

Joule-Thomson effect
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Joule-Thomson effect: Intermolecular attractive interactions cause the condensation of all gases. At temperatures slightly above the condensation temperature the interactions are strong enough that work against them during expansion causes significant cooling of the gas. If the cooling is sufficient, part of the gas will condensate.

(C. Kittel)

1. Cooling by external work in an expansion engine

The entropy of an ideal monatomic gas depends on the volume and the temperature.

$$S = Nk_B \left[\frac{5}{2} + \ln\left(\frac{n_Q}{n}\right) \right]$$

with

$$n_Q = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}$$

Then

$$\begin{aligned} S &= Nk_B \left[\frac{5}{2} + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{mk_B}{2\pi\hbar^2} \right) - \ln N + \ln V \right] \\ &= Nk_B \left(\frac{3}{2} \ln T + \ln V + \text{const} \right) \end{aligned}$$

So the entropy remains constant if

$$\frac{3}{2} \ln T + \ln V = \ln(T^{3/2}V) = \text{const}$$

or

$$T^{3/2}V = \text{const} .$$

In an expansion at constant entropy from V_1 to V_2 for an ideal monatomic gas

$$T_1^{3/2}V_1 = T_2^{3/2}V_2$$

We use the ideal gas law

$$PV = Nk_B T, \quad \text{or} \quad V = \frac{N}{P} k_B T$$

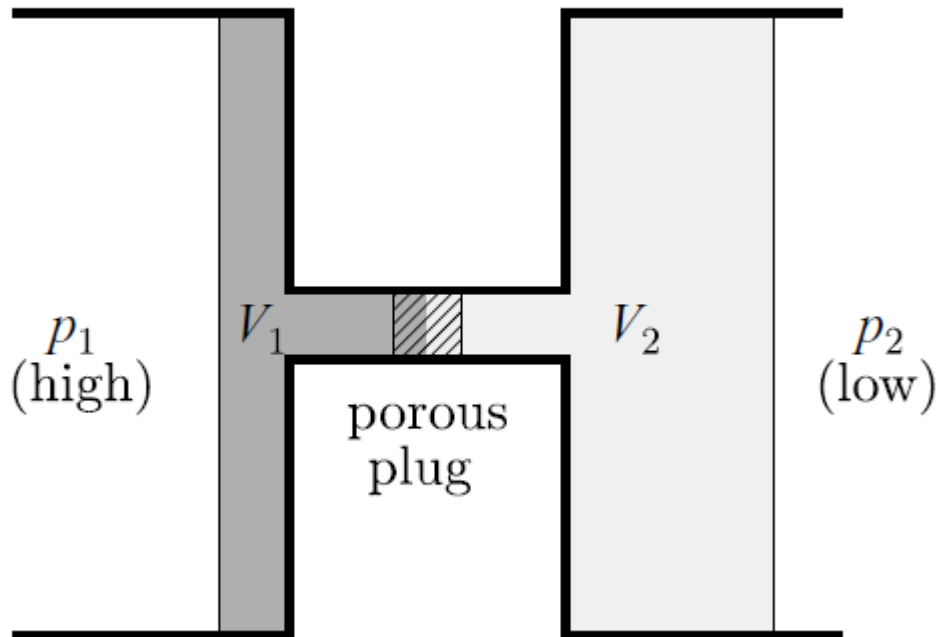
Then we get the relation

$$\frac{T_1^{5/2}}{P_1} = \frac{T_2^{5/2}}{P_2}, \quad \text{or} \quad T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{2/5}$$

((Example))

$P_1 = 32 \text{ atm}$. $T_1 = 300 \text{ K}$. When $P_2 = 1 \text{ atm}$, we have $T_2 = 75 \text{ K}$.

2. Gas liquefaction by the Joule-Thomson effect



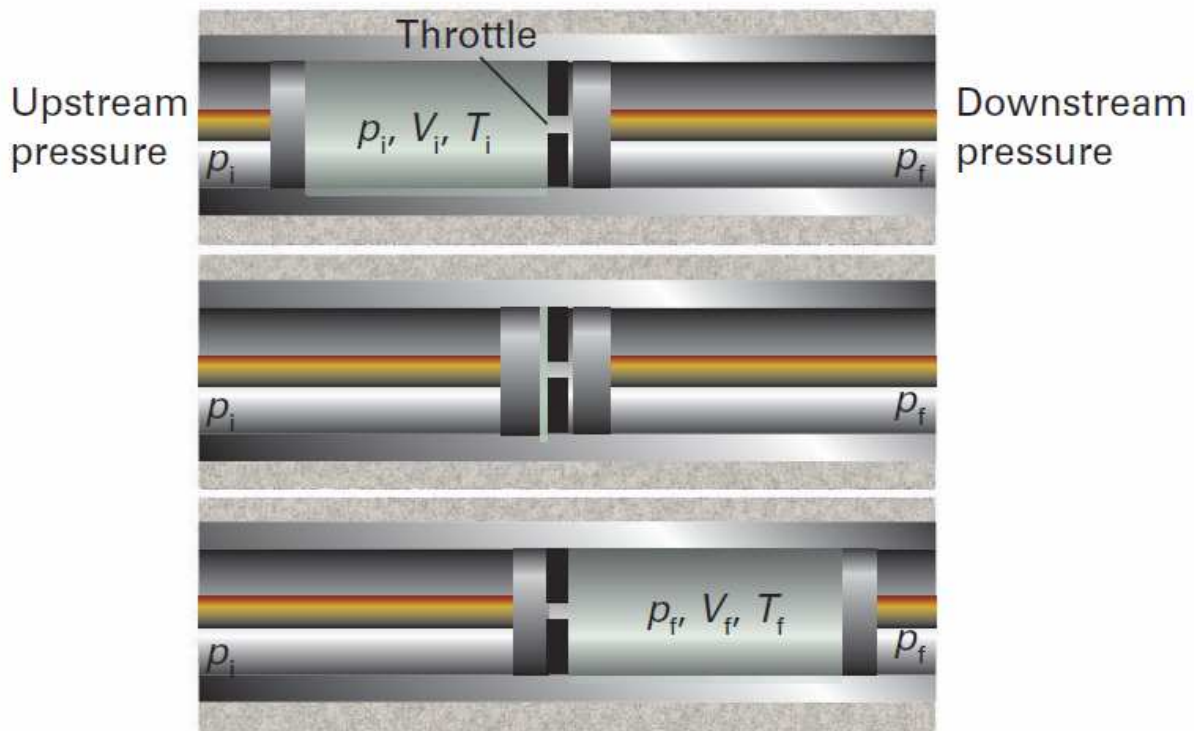


Fig. The thermodynamic basis of Joule–Thomson expansion. The pistons represent the upstream and downstream gases, which maintain constant pressures either side of the throttle. The transition from the top diagram to the bottom diagram, which represents the passage of a given amount of gas through the throttle, occurs without change of enthalpy. (Atkins, Physical Chemistry)

Intermolecular attraction interactions cause the condensation of all gases. At temperatures slightly above the condensation temperature the interactions are strong enough that work against them during expansion causes significant cooling of the gas. If the cooling is sufficient, part of the gas will condense. This is called the Joule-Thomson liquefaction. The pressure P_1 and P_2 remain constant through the process. Such a process may be diagrammatically represented as a passage of the gas through a porous partition. The constancy of pressure on either side of the partition is maintained by pistons moving inward and outward in an appropriate manner. If the hole in the partition are sufficiently small, the macroscopic flow velocity of the gas may be taken as zero. The gas is thermally isolated from the external medium.

This process is irreversible because of the presence of the partition with very small holes, which creates a large amount of friction and destroys the velocity of the gas.

The difference of energy between final and initial state;

$$\Delta Q = 0, \quad \Delta U = U_2 - U_1 = \Delta W = -P_1(0 - V_1) - P_2(V_2 - 0) = P_1V_1 - P_2V_2$$

or

$$H_2 = U_2 + P_2V_2 = U_1 + P_1V_1 = H_1$$

Then the enthalpy H remains constant. In other words, we have $H_1 = H_2$ in the Joule-Thomson effect. For a monoatomic gas,

$$H = E + PV = \frac{3}{2}Nk_B T + Nk_B T = \frac{5}{2}Nk_B T$$

So that $T_1 = T_2$ in the expansion. There is zero cooling for an ideal gas. Note that for an ideal gas the enthalpy is given by

$$H = U(T) + PV = U(T) + RT$$

Since the enthalpy depends only on T , the temperature remains unchanged.

The change in T caused by a small change of pressure in a Joule-Thomson process is given by

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T, H)}{\partial(P, H)} = \frac{\frac{\partial(T, H)}{\partial(P, T)}}{\frac{\partial(P, H)}{\partial(P, T)}} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P}$$

$$dH = TdS + VdP$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_P \quad (\text{Maxwell})$$

Then we have

$$\begin{aligned}
 \mu_{JK} &= \left(\frac{\partial T}{\partial P} \right)_H \\
 &= \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \\
 &= \frac{VT}{C_P} \left[\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P - \frac{1}{T} \right] \\
 &= \frac{TV}{C_P} \left[\alpha - \frac{1}{T} \right]
 \end{aligned}$$

where α is the co-efficient of thermal expansion and defined by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P.$$

The change in temperature for a gas following the Joule-Thomson expansion from pressure P_1 to pressure P_2 is given by

$$\Delta T = \int_{P_1}^{P_2} \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] dP$$

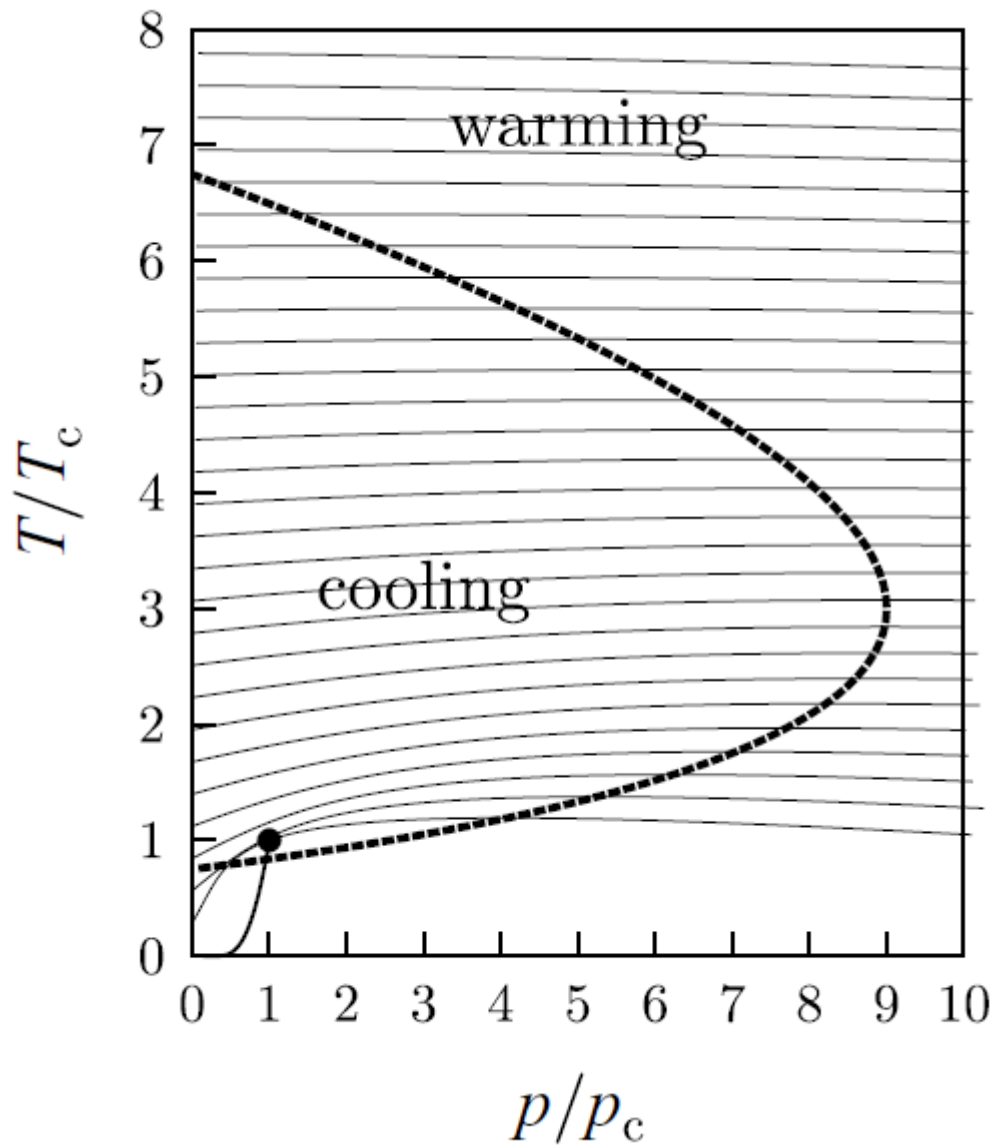


Fig. The inversion curve of the van der Waals gas is shown as the heavy dashed line. The isenthalps (lines of constant enthalpy) are shown as thin solid lines. When the gradients of the isenthalps on this diagram are positive, then cooling can be obtained when pressure is reduced at constant enthalpy (i.e. in a Joule–Kelvin expansion). Also shown (as a solid line near the bottom left-hand corner of the graph which terminates at the dot) is the line of coexistence of liquid and gas ending in the critical point ($P = P_c$, $T = T_c$, shown by the dot). (Blundell-Blundell)

3. The inversion temperature (the number density)

The van der Waals equation

$$P + \frac{aN^2}{V^2} = \frac{Nk_B T}{V - Nb}$$

We introduce a new variable (the number density)

$$\rho = \frac{N}{V},$$

Then the van der Waals equation can be rewritten as

$$P + a\rho^2 = \frac{k_B T \rho}{1 - b\rho}$$

Taking the derivative with respect to T at constant P , we get

$$2a\rho \left(\frac{\partial \rho}{\partial T} \right)_P = \frac{k_B \rho}{1 - b\rho} + \frac{k_B T}{(1 - b\rho)^2} \left(\frac{\partial \rho}{\partial T} \right)_P$$

or

$$\left(\frac{\partial \rho}{\partial T} \right)_P = \frac{k_B \rho (1 - b\rho)}{2a\rho (1 - b\rho)^2 - k_B T}$$

α (the co-efficient of thermal expansion) is obtained as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P = \frac{k_B (1 - b\rho)}{k_B T - 2a\rho (1 - b\rho)^2}.$$

$$\alpha T - 1 = \frac{\rho [-k_B T b + 2a(1 - b\rho)^2]}{k_B T - 2a\rho (1 - b\rho)^2} \approx \frac{\rho [-b + \frac{2a}{k_B T}]}{k_B T}$$

The inversion temperature is given by

$$-k_B T b + 2a(1 - b\rho)^2 = 0$$

or

$$-\frac{8}{27} t_r + 2 \left(1 - \frac{1}{3v_r} \right)^2 = 0$$

or

$$v_r = \frac{9 + 2\sqrt{3}\sqrt{t_r}}{27 - 4t_r}, \quad (1)$$

where

$$T_c = \frac{8a}{27k_b b}, \quad v_c = 3b, \quad P_c = \frac{a}{27b^2}$$

$$v_r = \frac{v}{v_c} = \frac{1}{\rho v_c}, \quad p_r = \frac{P}{P_c}, \quad t_r = \frac{T}{T_c}$$

The van der Waals equation:

$$p_r = -\frac{3}{v_r^2} + \frac{8}{3} \frac{t_r}{v_r - \frac{1}{3}} \quad (\text{van der Waals equation})$$

From Eq.(1), p_r can be obtained as

$$p_r = 3(-9 + 8\sqrt{3}\sqrt{t_r} - 4t_r); \quad \text{dimensionless form}$$

and

$$\frac{dp_r}{dt_r} = 12\left(-1 + \frac{\sqrt{3}}{\sqrt{t_r}}\right)$$

- (a) At $t_r = 3$, $p_r = 9$ (p_r has a local maximum at $t_r = 3$ in the p_r vs t_r)
- (b) p_r is equal to zero at $t_r = 3/4$ and $27/4$.

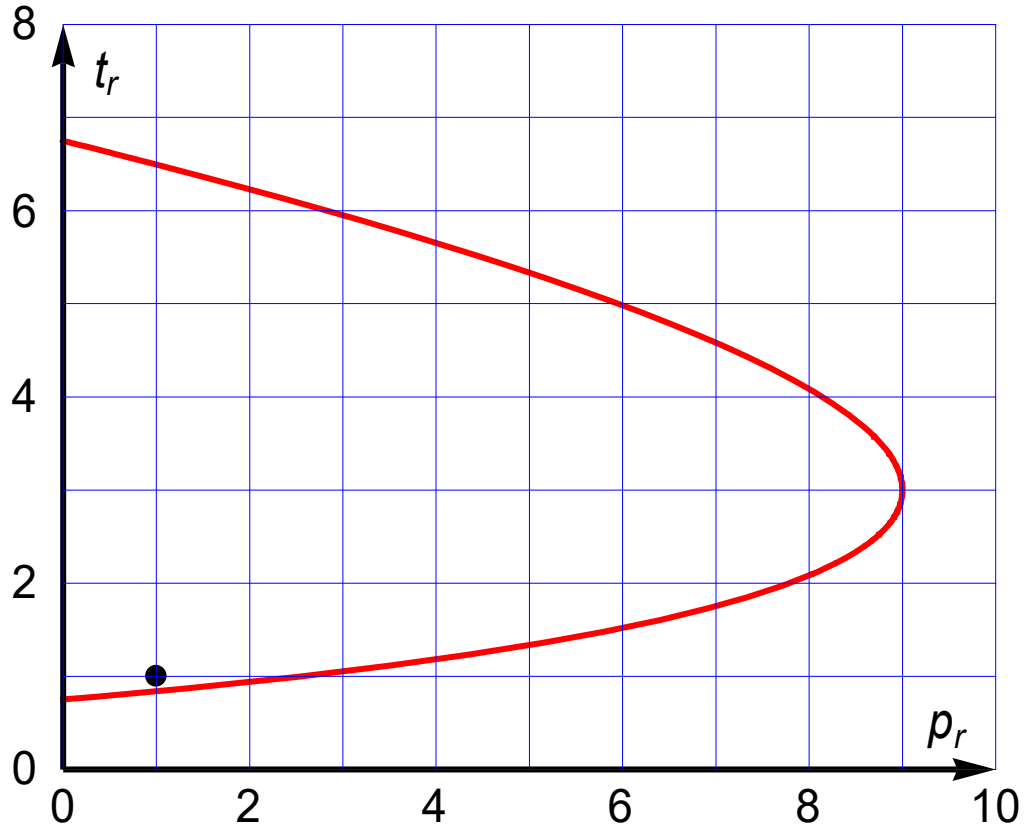


Fig. The inversion curve of the van der Waals gas (red line). The dot denotes the critical point.

((**Example-2**)) Ideal gas: $PV = Nk_B T$

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{\partial}{\partial T} \frac{Nk_B T}{P} \right)_P = \frac{Nk_B}{PV} = \frac{1}{T}$$

$$\left(\frac{\partial T}{\partial P} \right)_H = 0$$

((**Example-2**)) **van der Waals gas**

The van der Waals equation is given by

$$\left(P + \frac{aN^2}{V^2} \right) (V - Nb) = Nk_B T$$

The enthalpy H is given by

$$H = U + PV = \frac{5}{2} Nk_B T + NbP - \frac{2N}{k_B T} aP$$

where a and b are positive.

((Note))

We use the two equations

$$U = -\frac{aN^2}{V} + \frac{3}{2} Nk_B T$$

and

$$(P + \frac{aN^2}{V^2})(V - Nb) = Nk_B T$$

Noting that

$$PV = PNb - \frac{aN^2}{V} + \frac{N^3 ab}{V^2} + Nk_B T$$

we have the expression for H as

$$\begin{aligned} H &= U + PV \\ &= -\frac{aN^2}{V} + \frac{3}{2} Nk_B T + PNb - \frac{aN^2}{V} + \frac{N^3 ab}{V^2} + Nk_B T \\ &= \frac{5}{2} Nk_B T + PNb - \frac{2aN^2}{V} + \frac{N^3 ab}{V^2} \\ &\approx \frac{5}{2} Nk_B T + PNb - \frac{2aN^2}{V} \\ &= \frac{5}{2} Nk_B T + PNb - \frac{2NaP}{k_B T} \end{aligned}$$

The results are given to the first order in the van der Waals correction terms a and b .

$$\left(\frac{\partial H}{\partial P} \right)_T = Nb - \frac{2Na}{k_B T} = Nb \left(1 - \frac{T_{inv}}{T} \right)$$

where T_{inv} is defined as

$$T_{inv} = \frac{2a}{k_B b} = \frac{27}{4} T_c$$

with

$$T_c = \frac{8a}{2k_B b} = T_c,$$

and

$$\left(\frac{\partial H}{\partial T} \right)_P = \frac{5}{2} Nk_B + \frac{2N}{k_B T^2} aP$$

Then

$$\left(\frac{\partial T}{\partial P} \right)_H = - \frac{\left(\frac{\partial H}{\partial P} \right)_T}{\left(\frac{\partial H}{\partial T} \right)_P} = \frac{Nb \left(\frac{T_{inv}}{T} - 1 \right)}{\frac{5}{2} Nk_B + \frac{2N}{k_B T^2} aP} \propto Nb \left(\frac{T_{inv}}{T} - 1 \right) = \frac{Nb}{T} (T_{inv} - T)$$

$$\text{For } T < T_{inv}, \quad \left(\frac{\partial T}{\partial P} \right)_H > 0$$

$$\text{For } T > T_{inv}, \quad \left(\frac{\partial T}{\partial P} \right)_H < 0$$

All gases have a T_{inv} , below which an expansion cools, above which it heats the gas.

((Physical meaning))

$$\begin{aligned} H &= U + PV \\ &= \frac{5}{2} Nk_B T + \frac{N^2 b k_B}{V} \left(T - \frac{2a}{b k_B} \right) \\ &= \frac{5}{2} Nk_B T + \frac{N^2 b k_B}{V} (T - T_{inv}) \end{aligned}$$

- (a) For $T < T_{inv}$, H at fixed T increases as the volume increases; here in expansion the work done against the attractive interaction between molecules is dominant. In a process at

constant H , this increase is compensated by a decrease of $\frac{5}{2}Nk_B T$ term by cooling the gas.

- (b) For $T > T_{inv}$, H at fixed T decreases because the work done by the short range repulsive interactions is dominant. At the higher temperatures the molecules penetrate farther into the repulsive region.

$$T_{inv} = 621 \text{ K (N}_2\text{)}, 205 \text{ K (N}_2\text{)}, 193 \text{ K (H}_2\text{)}, 51 \text{ K (He)}.$$

The Joule-Thomson effect is essentially due to the interaction between molecules of gases. When the gas is expanded, the distance between molecules in gas becomes longer, leading to the increase of potential energy. In other words, the energy work done (ΔW) on the gas becomes increasing on expansion. Because of the energy conservation,

$$\Delta E = \Delta Q + \Delta W$$

the thermal energy ΔQ decreases, leading to the lowering of temperature. For the ideal gas without any attractive interaction between molecules in gas the Joule-Thomson effect does not occur.

ContourPlot of the enthalpy constant

$$\begin{aligned} H &= U + PV \\ &= -\frac{aN^2}{V} + \frac{3}{2}Nk_B T + PV \end{aligned}$$

with

$$P = -\frac{aN^2}{V^2} + \frac{Nk_B T}{V - Nb}$$

$$v = v_c v_r, \quad T = T_c t, \quad P = P_c p$$

$$\frac{H}{N} = \frac{a}{9b} \left(-\frac{3}{v_r} + 4t + p v_r \right)$$

((ContourPlot))

We make a plot of

$$p = -\frac{3}{v^2} + \frac{\frac{8}{3}t}{v - \frac{1}{3}}$$

$$h = \frac{H}{N} \frac{9b}{a} = -\frac{3}{v_r} + 4t + pv_r$$

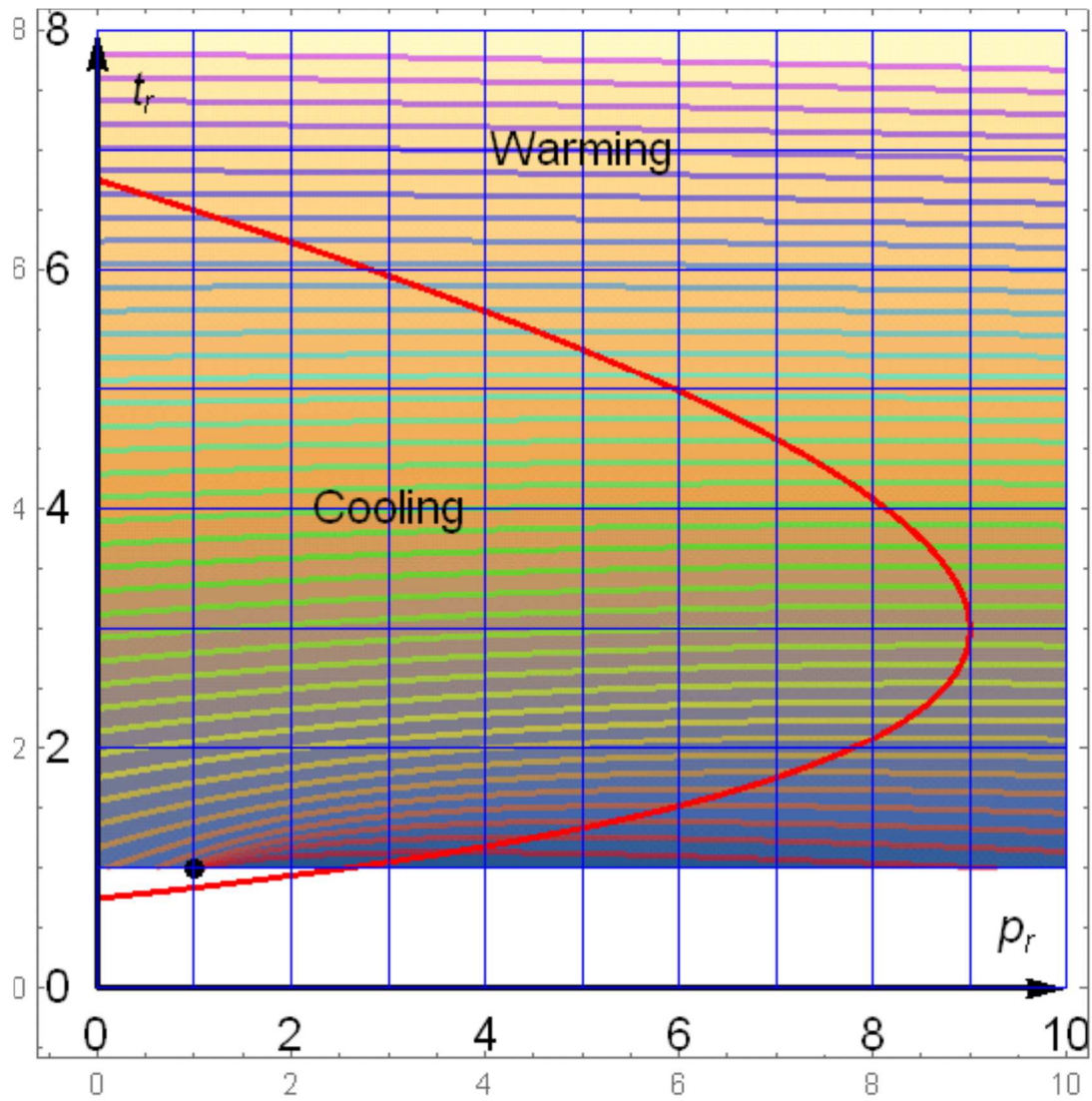
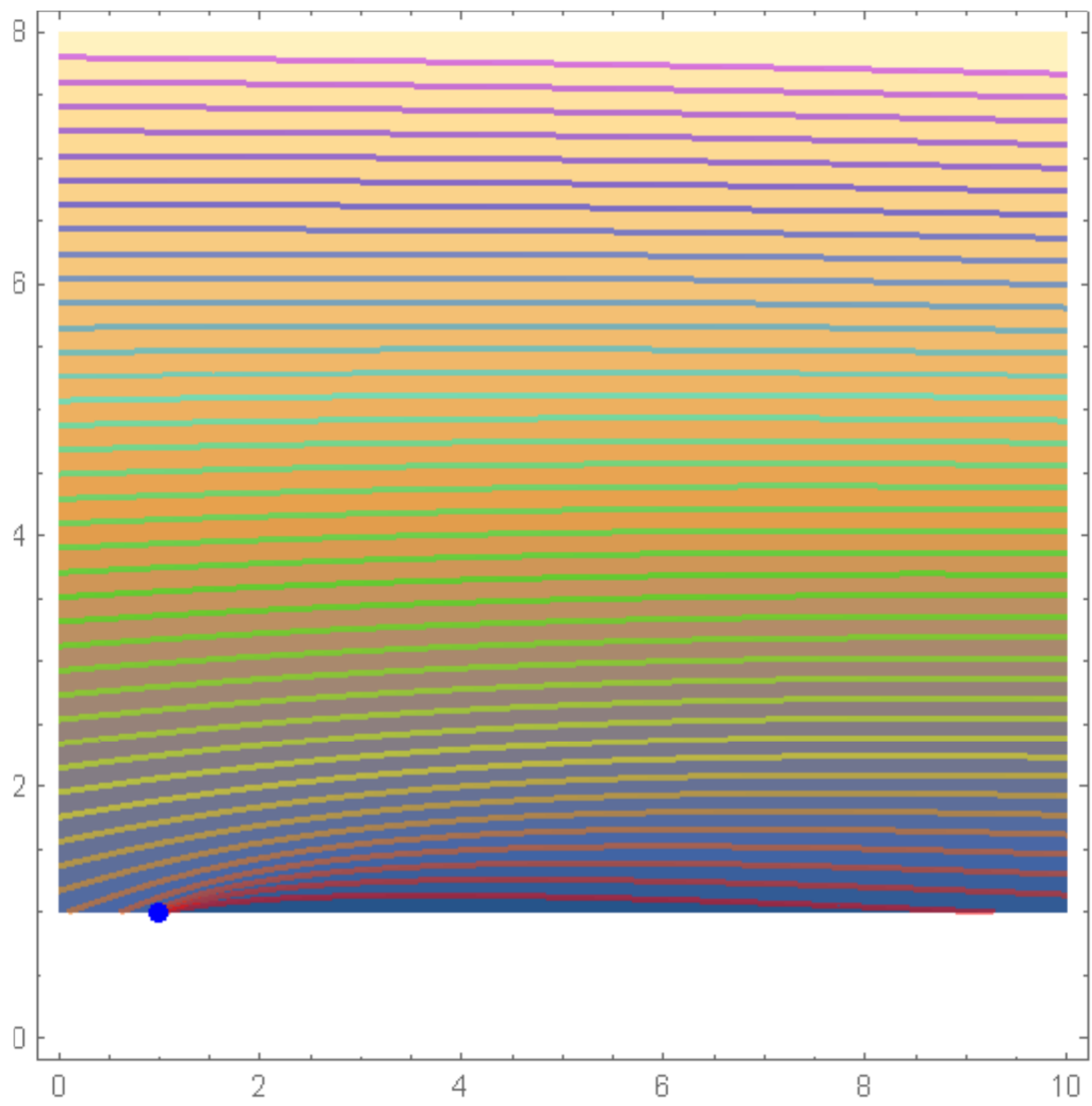


Fig. The isenthalps (lines of constant enthalpy). $t_r > 1$.



((Note))

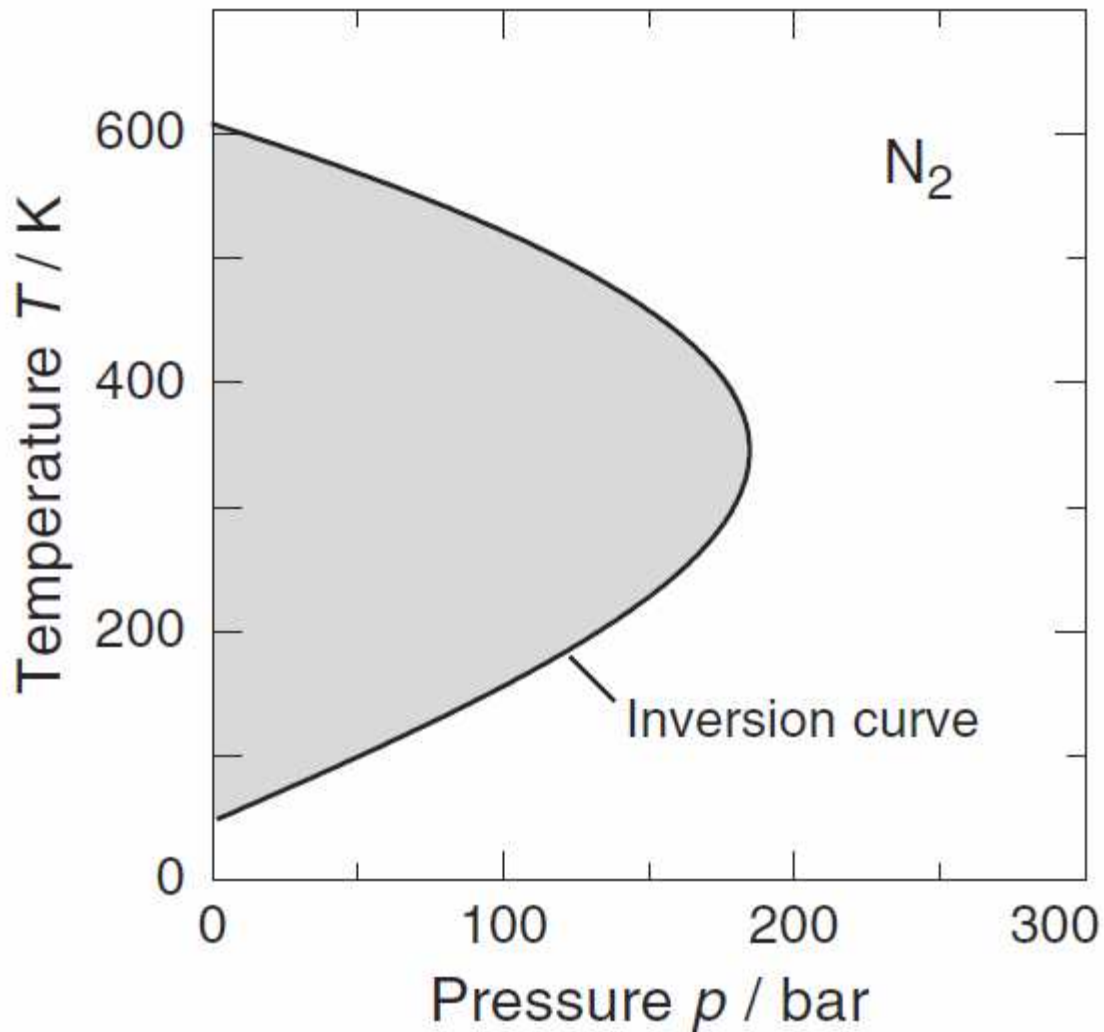


Fig. The inversion temperatures for nitrogen.

5. Linde liquefier

The arrangement with the heat exchanger and expansion valve connected in series leads to a process that takes place at constant enthalpy. It is often referred to as a *Linde liquefier*. If we denote the enthalpies of the gas streaming in, the liquid and the gas streaming back as H_{in} , H_l and H_{back} , respectively, we can write the relation

$$H_{in} = \lambda H_l + (1 - \lambda) H_{back} ,$$

where λ represents the fraction of gas that has been liquefied. Since the three enthalpies that enter here are well known from various experiments, one can easily calculate λ using the equation

$$\lambda = \frac{H_{back} - H_{in}}{H_{back} - H_l}$$

The magnitude of λ depends on the pressure difference as well as on the starting temperature of the expansion. Since, for a decent liquefaction $\lambda > 0.1$ is desirable, one usually needs to start with temperatures below $T_{inv}/3$. Because of this, it is sensible to use an expansion engine for precooling in the process of liquefaction of many gases. The combination of a Linde liquefier and an expansion engine is known as a *Claude cycle* (Enss and Hunklinger).

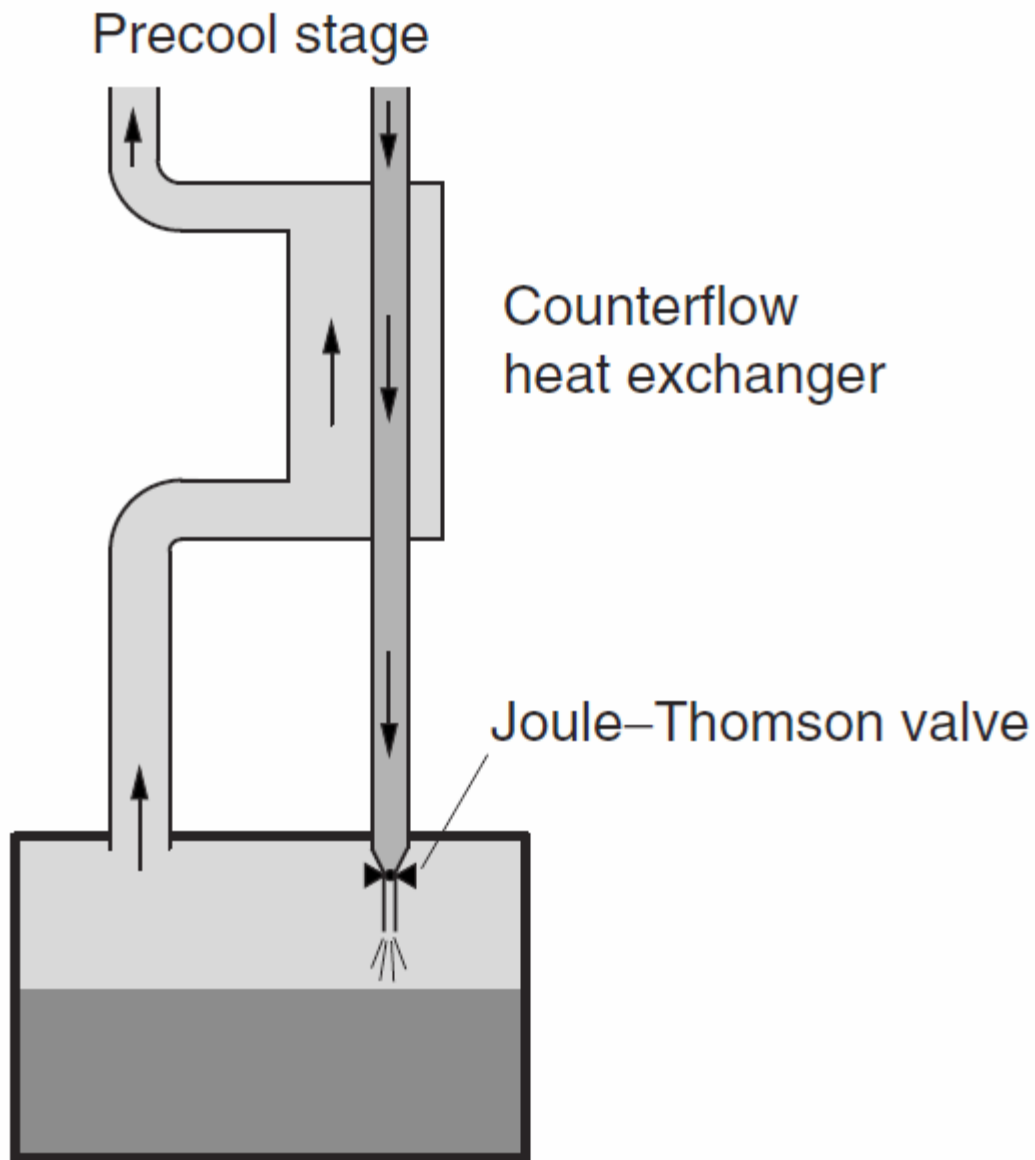


Fig. Schematic illustration of the setup of a gas liquefier with Joule–Thomson expansion and counterflow heat exchanger (C. Enss and S. Hunklinger).

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