

Correction in ex. 20): Note the new definition of the extensive isobaric expansion coefficient.

Please note: Exercises 20, 21 and 22 are mandatory and have to be submitted to the postboxes in the 5th floor of building 46.

Exercise 20.

On the last sheet you investigated the van-der-Waals gas given by the thermal equation of state:

$$\left(p + \frac{a}{v^2}\right)(v - b) = k_B T \quad (1)$$

and derived the Joule-Thomson coefficient $\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$, which can be expressed as a function of the isobaric expansion coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$.

The equation

$$\alpha = \frac{1}{T} \quad (2)$$

defines the so called inversion curve $p = p(v)$ at which a sign change of the Joule-Thomson coefficient occurs. Argue why the inversion curve yields the sign change and derive the temperature T_{inv} above which the Joule-Thomson coefficient is negative.

Exercise 21.

The Gibbs free energy of a magnetic substance is given by

$$dU = TdS + \vec{H} \cdot d\vec{M}, \quad (3)$$

where \vec{H} is the magnetic Field and \vec{M} is the magnetization of the substance. Assume that the volume is constant (solid state). Now consider the specific heats

$$C_X = T \left(\frac{\partial S}{\partial T}\right)_X, \quad X \in \{\vec{H}, \vec{M}\} \quad (4)$$

as well as the isothermal and isentropic susceptibility

$$\chi_X = \left(\frac{\partial \vec{M}}{\partial \vec{H}}\right)_X, \quad X \in \{S, T\} \quad (5)$$

Show that for an isotropic substance the following relations between the specific heats and the susceptibilities hold true:

$$C_{\vec{H}} - C_{\vec{M}} = VT\alpha_H^2/\chi_T \quad (6)$$

$$\chi_T - \chi_S = VT\alpha_H^2/C_H \quad (7)$$

$$\frac{C_{\vec{H}}}{C_{\vec{M}}} = \frac{\chi_T}{\chi_S}, \quad (8)$$

where $\alpha_H = \left(\frac{\partial \vec{M}}{\partial T}\right)_H$.

Exercise 22.

Now consider a paramagnetic substance. The relation between the H field and the magnetization M is

given by the Curie law: $M = \gamma H/T$, where $\gamma = \text{const.}$ Write down the differential dG_m of the magnetic Gibbs function G_m which is defined as

$$G_m = G_m(T, V, H) = U - TS - HM \quad (9)$$

and show that

$$S = - \left(\frac{\partial G_m}{\partial T} \right)_{V, H} \quad (10)$$

follows from this. Prove that

$$G_m(T, V, H) = G_0(T, V) - \gamma \frac{H^2}{2T}, \quad (11)$$

where $G_0(T, V) = G_m(T, V, H = 0)$ and derive the entropy $S(T, V, H)$ from this. Also show that the pressure does not explicitly depend on the magnetic field, i.e. $p = p(V, T)$.