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 1st and 2nd Laws) \[ ds = \frac{de}{T} + \frac{p}{T} dv \]
  – 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
  \[ p = \rho RT = \frac{\rho}{M}RT; \quad \overline{R} = 8.3143 \text{ J/mol} \cdot \text{K} = 8.3143 \text{ kJ/mol} \cdot \text{K} \]
  \[ = 1.9858 \text{ cal/mol} \cdot \text{K} = 1545.3 \text{ ft} \cdot \text{lb} / \text{lbmol} \cdot \text{R} \]

- “Energy” state equations (Specific Heats)
  \[ c_v \equiv \frac{de}{dT}; \quad c_p \equiv \frac{dh}{dT}; \quad c_p - c_v = R \]
  \[ \gamma = \frac{c_p}{c_v} = \frac{1}{1 - R/c_p} \]
  \[ \Rightarrow \frac{c_p}{R} = \left( \frac{\overline{c}_p}{\overline{R}} \right) = \frac{\gamma}{\gamma - 1} \]

bar means per mole

\[ \gamma_{\text{atom}} = 5/3; \quad \gamma_{\text{diatom}} = 7/5 \rightarrow 9/7; \quad \gamma_{\text{poly}} = 8/6 \rightarrow 1; \]

\[ \text{Temperature (K)} \]

Perfect Gas – Entropic State Eq’n.

- Gibbs Eq.
  \[ Tds = de + pdv = de + pdv + (vdp - vdp) \]
  \[ = de + d(pv) - vdp \]
  \[ = dh - vdp \]
  \[ ds = dh - \frac{v}{T} dp \]
  \[ = \frac{c_p(T) dT}{T} - \frac{R dp}{p} \]
  \[ \text{for a P.G.} \]
  \[ dh = c_p(T) dT \]
  \[ dT = R \ln \frac{p_2}{p_1} \]

From state 1 to state 2

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

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

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

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

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**

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

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

- if isentropic \((\Delta s_{12}=0)\)

\[ \frac{p_2}{p_1} = e^{\Delta \Phi_{12}/R} \]

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

\[ \gamma = \frac{y}{y-1} \]

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

\[ T \, ds = c_p \, dT - v \, dp \]

\[ dT = \left(T/c_p\right) ds + \left(v/c_p\right) dp \]

\[ = \frac{\partial T}{\partial s} \left|_p \right. \, ds + \left. \frac{\partial T}{\partial p}\right|_s \, dp \]