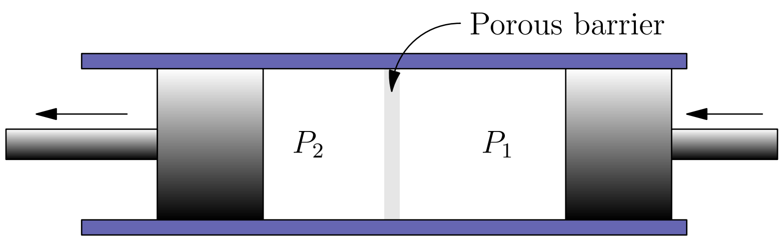
J02T.1—Joule-Thomson Process

Problem

A thermally isolated vessel containing a non-ideal gas is separated in two parts by a porous barrier. Initially all of the gas is on one side of the barrier and occupies a volume V. The gas is transferred slowly through the barrier by moving two pistons inward and outward, while keeping the pressures P_1 and P_2 fixed on both sides of the barrier. This is called a Joule-Thomson process. For an ideal gas the temperatures T_1 and T_2 before and after the process are the same. For a non-ideal gas there will be a small difference $\Delta T = T_2 - T_1$. The problem is to determine ΔT for a non-ideal gas described by the van der Waals equation of state

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$



In this problem we assume that the pressure difference is small, so that after the process the volume has increased only by a small amount $\Delta V = V_2 - V_1$.

a) Calculate the free energy $F(V, T)$ for a van der Waals gas with total specific heat C_V.

b) Show that the enthalpy $H \equiv U + PV$ is constant for a Joule-Thomson process.

Hint: Argue that

$$\Delta T = \left(\frac{\partial T}{\partial V}\right)_H \Delta V.$$

c) Find the enthalpy H for a van der Waals gas as a function of V and T.

d) Show that ΔT is positive for high temperature and negative at low temperatures. The temperature T_{inv} at which ΔT changes sign is called the inversion temperature. Derive that

$$T_{\text{inv}} = \frac{2a}{bR}\left(1 - \frac{b}{V}\right)^2.$$