

PHYS 813: Statistical Mechanics and Thermodynamics, Assignment 2

Due 3/20/09

1. Consider a completely isolated system consisting of subsystems A and A'. Assume that A' is so large that the changes within A do not influence the temperature and pressure of A'. Subsystem A is separated from subsystem A' by a moving piston that conducts heat. The system is initially in equilibrium. Consider an arbitrary spontaneous process, resulting from the removal of some internal restrictions within A (the piston is free to move and is conducting at all times). In the initial and final states, the temperature and pressure of A are the same as of A' (since both states are equilibria). Within the process, the volume of A changes and heat is exchanged between A and A'.
 - (a) Give examples of processes that can lead to volume work and heat exchange in the process described above.
 - (b) Show that when the system reaches equilibrium, the Gibbs free energy for system A will be at the minimum. Hint: Start from the second postulate of thermodynamics.
2. Consider a liquid in coexistence with its vapor.
 - (a) Find the equation for the derivative dp/dT along the coexistence curve as a function of the molar volumes of the liquid v_L and the vapor v_V , temperature, and the molar heat of vaporization q . *Hint*: Relate the differentials of the chemical potentials on both sides of the coexistence line.
 - (b) Assume that the vapor follows the ideal gas law, has a density which is much less than that of the liquid, and q is independent of T . Show that then $p \sim \exp(-q/RT)$.
3. In the so-called Joule-Thompson experiment, two cylinders filled with a gas are separated by a porous plug (called throttle) allowing the gas to expand slowly from one cylinder to another. Pistons keep the pressure constant in each cylinder. One can show (but do not show it) that this setup results in a process with a constant enthalpy H :

$$H(T_1, p_1) = H(T_2, p_2) = \text{const.}$$

where T_i and p_i are the temperatures and pressures of the gas in the two cylinders. The dependence $H(T, p) = \text{const.}$ allows one to calculate $T(p)$. Find the derivative of this curve

$$\delta = \left(\frac{\partial T}{\partial p} \right)_H$$

in terms of the volume, temperature, heat capacity at constant pressure, and molar coefficient of thermal expansion of the gas. The latter two quantities are defined as

$$C_p = \left(\frac{dQ}{dT} \right)_p, \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p.$$

Hints: Start from the expression for δ resulting from the “three-derivatives” formula applied to $H(T, p)$. To transform one of the derivatives that will appear in this expression, compare $dH(T, p)$ and $dH(S, p)$. Finally, use a Maxwell formula.

4. Consider first a general system.

(a) Show that the difference of the molar specific heats can be written as

$$c_p - c_V = \frac{1}{N} \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p$$

(b) Show that

$$p + \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V$$

(c) Using the results of (a) and (b), find the difference $c_p - c_V$ for a van der Waals gas fulfilling

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

where v is the molar volume and a and b are constants.

(d) Show that for $v \rightarrow \infty$ at constant p , one recovers the ideal gas result for the difference.

5. A van der Waals gas fulfilling

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

where v is the molar volume and a and b are constants, undergoes an isothermal expansion from volume V_1 to volume V_2 .

(a) Calculate the change in Helmholtz free energy.

(b) Calculate the change in internal energy.

6. Consider a Carnot engine filled with ideal gas.

(a) Without an explicit consideration of the p - V dependence on the adiabatic segments, show that the sum of the work performed on these segments is zero.

(b) To confirm this result, use direct integration of the p - V dependence to find explicit expressions for the work on each of the adiabatic segments.

7. Consider a classical gas of hard spheres of diameter σ . Show that for such a gas the volume V in the ideal gas law should be replaced by $V - b$, where b is proportional to the number of particles N and to σ^3 . Find the proportionality constant.

8. Consider a mixture of two ideal gases with different $\gamma = C_p/C_V$. Find the effective γ for the mixture.

9. The elasticity of a rubber band can be described by a “one-dimensional” model of a polymer involving $N + 1$ molecules linked together end-to-end. There are N such links, each of length d . The angle between successive links is equally likely to be 0 or π . Assume there are no interactions between the molecules.

(a) Find the number of arrangements $g(N, m)$ that give an overall length $L = 2md$.

(b) Show that for $m \ll N$, $g(N, m)$ can be written as

$$g(N, m) = g(N, 0)e^{-4m^2/N}.$$

- (c) Find the entropy of the system as a function of L for $N \gg 1$ and $L \ll Nd$.
- (d) Assume that the system is in equilibrium with a heat bath of temperature T . Using the expression derived in (c) and appropriate thermodynamic relations, find the external force required to maintain the length L .