

Problem 6.1: Absolute Zero

[Oral | 4 pt(s)]

ID: ex_absolute_zero:sm2324

Learning objective

Here we show that absolute zero cannot be reached by an adiabatic expansion.

From the lecture, we know that

$$c_p \rightarrow 0 \quad \text{for} \quad T \rightarrow 0. \tag{1}$$

Thus the specific heat at constant pressure takes on the form

$$c_p = T^x (a_0 + a_1 T + a_2 T^2 + \dots) \tag{2}$$

where x is a positive exponent.

a) Show that

1pt(s)

$$\frac{V}{c_p} = \text{const} \neq 0 \quad \text{for} \quad T \rightarrow 0 \tag{3}$$

b) Using the result from (a), show that absolute zero cannot be reached by an adiabatic expansion.

1pt(s)

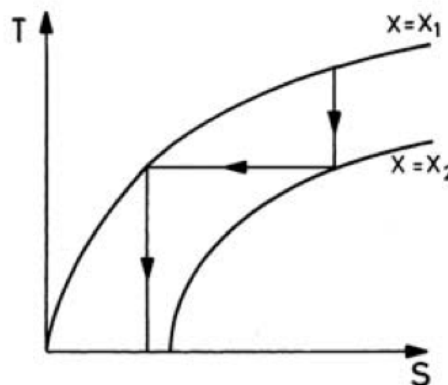
In the following, we gain intuition whether absolute zero can be reached at all. We consider the fact that cooling processes always take place between two curves with $X = \text{const.}$, e.g., $X_1 = P_1, X_2 = P_2 (P_1 > P_2)$.

c) Draw the T - S diagram and show that absolute zero could only be reached by infinitely many steps. To this end, consider steps consisting of adiabatic cooling and isothermal compression between two isobars. Is it possible to decrease the entropy better than by doing it at $T = \text{const.}$?

1pt(s)

d) Imagine a substance described by the T - S diagram as shown in the hypothetical diagram below. This substance would reach $T = 0$ after a finite number of adiabatic coolings and isothermal compressions. Why such a substance cannot exist?

1pt(s)



Problem 6.2: Adiabatic Demagnetization: The Way to Millikelvin Temperatures [Oral | 4 pt(s)]

ID: ex_adiabatic_demagnetization:sm2324

Learning objective

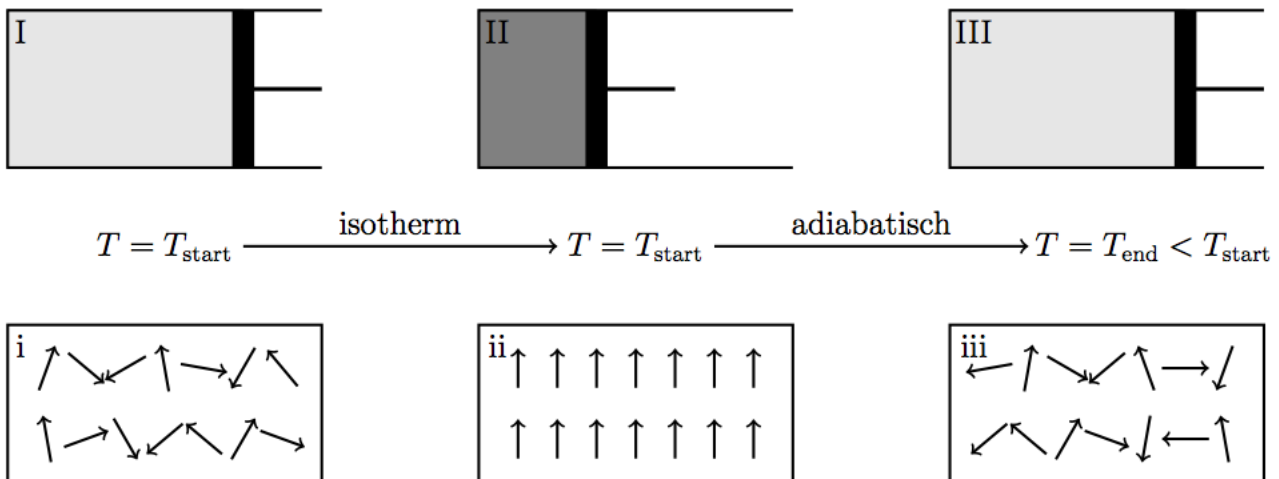
In this exercise we analyze how low temperatures can be reached using adiabatic demagnetization.

In adiabatic processes, the temperature of a system changes; for example, an expanding (ideal) gas cools down. The analogous phenomenon for magnetic substances is called the magnetocaloric effect: a paramagnet cools down during adiabatic demagnetization. In this way, temperatures of a few millikelvin can be reached.

As in previous exercises, the work is given by $W = -HdM$, and the Curie law can be formulated as $M(T, H) = \frac{KH}{T}$. The specific heat at $H = 0$ is given by

$$c_H(T, H = 0) = T \left(\frac{\partial S}{\partial T} \right)_H = \frac{b}{T^2}, \tag{4}$$

with positive, material-dependent constants $K, b > 0$.



- a) **The Gibbs Potential:** Derive, using the internal energy $U(S, M)$, the Gibbs potential for the paramagnetic substance $G(T, H)$. Next, calculate its differential dG . Which Maxwell relation can be derived from G ? 1pt(s)
- b) **Adiabatic Equation:** Use the result from (a) to calculate the entropy of the system $S(T, H)$. How does the temperature T change with the change of the magnetic field H for constant entropy S ? 1pt(s)
Hint: Using the expression for $c_H(T, H = 0)$ (see above), one can determine the 'integration constant'.
- c) **Experimental Procedure:** Sketch the process for the ideal gas (I \rightarrow II \rightarrow III) in the T - V diagram, and respectively for the paramagnet (i \rightarrow ii \rightarrow iii) in the T - H diagram. To do this, use the entropy relations for the corresponding systems. 1pt(s)
- d) **Lowest Temperature Record:** How must the experimental parameters T, H , and the material properties K and b be chosen to achieve the lowest possible temperature? What are the limiting factors? 1pt(s)

Problem 6.3: Van der Waals gas

[Written | 4 pt(s)]

ID: ex_van_der_waals_gas:sm2324

Learning objective

Here, we revisit the phase transition of the van der Waals gas and consider its thermodynamic stability.

In the lecture, the equation of state for the van der Waals gas was introduced as

$$(v - b) \left(p + \frac{a}{v^2} \right) = RT \quad (5)$$

with molar volume $v = V/n$ and the (molar) parameters a and b .

a) Calculate the isothermal compressibility

1pt(s)

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T, \quad (6)$$

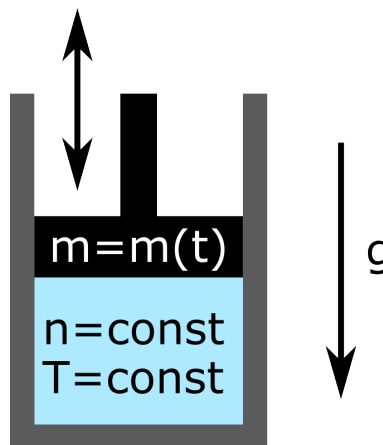
for the critical molar volume $v_c = 3b$ as a function of T . Describe the behavior of β_T for $T \rightarrow T_c^+$, where $(T_c = \frac{8a}{27bR})$

b) Using these results, discuss the thermodynamic stability of the van der Waals gas for $T < T_c$ and $T \geq T_c$.

1pt(s)

c) Consider the following setup. A vertical cylinder is filled with a van der Waals gas which stabilizes a piston of mass m . Assume the temperature is fixed at $T < T_c$. What happens if the mass $m = m(t)$ is slowly increased as a function of time? (Let $m(t = 0)$ be very small.)

1pt(s)



d) Calculate the (molar) free energy $f(T, v)$ for fixed temperature T as a function of v and discuss the qualitative differences for $T > T_c$ and $T < T_c$, respectively. Sketch the (molar) Gibbs free energy $g(T, p)$ for fixed T as a function of p for $T > T_c$ and $T < T_c$.

1pt(s)

Hints: The Gibbs free energy is defined as the Legendre transform of $f(T, v)$, i.e.,

$$g(T, p) := \inf_v [f(T, v) + pv] = \inf_v [f(T, v) - (-pv)] = -\sup_v [-pv - f(T, v)]. \quad (7)$$

Sketch this function by hand or use a CAS to derive a qualitative result.