Thermodynamics Properties

- **Property**
  - any characteristic of a system which can be quantitatively evaluated and which is related to energy of system
  - examples: \( m, V, E, p, T, S, H, ... \)

- **Independent Properties**
  - Question: How many intensive properties does it take to define a unique state for a known substance?
  - Answer: Two - for simple compressible substances
    - useful work done only by compression/expansion; no E&M fields, no liquid surface tension,...
  - So if you know two properties, can predict the rest

State Equations

- Relate TD properties
  - e.g., \( Y = Y(T, p) \)

- **Examples**
  - Gibbs equation (from 1\textsuperscript{st} and 2\textsuperscript{nd} Laws)
    \[
    ds = \frac{de}{T} + \frac{p}{T} \, dv \quad \text{(II.5)}
    \]
  - caloric equations of state
    \[
    h = h(T, \rho)
    \]
    \[
    e = e(T, \rho)
    \]

- **Simplify by restricting ourselves to perfect gases**
  - obey **Perfect Gas** relation
    \[
    p = \rho RT
    \]
    \[
    \text{or}\quad pv = RT \quad \text{(II.6)}
    \]
Perfect (Ideal) Gases

• Thermal (virial) state equation
  
  \[ p = \rho RT = \frac{\rho R}{M}T; \quad \overline{R} = 8.3143 \text{J/mol} \cdot \text{K} = 8.3143 \text{kJ/kmol} \cdot \text{K} \]
  
  \[ = 1.9855 \text{cal/mol} \cdot \text{K} = 1545.3 \text{ft} \cdot \text{lb} \cdot \text{s}^2/\text{lb mol} \cdot \text{ft} \]

• “Energy” state equations (Specific Heats)

  \[ \gamma \equiv \frac{c_p}{c_v} = \frac{v}{R} = \frac{1}{1 - \frac{R}{c_p}} \]

  \[ = \frac{c_p}{R} = \frac{c_p}{c_v} \]

  \[ \gamma \equiv \frac{c_p}{c_v} = 1 + \frac{\gamma - 1}{c_p} \]

  \[ \overbrace{\gamma}^{\text{bar means per mole}} \]

  \[ \gamma_{\text{atom}} = \frac{5}{3}; \quad \gamma_{\text{diatom}} = \frac{7}{5} \rightarrow \frac{9}{7}; \quad \gamma_{\text{poly}} = \frac{7}{5} \rightarrow 1; \quad \text{Temperature (K)} \]

Perfect Gas – Entropic State Eq’n.

• Gibbs Eq.  \[ Tds = de + pdv = de + pdv + (vdp - vdp) \]

  \[ = de + \frac{d(pv)}{\gamma} - vdp \]

  \[ = dh - vdp \]

  \[ ds = dh \frac{v}{T} \frac{dp}{\gamma} \]

  \[ = \frac{c_p(T)TdT}{R} \frac{dp}{p} \quad \text{for a P.G.,} \quad dh = c_p dT \]

  \[ p\nu = RT \]

  From state 1 to state 2

  \[ \int_{s_1}^{s_2} ds = s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p(T)TdT}{R} \frac{dp}{p} = \int_{T_1}^{T_2} \frac{c_p(T)TdT}{R} \frac{dp}{p} - R \ln \frac{p_2}{p_1} \]

  \[ s_2 - s_1 = \left[ \phi(T_2) - \phi(T_1) \right] - R \ln \left( \frac{p_2}{p_1} \right) \]

  \[ \text{fn of T only} \quad \text{fn of p only} \]
\textbf{p-T-s State Equation}

\[ s_2 - s_1 = \Delta s_{12} = \left[ \Delta \phi_{12} \right] - R \ln \left( \frac{p_2}{p_1} \right) = \frac{\int_{T_1}^{T_2} c_p(T) \, dT}{T_1} - R \ln \left( \frac{p_2}{p_1} \right) \]

Cal. Perf. \[ \Delta s_{12} = c_p \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{p_2}{p_1} \right) \] (II.9)

- **Pressure ratio**

  \[ \frac{p_2}{p_1} = e^{(\Delta s_{12})/R} \]

  \[ \frac{p_2}{p_1} = \left( \frac{T_2}{T_1} \right)^{c_p/R} e^{-\Delta s_{12}/R} \]

  \[ \frac{p_2}{p_1} = \left( \frac{T_2}{T_1} \right)^{c_p/R} \]

  \[ \Delta s_{12} = \gamma - 1 \]

  (II.10)

  must be absolute \( p, T \)

\textbf{State Diagrams}

- Useful to be able to visualize/graph state relationships

  - in engine (cycle) analysis, \( T-s \) an important diagram

  \[ T \text{ds} = c_p \text{dT} - v \text{dp} \]

  \[ dT = \left( \frac{T}{c_p} \right) ds + \left( \frac{v}{c_p} \right) dp \]

  \[ \begin{align*}
  \frac{\partial T}{\partial s} & = \frac{\partial T}{\partial p} \\
  ds & + \frac{\partial T}{\partial p} \, dp \\
  >0 & \text{ w/ } T \uparrow \quad >0
  \end{align*} \]

  \( s \uparrow \) for \( T \uparrow \)

  @ constant \( p \)

  \( T \uparrow \) for \( p \uparrow \)

  @ constant \( s \)