Sheet 5

Hand in via OLAT until 08.12.2020 18:00.

13) Thermodynamic variables *(10=2+4+4 Punkte)*

(i) Derive the following Maxwell relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

(ii) Use the derived Maxwell relation, to show that

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right].$$

Hint: Use the identities a) and b) of the Lemma presented in the lecture and familiar from the previous exercise sheet (eq. 2.67 and 2.68 in the script).

(iii) Compute $\left(\frac{\partial T}{\partial V}\right)_E$ for the van der Waals gas with equation of state

$$P = \frac{Nk_BT}{V-Nb} - a\frac{N^2}{V}$$

and for the ideal gas ($a = 0$, $b = 0$). Does the gas cool down, heat up, or remain at the same temperature during expansion?

14) Joule-Thomson effect *(6=2+4 Punkte)*

For the Joule-Thomson process one considers a system composed of two volumes, and the system being thermally isolated. By making use of a throttle, gas is pushed at constant pressure P_1 from system 1 at initial volume V_1 into system 2. At system 2, the pressure $P_2 < P_1$ is also kept constant, and the gas takes the final volume V_2. The throttle prevents the production of kinetic energy and ensures that the expansion is adiabatic (no heat is generated).

(i) Show that the enthalpie H is constant, and that the process is irreversible.

(ii) The Joule-Thomson coefficient is defined as $\delta = \left(\frac{\partial T}{\partial P}\right)_H$. Use your result from (i) to show that

$$\delta = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right].$$

The equation of state for an ideal gas is given as

$$PV = NT.$$

Show that for an ideal gas one has $\delta = 0$.
Hint: Use the same procedure as in exercise 13) ii).

15) Free entropy ***(4=2+2 points)***

The entropy can also be considered as a thermodynamic potential, with energie and volume as natural variables:

$$S = S(E, V), \qquad dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV = \frac{1}{T} dE + \frac{P}{T} dV$$
$$= \beta dE + \pi dV, \qquad \beta = \frac{1}{T}, \qquad \pi = \frac{P}{T}.$$

(i) Compute the so-called Planck potential $\Xi(\beta, \pi)$ by Legendre transforming twice.

(ii) Show that $d\Xi = -\frac{1}{T} dG$ with G the Gibbs free energy.

$$dG = -SdT + VdP.$$

Hint: Use the total differentials of $d\pi$ and $d\beta$.