Physics Department
Paderborn University

Theoretical Physics - Thermodynamics
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Sheet IV
Preparation until Tuesday, 11.11.2008

10. Thermodynamic potentials

a) Read from the Guggenheim scheme on which natural variables v_1, v_2 does the Gibbs free energy $G = G(v_1, v_2)$ depend. What is the result of the partial derivative

$$\left(\frac{\partial G}{\partial v_1}\right)_{v_2} \quad \text{or} \quad \left(\frac{\partial G}{\partial v_2}\right)_{v_1} ? \tag{17}$$

With the help of these relations find the thermal equation of state for

$$G = Nk_bT \ln p + p\left(Nc_1 - \frac{Nc_2}{k_BT}\right), \tag{18}$$

where $c_1 = \text{const.}$ and $c_2 = \text{const.}$

b) Show that the result for $c_1 = b$ and $c_2 = a$ agree with the van der Waals equation Eq. (3) Sheet I, when second order terms in a and b are neglected.

11. Grand potential

The grand potential for a pVT-system is given by

$$\Omega = \Omega(T, V, \{\mu_i\}). \tag{19}$$

Try to construct a potential which depends on pressure p instead of volume V. Justify your failure!
Instructions:

- First, with the help of the exact differential, show that the grand potential

$$\Omega = U - TS - \sum_i \mu_i N_i \tag{20}$$

  can be indeed written as one depending on $T, V, \{\mu_i\}$. Check quickly whether the remaining thermodynamic parameters $S, p, \{\mu_i\}$ can be obtained by partial derivative.

- Carry out a corresponding Legendre transformation $\tilde{\Omega} = L[\Omega]$ and show once again via the exact differential that you are apparently close to the target $\tilde{\Omega} = \tilde{\Omega}(T, p, \{\mu_i\})$.

- Why does the Euler equation for the system (to be shown in the Lecture)

$$U = TS - pV + \sum_i \mu_i N_i \tag{21}$$

  undo the result for $\tilde{\Omega}$? Why should one expect such a result?

12. Condition of equilibrium

Consider a mixture of n ideal gases with particle number N_i. Show that the system is in equilibrium when the i-th chemical potential is given by

$$\mu_i = \mu_i(p, T, N_i) = \mu_i^0(p, T) + k_B T \ln \frac{N_i}{N}. \tag{22}$$

a) Consider which thermodynamic potential in the process must be minimal. What is, in general the condition of equilibrium (which depends on μ_i and N_i)?

b) Use Eq. (22) to check 12 a) explicitly (remember that $N = \sum_i^n N_i$ when you take derivation $\partial/\partial N_i$.)

13. Magic exercise

Hogwarts consists of two adjacent isolated "horror chambers" 1 and 2 which have the volume V_1 and V_2, respectively, and are kept at temperature T. Since the magicians can easily spirit off their extension or interactions, they can be treated as ideal gas. There are present in each room the magicians of two kinds (G)ryffindor and (S)lytherin; the beginning of the school year is described via the state

Chamber 1	Chamber 2
T, V_1, N_1^G, N_1^S	T, V_2, N_2^G, N_2^S.

A spell of a certain Potter makes the wall between the chambers penetrable for Gryffindors.

a) Which variables have to be extremal by the redistribution of the Gryffindors? What does it mean for the chemical potential? Eliminate the number of Gryffindors in chamber 2, in which you can release them via their total number N_{ges}^G.

b) With the heat capacity C_z of the magician it is possible to write the chemical potential for magician mixture in volume V

$$\mu_l = k_B T \left(\frac{5}{2} - \ln \left(C_z T^{3/2} \frac{V}{N_l} \right) \right). \tag{23}$$

What is the consequence for the numbers N_1^G and N_2^G of the Gryffindors in chamber 1 and 2. How big is the total number of the magicians (Gryffinfor + Slytherin) in particular chambers?

c) How strong is the pressure in the chambers?

d) What happens with the pressure if *Malfoy* also performs magic and the wall in between is penetrable for Slytherins?

e) What happens with the pressure if instead of the spell of Malfoys, *Longbottom* performs magic that makes all the Slytherins disappear, i.e. $N_{ges}^S = 0$.