1. Joule-Thomson Expansion

- For a substance flowing adiabatically through a throttle (valve or porous plug):
  \[ P_{\text{in}} > P_{\text{out}} \]
  and negligible change in kinetic and potential energy,
  \[ \Delta h = q_{\text{in}} - w_{\text{b,y}} = 0 \rightarrow \text{isenthalpic} \]
- Points of interest: given \( P_{\text{in}}, T_{\text{in}} \) and \( P_{\text{out}} \), what is \( T_{\text{out}} \) and/or phase condition?
- If fluid is an ideal gas, \( T_{\text{out}} = T_{\text{in}} \): no cooling or heating will occur
  \( \rightarrow \) Joule-Thomson expansion effects are due to real gas behavior
- can characterize the effect using the “Joule-Thomson Coefficient”, \( \mu_{JT} \)
  \[ \mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_h \]

- Q: If we want temperature to decrease as the fluid goes through the adiabatic throttle, do we want \( \mu_{JT} > 0 \) or \( \mu_{JT} < 0 \)?

- Values of \( \mu_{JT} \) could be found from laboratory data/studies. Alternatively, could use thermodynamic estimation:
  \[ dh = c_p dT + \left( v - \left( \frac{\partial v}{\partial T} \right)_p \right) dP \]
  \[ \left( \frac{\partial T}{\partial P} \right)_h = \frac{\left( \frac{\partial v}{\partial T} \right)_p - v}{c_p^{\text{real}}} = \frac{c_p^{\text{id gas}} - \int_{P_{\text{ideal}}}^P \left[ \frac{\partial^2 v}{\partial T^2} \right] dP}{c_p^{\text{ideal}}} \]
- Since \( c_p^{\text{real}} \) is quite complicated to evaluate using cubic EOS (e.g. Van der Waals, Peng Robinson, etc.), a more tractable alternative is to use the virial EOS based on pressure expansion (see example 5.9, pp.300-301)
- **Main application**: refrigeration and gas liquefaction
- Joule-Thomson Inversion Curves


Note: equation 5 referred to in Figure 2 is given by:

\[ P_r = 24.21 - \left( \frac{18.54}{T_r} \right) - 0.825 \left( T_r \right)^2 \]

- Two competing molecular activity:

  a) \( \mu_J T > 0 \). When molecular attraction dominates, expansion increases potential energy and kinetic energy decreases \( \Rightarrow \) decrease in temperature

  b) \( \mu_J T < 0 \). When molecular repulsion dominates, expansion decreases potential energy and kinetic energy increases \( \Rightarrow \) increase in temperature

- The inversion curve is when \( \mu_J T = 0 \). For a given pressure, the temperature where \( \mu_J T = 0 \) is known as the Boyle temperature, i.e. \( T_{Boyle} = \left[ T(P) \right]_{\mu_J T=0} \)

- Inside the dome is where \( \mu_J T > 0 \). Note: this dome is not a vapor-liquid dome!
2. Gas Liquefaction

- Basic units:
  
a) Compressor: this will increase the pressure to desired condition of the throttle (but temperature will increase)
  
b) Cooler: reduces temperature before throttle process

  \[ \text{Compression+cooling must move the condition to be inside the JT-inversion dome.} \]

c) Throttle: Joule-Thomson (isenthalpic) expansion \( \rightarrow \) gas has cooled significantly to attain partial liquefaction
  
d) Separator: extract the liquefied product

Draw the gas liquefaction diagram:

- Improvements (Linde process):

  a) Use cold vapor from the separator and cool the gas before it enters the throttle
  
b) After the heat exchanger, mix with gas feed
Example 5.10 (page 302)

Given: \( N_2 \), enters throttle at \( T_{\text{in}} = -122^\circ C \) and \( P_{\text{in}} = 100 \text{ bar} \).

exits at \( P_{\text{out}} = 1 \text{ bar} \).

Data: \( T_c = 126.2K \), \( P_c = 33.8 \text{ bar} \), \( \omega = 0.039 \)

Required: percentage liquefaction (if any)

Solution: use departure functions instead

\[
\Delta h = \int_{T_{\text{in}}}^{T_{\text{out}}} c_p \text{ideal} \, dT + \left[ \Delta h_{\text{out},P_{\text{out}}}^{\text{dep}} - \Delta h_{T_{\text{in}},P_{\text{in}}}^{\text{dep}} \right]
\]

Assuming outlet is a vapor-liquid mixture, can use Antoine equation:

\[
\ln(P_{\text{out}}) = 8.334 - \frac{588.72}{T_{\text{out}} - 6.60} \to T_{\text{out}} = 77.15K
\]

\[
\int_{T_{\text{in}}}^{T_{\text{out}}} c_p \text{ideal} \, dT = -2270 \frac{J}{mol}
\]

At the inlet: \( T_{r,\text{in}} = 1.20 \) and \( P_{r,\text{in}} = 2.96 \)

\[
\Delta h_{T_{\text{in}},P_{\text{in}}}^{\text{dep}} = RT_c \left( -2.807 + (0.039)(-0.934) \right) = -2983 \frac{J}{mol}
\]

Since the process is isenthalpic, \( \Delta h = 0 \)

\[
0 = -2270 \frac{J}{mol} + \left[ \Delta h_{T_{\text{out}},P_{\text{out}}}^{\text{dep}} + 2983 \frac{J}{mol} \right]
\]

\[
\frac{\Delta h_{T_{\text{out}},P_{\text{out}}}^{\text{dep}}}{RT_c} = \frac{-713}{(8.314)(126.2)} = -0.683
\]

From departure plots, at \( P_{r,\text{out}} = 0.03 \)

\[
\Delta h_{T_{\text{out}},P_{\text{out}}}^{\text{dep}}(\text{vap}) = -0.1
\]

\[
\Delta h_{T_{\text{out}},P_{\text{out}}}^{\text{dep}}(\text{liq}) = -5.1 + (0.039)(-7.5) = -5.7
\]

\[
x(-0.1) + (1 - x)(-5.7) = -0.683
\]

\[
x = 0.9
\]

\to per cent liquefaction: 10%
Some notable features of Figure 1:

- Isenthalpic lines appear flat when $P < 2 \text{ bars}$ → ideal gas behavior, i.e. isenthalpic implies isothermal

- Downward slopes in the T-s diagram locates the positive Joule-Thomson coefficients (pressure decreases as entropy increases along the isenthalpic curves)

- Just operating in the region where $\mu_{JT} > 0$ is not sufficient for liquefaction → still needs the initial condition to be chosen such that the isenthalpic expansion path will enter the vapor-liquid dome while exiting to the outlet pressure