## Real gas expansions

## Joule expansion

A Joule expansion is an irreversible expansion of a gas into an initially evacuated container with adiathermal 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,

$$
\begin{equation*}
\mu_{\mathrm{J}}=\left(\frac{\partial T}{\partial V}\right)_{U}=-\frac{1}{C_{V}}\left[T\left(\frac{\partial p}{\partial T}\right)_{V}-p\right] \tag{1}
\end{equation*}
$$

For an ideal gas, $\mu_{\mathrm{J}}=0$. For a van der Waals gas, $\mu_{\mathrm{J}}=-a /\left(C_{V} V^{2}\right)$.

## Joule-Kelvin (Joule-Thomson) expansion

In a Joule-Kelvin expansion, the gas is expanded adiathermally from pressure $p_{1}$ to $p_{2}$ by a steady flow through a porous plug (throttle valve). $\Delta Q=0$, so enthalpy is conserved:

$$
\begin{align*}
\Delta U & =\Delta W \\
\Rightarrow U_{2}-U_{1} & =p_{1} V_{1}-p_{2} V_{2} \\
\Rightarrow H_{1} & =H_{2} . \tag{2}
\end{align*}
$$

The temperature change is described by the Joule-Kelvin coefficient,

$$
\begin{equation*}
\mu_{\mathrm{JK}}=\left(\frac{\partial T}{\partial p}\right)_{H}=\frac{1}{C_{p}}\left[T\left(\frac{\partial V}{\partial T}\right)_{p}-V\right] . \tag{3}
\end{equation*}
$$

For a van der Waals gas,

$$
\begin{equation*}
\lim _{p \rightarrow 0} \mu_{\mathrm{JK}}=\frac{1}{C_{p}}\left(\frac{2 a}{R T}-b\right) . \tag{4}
\end{equation*}
$$

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 $\mu_{\mathrm{JK}}>0$ and $\mu_{\mathrm{JK}}<0$.
[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 $\mu_{\mathrm{JK}}<0$ to the region where $\mu_{\mathrm{JK}}>0$ 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 $p_{\mathrm{L}} \sim 1 \mathrm{~atm}$. 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 $T_{1}<T_{\mathrm{i}}^{\mathrm{max}}$, the maximum inversion temperature. Values of $T_{\mathrm{i}}^{\max }$ for various gases are given in the table:

| Gas | He | $\mathrm{H}_{2}$ | $\mathrm{~N}_{2}$ | Ar | $\mathrm{CO}_{2}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| $T_{\mathrm{i}}^{\max }(\mathrm{K})$ | 43 | 204 | 607 | 794 | 1275 |

Liquefaction of He and $\mathrm{H}_{2}$ starting from room temperature is therefore only possible if the inlet gas is pre-cooled.

