

## Real gas expansions

### Joule expansion

A **Joule expansion** is an irreversible expansion of a gas into an initially evacuated container with adiabatic walls. No work is done on the gas and no heat enters the gas, so  $\Delta U = 0$ . The temperature change is described by the **Joule coefficient**,

$$\mu_J = \left( \frac{\partial T}{\partial V} \right)_U = -\frac{1}{C_V} \left[ T \left( \frac{\partial p}{\partial T} \right)_V - p \right]. \quad (1)$$

For an ideal gas,  $\mu_J = 0$ . For a van der Waals gas,  $\mu_J = -a/(C_V V^2)$ .

### Joule–Kelvin (Joule–Thomson) expansion

In a **Joule–Kelvin expansion**, the gas is expanded adiabatically from pressure  $p_1$  to  $p_2$  by a steady flow through a porous plug (throttle valve).  $\Delta Q = 0$ , so **enthalpy is conserved**:

$$\begin{aligned} \Delta U &= \Delta W \\ \Rightarrow U_2 - U_1 &= p_1 V_1 - p_2 V_2 \\ \Rightarrow H_1 &= H_2. \end{aligned} \quad (2)$$

The temperature change is described by the **Joule–Kelvin coefficient**,

$$\mu_{JK} = \left( \frac{\partial T}{\partial p} \right)_H = \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_p - V \right]. \quad (3)$$

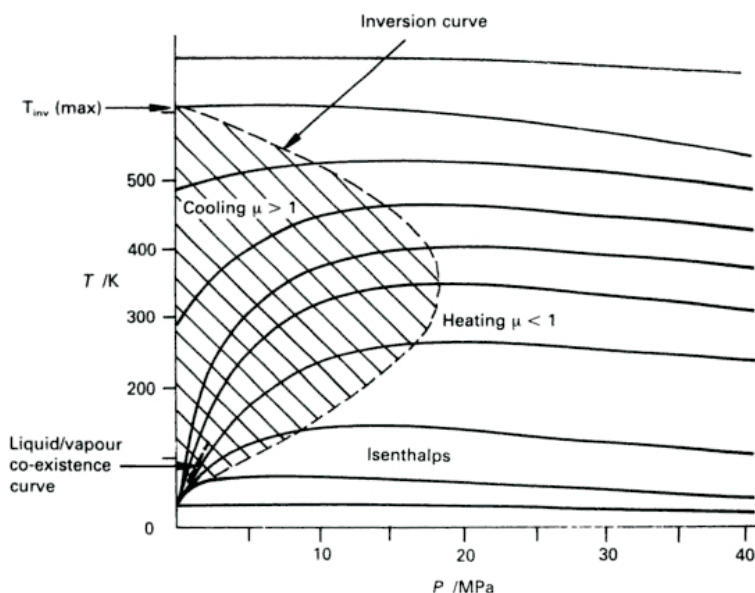
For a van der Waals gas,

$$\lim_{p \rightarrow 0} \mu_{JK} = \frac{1}{C_p} \left( \frac{2a}{RT} - b \right). \quad (4)$$

This can be positive or negative, so both heating and cooling are possible.

The diagram on the right shows the isenthalps of nitrogen in the  $p - T$  plane. The **inversion curve** is the line separating regions with  $\mu_{JK} > 0$  and  $\mu_{JK} < 0$ .

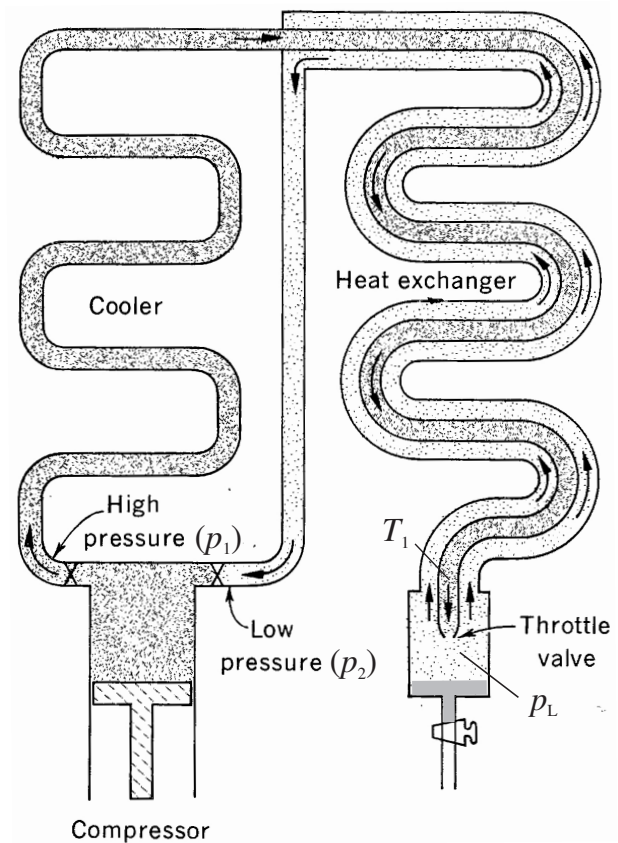
[From A. Kent, *Experimental Low Temperature Physics* (MacMillan, 1993).]



## Liquefaction of gases

Liquefaction by the Linde cycle. A Joule–Kelvin gas expansion from the region in the  $p - T$  diagram where  $\mu_{JK} < 0$  to the region where  $\mu_{JK} > 0$  can produce strong cooling. Gas at a high initial pressure  $p_1$  and temperature  $T_1$  expands into a chamber at a much lower pressure  $p_L \sim 1$  atm. The exhaust gas flows back to the compressor at a pressure  $p_2$ , where it is re-pressurized and the cycle repeated. The cold exhaust gas is passed through a heat exchanger in order to cool the incoming gas. This increases the efficiency of the process.

[Figure adapted from Fig. 13.5 in M.W. Zemansky and R.H. Dittman, *Heat and Thermodynamics* (McGraw-Hill, 6th ed. 1981).]



An advantage of the Joule–Kelvin liquefier is that the lower the temperature, the larger the drop in temperature for a given pressure drop. This is because the slope of the isenthalps increases as the temperature decreases (see curves for nitrogen on the previous page).

Cooling by the Joule–Kelvin process is possible when  $T_1 < T_i^{\max}$ , the maximum inversion temperature. Values of  $T_i^{\max}$  for various gases are given in the table:

Gas	He	H <sub>2</sub>	N <sub>2</sub>	Ar	CO <sub>2</sub>
$T_i^{\max}$ (K)	43	204	607	794	1275

Liquefaction of He and H<sub>2</sub> starting from room temperature is therefore only possible if the inlet gas is pre-cooled.