

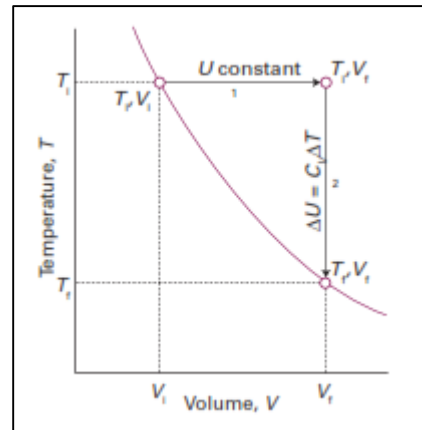
**Adiabatic changes**

We are now equipped to deal with the changes that occur when a perfect gas expands adiabatically. A decrease in temperature should be expected: because work is done but no heat enters the system, the internal energy falls, and therefore the temperature of the working gas also falls. In molecular terms, the kinetic energy of the molecules falls as work is done, so their average speed decreases, and hence the temperature falls.

$$W_{ad} = dU$$

Because the expansion is adiabatic, we know that  $q = 0$

$$W_{ad} = C_V dT$$



That is, the work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states. That is exactly what we expect on molecular grounds, because the mean kinetic energy is proportional to  $T$ .

$$C_V dT = -PdV$$

$$C_V dT = -\frac{RT}{V}dV$$

$$C_V \frac{dT}{T} = -R \frac{dV}{V}$$

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$\left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_1}{V_2}\right)^R$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V}$$

Since

$$\frac{R}{C_V} = \frac{C_P - C_V}{C_V} = \gamma - 1$$

then

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}} = \frac{V_1}{V_2}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

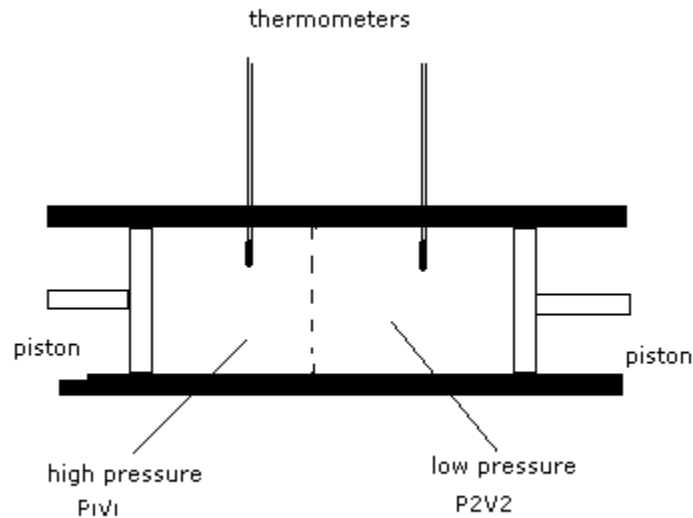
EX) Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25°C, from 0.50 dm<sup>3</sup> to 1.00 dm<sup>3</sup>. The molar heat capacity of argon at constant volume is 12.48 J mol<sup>-1</sup> K<sup>-1</sup>.

Q) When a sample of argon (for which  $\gamma = 5/3$ ) at 100 kPa expands reversibly and adiabatically to twice its initial volume, the final pressure will be?

Q) Calculate the final pressure of a sample of water vapour that expand Reversibly and adiabatically from 87.3 Torr and 500 cm<sup>3</sup> to a final volume of 3.0 dm<sup>3</sup>. Take  $\gamma = 1.3$ .

### Joule-Thomson Effect

The Joule-Thomson (JT) effect is a thermodynamic process that occurs when a fluid expands from high pressure to low pressure at constant enthalpy (an isenthalpic process). Such a process can be approximated in the real world by expanding a fluid from high pressure to low pressure across a valve. Under the right conditions, this can cause cooling of the fluid.



This effect was first observed in an experiment conducted by James Joule and Thomson in 1852 in which they flowed high pressure air through a small porous plug causing the pressure to drop. Joule and Thomson noted that the air was cooled by this procedure (which is a good approximation of an isenthalpic process (process done at constant enthalpy)).

$$H_f = H_i$$

H.W) provide that  $H_f = H_i$  in The Joule–Thomson experiment

An important property of a given gas is its Joule-Thomson coefficient. These coefficients are important from two standpoints;

(i) Intermolecular interaction, and (ii) liquefaction of gases.

The Joule-Thomson coefficient for gas,  $\mu$  is defined by the following equation:

$$\mu_T = \left( \frac{\partial T}{\partial P} \right)_H$$

For all gases (except helium and hydrogen) at 298 K and moderate pressures  $\mu_T > 0$ . At room temperature and ambient pressure,  $\mu$  is  $0.002 \text{ K Pa}^{-1}$  for nitrogen and  $0.025 \text{ K Pa}^{-1}$  for 2,2-dimethylpropane.

EX) A vapor at 22 atm and  $5^\circ\text{C}$  was allowed to expand adiabatically to a final pressure of 1.00 atm; the temperature fell by 10 K. Calculate the Joule-Thomson coefficient,  $\mu$ , at  $5^\circ\text{C}$ , assuming it remains constant over this temperature range.

$$\mu_T = \left( \frac{\partial T}{\partial P} \right)_H = \frac{\Delta T}{\Delta P} = \frac{-10\text{K}}{(1.00 - 22)\text{atm}} = 0.48\text{K atm}^{-1}$$

H.W) when a certain freon used in refrigeration was expanded adiabatically from an initial pressure of 32 atm and  $0^\circ\text{C}$  to a final pressure of 1.00 atm, the temperature fell by 22 K. Calculate the Joule-Thomson coefficient,  $\mu_T$ , at  $0^\circ\text{C}$ , assuming it remains constant over this temperature range.