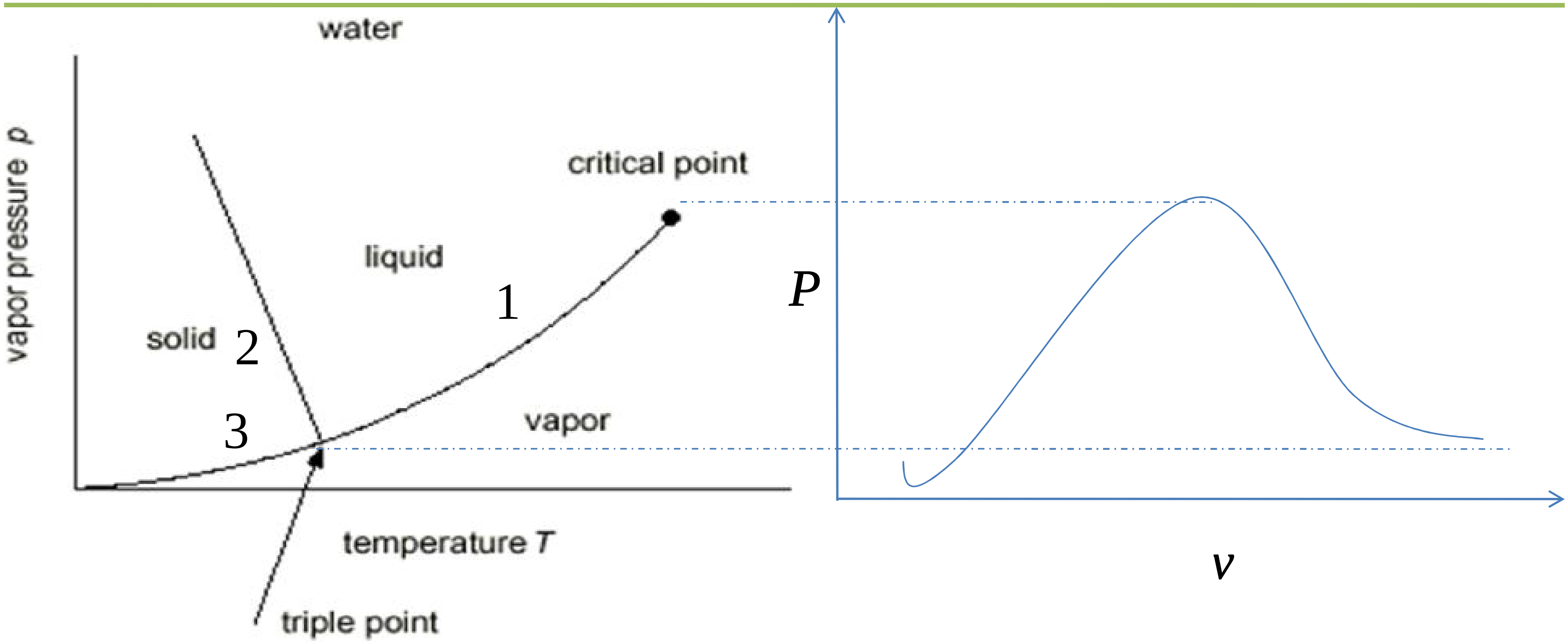
$$U = U[S, V] \Longrightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$H = H[S, p] \Longrightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$F = F[T, V] \Longrightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$G = G[T, p] \Longrightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

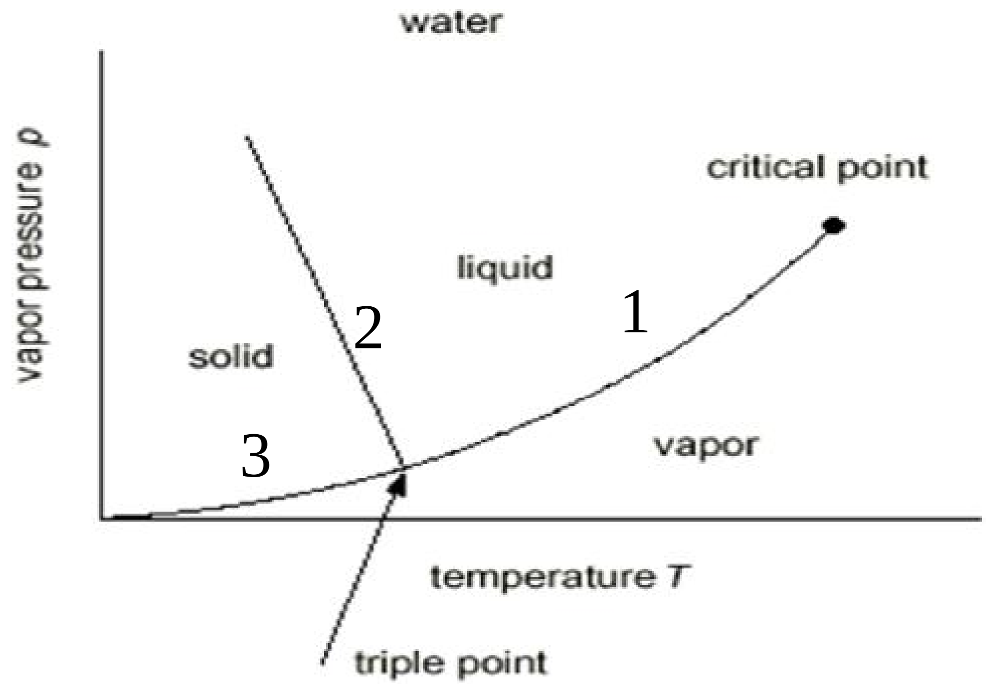




$$\left(\frac{dP}{dT}\right)_{sat.}=\frac{\Delta s}{\Delta v}=\frac{s_g-s_f}{v_g-v_f}\rightarrow\left(\frac{dP}{dT}\right)_{sat.}=\frac{h_{fg}}{T\left(v_g-v_f\right)}$$

- Assumptions: $v_g >> v_f$ and $v_g \approx \frac{RT}{P} \rightarrow \left(\frac{dP}{dT}\right)_{sat.}=\frac{Ph_{fg}}{RT^2}$

Tripple Point is like a bridge



- For line 1:

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{P_1}^{P_2} \frac{h_{fg}}{R} \frac{dT}{T^2} \rightarrow \ln\left(\frac{P_2}{P_1}\right) = \frac{h_{fg}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$ Clayperon Relation

- For line 2:

$$\frac{dP}{dT} = \frac{h_{if}}{T(v_f - v_i)}$$

- For line 3:

$$\frac{dP}{dT} = \frac{h_{ig}}{T(v_g - v_i)}$$

Generalized Enthalpy Chart …

$$h = f\,(T\,,\;P) \rightarrow dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP = c_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

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

$$\Rightarrow dh = c_P dT + \underbrace{\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]}_{\text{For ideal gas } = 0} dP$$

$$dh = dh_P + dh_T$$

$$dh_P = c_P dT +$$

$$dh_T = \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

Generalized Enthalpy Chart …

$$P_r = \frac{P}{P_C},\ v_r = \frac{v}{v_C},\ \text{and } T_r = \frac{T}{T_C}$$

$$P_r v_r = ZRT_r$$

$$dh_T = \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP$$

$$\rightarrow dh_{Tr} = -\frac{RT_r^{\,2} T_C^{\,2}}{P_r P_C}\left(\frac{\partial Z}{\partial (T_r T_C)}\right)_{P_r} P_C dP_r$$

$$\Rightarrow \frac{dh_{Tr}}{RT_C} = -\frac{T_r^{\,2}}{P_r}\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} dP_r$$

$$\int_{h^*}^{h} \frac{dh_{Tr}}{RT_C} = -\int_{P^*}^{P_r} \frac{T_r^{\,2}}{P_r}\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} dP_r$$

- * is a ideal state

Generalized Enthalpy Chart …