Statistical Mechanics WS 2013/14 Sheet 6

Please hand in your solutions (in pairs) before the Monday lecture.

Problem 1 : Thermodynamic potentials, Maxwell relations and response functions (25 points)

a) (8 points) Using the respective total diferential show that

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T}$$

$$\left(\frac{\partial S}{\partial p}\right)_{H,N} = -\frac{V}{T}$$

$$\left(\frac{\partial T}{\partial V}\right)_{F,N} = -\frac{p}{S}$$

$$\left(\frac{\partial T}{\partial p}\right)_{G,N} = \frac{V}{S}$$

b) (5 points) Express the following response functions as a second derivative of an appropriate thermodynamic potential (N=const)

heat capacity at constant volume

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_{V,N} = T\left(\frac{dS}{dT}\right)_V$$

heat capacity at constant pressure

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_{p,N} = T\left(\frac{dS}{dT}\right)_p$$

isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$

adiabatic compressibility

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,N}$$

thermal expansion coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

c) (12 points) The second derivatives of Gibb's Free energy (at N=const.) give three independent relations which can be combined to give the other second derivatives. Express all of the above response functions as combinations of the second derivatives of Gibb's Free energy.

Problem 2 : Heat and work (12 points)

A container is composed of two, separated compartments, a and b filled with two ideal, but different gases. The separating wall between the two compartments is movable and allows heat exchabge (but not particle exchange). Gas a and b have initial volume V_a , V_b, respectively and number of particles N_a and N_b, respectively.

a) (6 points) The pressure is the same for both gases $p = p_a = p_b$ but the temperatures are different $T_a \neq T_b$. Calculate the entropy change between the initial and the equilibrium state. Calculate the change in energy ΔU_a , enthalpy ΔH_a and the work ΔW_a done on subsystem a .

b) (6 points) Pressure and initial temperature are the same for both gases $p = p_a = p_b$ and $T = T_a = T_b$ but the initial voumes are different $V_a \neq V_b$. Now the separating wall is removed. Calculate the change in total entropy, change in energy ΔU_a , enthalpy ΔH_a and the work ΔW_a done on subsystem a (the process is isobaric).

Problem 3 : Heat capacity (8 points)

An ideal gas has a mass of 28g/mol. One mol of gas is expanded adiabatically such that its volume doubles. The temperatures before and after the expansion are T_{before} =298K and T_{after} =248K and the pressures are p_{before}= 2030 mbar and p_{after}= 820 mbar.

a) (2 points) Calculate the molar heat capacities $C_{V,m}$ and $C_{p,m}$

b) (2 points) Calculate the change in internal energy ΔU and the change in enthalpy ΔH.

c) (2 points) The speed of sound v_s is related to the heat capacity via $v_s = \sqrt{\frac{RT\gamma}{M_m}}$ where M_m is the molar mass of the gas, R is the gas constant 8,314 J mol^{-1} K^{-1}, and $\gamma = \frac{C_{p,m}}{C_{V,m}}$. Calculate the speed of sound in the ideal gas before and after the expansion.

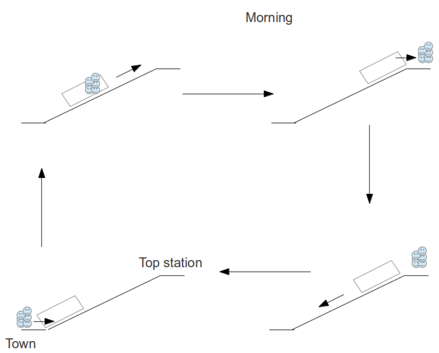
d) (4 points) What is the ratio of the number of gas atoms with velocity v_s to the number of gas atoms at most probable velocity?

Problem 4 : Soup (20 points)

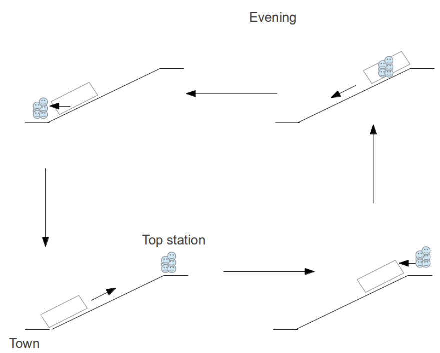
A friend claims that soup heated in a pot "stores" heat longer than soup heated in a microwave oven. Discuss your friend's opinion considering the heat capacity as a measure for the soup's ability to "store heat". Assume that the soup consists only of diatomic molecules. Furthermore, assume that the microwave oven only excites rotational degrees of freedom and heating in a pot leads only to vibrational excitations. Calculate the rotational and the vibrational heat capacity, C_{rot} and C_{vib} from the respective partition functions using $\langle E \rangle = kT^2 \frac{\partial}{\partial T} \ln Z$ with k : Boltzmann constant, T: temperature, h : Planck constant ν : vibrational frequency. You can use the rigid rotor and harmonic oscillator approximations. (Note that the partition function Z has to be related to the molecular partition functions z of the N soup molecules.)

Problem 5 : Cyclic processes (10 points)

In a small town at the foot of a small mountain many of the citizens work at a company on the top of the hill. A "cycle train" connects the town and the company building. The "cycle train" can be driven by its passengers cycling, i.e. using pedals like on a bicycle. In the morning N passengers enter the train that allows it to go uphill. At the upper station, the N passengers leave the train and go to work. The train, now empty, except for the conductor, goes downhill, back to town. In the evening the process is reversed: the empty train goes uphill (now driven by an external energy source, e.g. electricty). The passengers enter the train. They are tired from work and appreciate that the train runs downhill without them cycling. Back at the town station, the passengers leave the train.



a)



b)

Fig. 1: Cycle train transporting passengers uphill in the morning and back in the evening.

a) (4 points) What are the efficiencies, i.e. ratio of climbing work to passenger uptake, for the process in the morning and the reverse one in the evening.

b) (6 points) Would it be more efficient to transport every passenger individually? A single passenger can cycle uphill, however it takes longer. (For safety reasons the conductor has to be on the train)

Problem 6 : Guggenheim scheme / thermodynamic square (5 points)

Give an example for how the Guggenheim scheme works

a) (1 points) for differentials

b) (1 points) for coefficients

c) (3 points) find a nice new mnemonic for the Guggenheim scheme