

Joule Thomson Expansion

Several times, we have noted that the free adiabatic expansion of an ideal gas does not result in a change of temperature; this is because the energy depends only on the temperature and not on the volume, so if the internal energy is unchanged, so is the temperature. This is not true for a real gas though. In general a free expansion will result in cooling as internal work is done against the forces of attraction between the molecules. More formally

$$\left(\frac{\partial T}{\partial V}\right)_E = -\left(\frac{\partial E}{\partial V}\right)_T / \left(\frac{\partial E}{\partial T}\right)_V = -\frac{1}{C_V} \left(T \left(\frac{\partial P}{\partial T}\right)_V - P\right)$$

where we have used the FTR and a Maxwell relation in the last step. For an ideal gas this is zero, but for a van der Waal gas, it gives

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{1}{c_v} \frac{a}{V^2} < 0.$$

Something like this can be used to cool gases to low temperatures, but the process is a little more complicated. For practical purposes we want a continuous flow of coolant which passes through a throttle from a region of higher to lower pressure. If we consider a certain

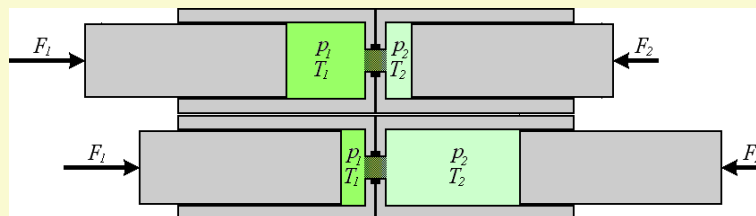


Figure 1: Schematic diagram of the throttling process, considering a certain mass of gas.

amount of gas, starting at (V_1, P_1, T_1) and ending after passing through the throttle at (V_2, P_2, T_2) , with no heat flow, the energy change is due only to the work done by the pressures on either side, so

$$E_2 - E_1 = P_1 V_1 - P_2 V_2 \quad \Rightarrow \quad H_1 = H_2$$

In other words, the continuous-flow throttling process is isenthalpic (constant enthalpy). Now the rate of change of temperature with pressure, which should be positive if cooling is to occur as the pressure falls, is

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

This can be positive or negative, as can be seen from the lines of constant enthalpy on the plot above. The line on which the slope

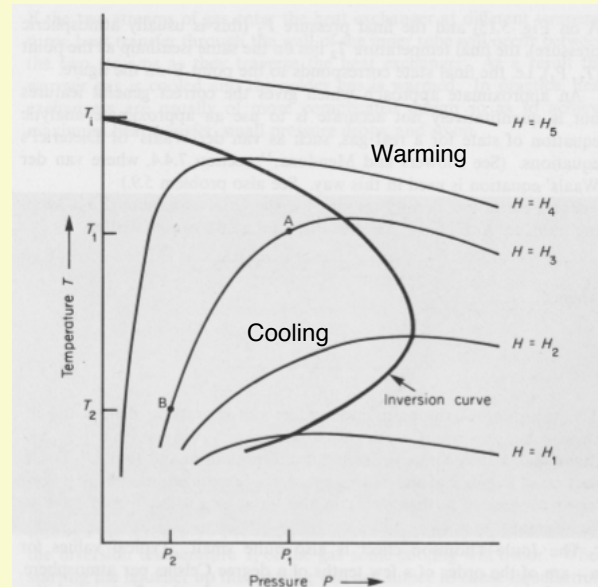


Figure 2: Isenthals and the inversion curve for a typical gas. Figure taken from Mandl

vanishes is called the inversion curve, and cooling will only take place if we start at temperatures and pressures to the left of it. The inversion curve intersects the T axis at a temperature T_i above which no cooling can occur, so pre-cooling may be necessary e.g. for hydrogen. In the plot, if we start at point A and lower the pressure, we can end up at the cooler, lower-pressure point B.

This effect, with recycling of the cooled gas to obtain further cooling, was pioneered by James Joule and William Thomson (later Lord Kelvin) in Salford in 1852, and formed the basis for the first successful liquefaction of oxygen and carbon monoxide in 1877 by Louis Cailletet. See an interesting discussion by [“Carnocycle”](#).