Freie Universität Berlin
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Statistical Physics and Thermodynamics (SS 2016)

Problem sheet 9

Hand in: Thursday, June 23 during the lecture

http://www.physik.fu-berlin.de/en/einrichtungen/ag/ag-netz/lehre/

1 Law of mass action for hydrogen (9 points)

In this exercise you will derive the law of mass action from the canonical partition function. Consider N_H H-atoms (mass m) and N_{H_2} H_2-molecules (mass $2m$) in thermodynamic equilibrium in a volume V. The following reaction takes place

$$H + H \rightleftharpoons H_2.$$
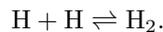
The system can be treated as an ideal gas.

a) Write down the canonical free energy F_H of the H-particles and the canonical free energy F_{H_2} of the H_2 particles. (**1 point**)

b) Derive the free energy $F(N_H, N_{H_2}, V, T) = F_H + F_{H_2} - N_{H_2}\Delta\mu$ of the entire system. The reaction energy $\Delta\mu$ is the energy released in the single reaction $2H \rightarrow H_2$. Express the free energy in terms of the thermal wave length $\lambda = h/\sqrt{2\pi m k_B T}$ and the particle numbers N_H and $N = N_H + 2N_{H_2}$. (**2 points**)

c) Calculate the equilibrium fraction $(N_H/V)^2/(N_{H_2}/V)$ in terms of $\Delta\mu$ and λ by minimizing the free energy according to $\partial F(N, N_H, V, T)/\partial N_H = 0$. (**3 points**)

d) Express the equilibrium density of hydrogen in atomic form, $c_H = N_H/V$, in terms of the total atomic density $c = N/V$ with $N = N_H + 2N_{H_2}$. (**1 point**)

e) Calculate the density c at which the majority of the hydrogen dissociates, given by the condition $c_H/c = 1/2$. (**1 point**)

f) The interstellar medium consists largely of hydrogen at low density $c = 10^7$ m^{-3} at $T = 100$ K, interspersed with clouds of $c = 10^{12}$ m^{-3} at $T = 10$ K. Based on the present calculation, in which form do you expect the hydrogen to be in the two different regions? Use the following constants:

$$h = 6.63 \cdot 10^{-34} \text{ J s}$$
$$m = 1.67 \cdot 10^{-27} \text{ J s}^2/\text{m}^2$$
$$k_B = 1.38 \cdot 10^{-23} \text{ J/K}$$
$$\Delta\mu = 7.24 \cdot 10^{-19} \text{ J.}$$

Comment: In fact, the hydrogen in the low-density regions of the interstellar space exists mainly in atomic form due to photodissociation under the influence of UV light. For details, see: Stecher and Williams, The Astrophysical Journal, Vol. 149, L29 (1967). (**1 point**)

2 Conformational changes in butane (5 points)

A butane molecule (C_4H_{10}) can take one of three conformations, A, B, or C, see Fig. 1. The molecule changes its conformation according to the following reaction,

$$A \rightleftharpoons B \rightleftharpoons C,$$

taking place in equilibrium, in a gas state that can be considered as ideal. The conformations A, B, and C have chemical potentials μ_A, μ_B and μ_C, respectively, and all conformations have the same mass m.
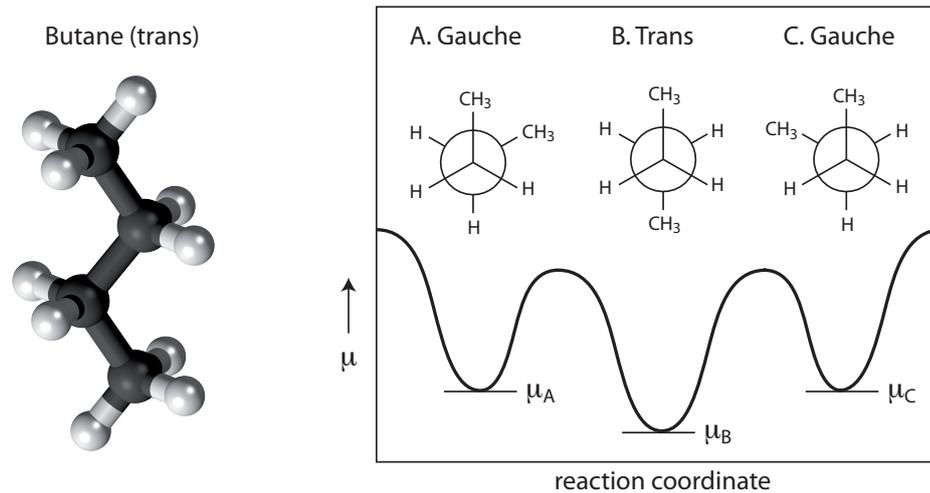

Figure 1: Conformational changes in butane. The three diagrams inside the graph show the view along the axis connecting the two central C atoms.

a) Write down the grand canonical partition function $\mathcal{Z}(\mu_A, \mu_B, \mu_C, V, T)$. (**1 point**)

b) Calculate the mean number of molecules in conformation i, $\langle N_i \rangle$, for $i = A, B, C$ from suitable derivatives of the grand canonical partition function. (**1 point**)

c) The reaction energy of the first part of the reaction is given by $\Delta\mu_1 = \mu_B - \mu_A$ and the reaction energy of the second reaction by $\Delta\mu_2 = \mu_C - \mu_B$. Express the fraction $\langle N_C \rangle / \langle N_A \rangle$ in terms of $\Delta\mu_1$ and $\Delta\mu_2$. (**1 point**)

d) Explain why the result of part (c) does not depend on μ_B. (**2 points**)

3 Thermodynamic potentials (6 points)

Consider the thermodynamic potentials depending on three state variables. Legendre transforms replace these variables by their conjugates.

a) How many different thermodynamic potentials can be defined? (**1 point**)

b) Starting from the Helmholtz free energy $F(T, V, N) = U - TS$, perform a Legendre transform to obtain the Gibbs free energy $G(T, p, N)$. (**1 point**)

c) Again starting from the Helmholtz free energy, perform a Legendre transform to obtain the grand potential $\Omega(T, V, \mu)$. (**1 point**)

d) Derive from $G(T, p, N)$ the potential $L(T, p, \mu)$ (which has no name because it is rarely used). Verify your result using the grand potential $\Omega(T, V, \mu)$. (**2 points**)

e) Explain your result for $L(T, p, \mu)$ in the view of the Gibbs-Duhem equation. (**1 point**)