1. The Joule-Thomson coefficient represents how the temperature of a gas changes under an isenthalpic (constant enthalpy) expansion. It is defined as $\mu_{\mathrm{JT}} \equiv \left(\frac{\partial T}{\partial P}\right)_H$

   (a) Starting from a total differential of enthalpy $H(T, P)$, derive this equivalent form:

$$\mu_{\mathrm{JT}} \equiv \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

Set total differential to 0 for constant enthalpy:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

Using $C_P = \left(\frac{\partial H}{\partial T}\right)_P$:

$$C_P\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

$$dT = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T}$$

   (b) Derive the same expression, but use a triple product rule.

Using the triple product rule:

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_P = -1$$

Substitute $C_P = \left(\frac{\partial H}{\partial T}\right)_P$:

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial H}\right)_T C_P = -1$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T}$$

2. A real gas obeys an equation of state:

$$V = \frac{RT}{P} + b$$

Given $b = 0.02\,\mathrm{L/mol}$, use Joule–Thompson to determine whether the gas cools or heats during an isenthalpic expansion. You can use your result from Activity 21 Problem 1.

$$\mu_{\mathrm{JT}} \equiv \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

From Activity 21:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

Evaluate derivative: $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

Substituting back in:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{RT}{P} + b\right) - T\left(\frac{R}{P}\right) = b > 0$$

$$\mu_{\mathrm{JT}} = -\frac{b}{C_P} \implies \mu_{\mathrm{JT}} \equiv \left(\frac{\partial T}{\partial P}\right)_H < 0$$

During expansion $dP < 0 \implies dT > 0$, so temperature increases

3. Show that the Joule-Thompson coefficient can be written as:

$$\mu_{\mathrm{JT}} \equiv -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

Use definition of enthalpy $H = U + PV$ and take partial $\left(\frac{\partial}{\partial P}\right)_T$:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T$$

Apply chain rule for first term:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T$$

Substituting yields desired result:

$$\mu_{\mathrm{JT}} = -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

Key idea: Just because partials does not mean Maxwell, chain rule when same variable is held constant

Homework Problem 22

1. Starting from the first law, show that:

$$T\,dS = c_V\,dT + \left(\left(\frac{\partial U}{\partial V} \right)_T + P \right) dV$$