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)
    \[ ds = \left( \frac{de}{T} + \frac{p}{T} \right) dv \]
  – caloric equations of state
    \[ h = h(T, \rho) \]
    \[ e = e(T, \rho) \]

• Simplify by restricting ourselves to perfect gases
  – obey **Perfect Gas** relation
    \[ p = \rho RT \]
    or
    \[ pv = RT \]
Perfect (Ideal) Gases

• Thermal (virial) state equation

\[ p = \rho RT = \rho \frac{\bar{R}}{M} T; \quad \bar{R} = 8.3143 \text{ J/mol} \cdot \text{K} = 8.3143 \text{ kJ/kmol} \cdot \text{K} = 1.9858 \text{ cal/mol} \cdot \text{K} = 1545.3 \text{ ft} \cdot \text{lb}_f / \text{lbmol} \cdot \text{R} \]

• “Energy” state equations (Specific Heats)

\[ c_v \equiv \frac{de}{dT}; \quad c_p \equiv \frac{dh}{dT}; \quad c_p - c_v = R \]

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

\[ \Rightarrow \frac{c_p}{R} \left( \frac{\bar{c}_p}{\bar{R}} \right) = \frac{\gamma}{\gamma - 1} \]

bar means per mole

\[ \gamma_{\text{atom}} = 5/3; \quad \gamma_{\text{diatom}} = 7/5 \rightarrow 9/7; \quad \gamma_{\text{poly}} = 8/6 \rightarrow 1; \]
Perfect Gas – Entropic State Eq’n.

• Gibbs Eq.  \( T ds = de + pdv \)
  \( = de + pdv + (vd\rho - vd\rho) \)
  \( = de + d(pv) - vd\rho \)
  \( = dh - vd\rho \)

\[ ds = \frac{dh}{T} - \frac{v}{T} d\rho \]

for a P.G.,
\[ dh = c_p dT \quad pv = RT \]

From state 1 to state 2
\[ \int_{s_1}^{s_2} ds = s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p(T)dT}{T} - R \int_{p_1}^{p_2} \frac{d\rho}{\rho} = \int_{T_1}^{T_2} \frac{c_p(T)dT}{T} - R \ln \frac{p_2}{p_1} \]

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

\( \text{fn of } T \text{ only} \quad \text{fn of } p \text{ only} \)
**p-T-s State Equation**

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

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

- **Pressure ratio**
  
  **General**
  \[
  \frac{p_2}{p_1} = e^{(\Delta \phi_{12} - \Delta s_{12})/R}
  \]

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

  - if isentropic \((\Delta s_{12}=0)\)
  \[
  \frac{p_2}{p_1} = e^{\Delta \phi_{12}/R}
  \]

  \[
  \frac{p_2}{p_1} = \left(\frac{T_2}{T_1}\right)^{c_p/R} = \frac{\gamma}{\gamma - 1}
  \]

  must be absolute \(p,T\)
State Diagrams

- Useful to be able to visualize/graph state relationships
  - in engine (cycle) analysis, $T$-$s$ an important diagram

\[
\begin{align*}
T ds &= c_p dT - v dp \\
dT &= \left( \frac{T}{c_p} \right) ds + \left( \frac{v}{c_p} \right) dp \\
&= \left. \frac{\partial T}{\partial s} \right|_p ds + \left. \frac{\partial T}{\partial p} \right|_s dp
\end{align*}
\]