Exercise 11

Name:	Matriculation number:
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The exercise is due on Wednesday, July 11, 8 am.

11.1 Text book

Read sections 7.1 and 7.2 in G.H. Findenegg, T. Hellweg „Statistische Thermodynamik"

11.2 Rotational-vibrational spectrum of $^{1}H^{127}I$

The absorption lines of the rotational-vibrational spectrum of $^{1}H^{127}I$ occur at the following wavenumbers

- P-Branch: 2275.90 cm^{-1}, 2263.05 cm^{-1}, 2250.20 cm^{-1}, 2237.35 cm^{-1},...
- R-Branch: 2301.60 cm^{-1}, 2314.45 cm^{-1}, 2327.30 cm^{-1}, 2340.14 cm^{-1},...

(a) Calculate the characteristic vibrational temperature Θ_{vib} and the characteristic rotational temperature Θ_{rot} of $^{1}H^{127}I$. Explain how you arrived at the results.

(b) From the characteristic vibrational temperature Θ_{vib}, calculate the ground state vibrational frequency and the bond force constant k.

(c) From the characteristic rotational temperature Θ_{rot}, calculate the moment of inertia and the bond length r.

(d) Compare your results with tabulated values for $^{1}H^{127}I$.

11.3 Mixing CO and O_2

Consider a container of volume $V = 0.05\text{m}^3$ which is split into two compartments with volumes $V_1 = V_2 = 0.025\text{m}^3$ by a wall. The first compartment is filled with 1 mol of ^{16}O-^{16}O. The second compartment is filled with 2 mol of ^{12}C-^{16}O. The temperature is 300 K. The characteristic temperatures for vibration and rotation of the two substances are

- ^{12}C-^{16}O: $\Theta_{\text{vib}} = 3112$ K and $\Theta_{\text{rot}} = 2.766$ K
- ^{16}O-^{16}O: $\Theta_{\text{vib}} = 2265$ K and $\Theta_{\text{rot}} = 2.068$ K

(a) Calculate the pressure in the two compartments.

(b) Calculate the free energy of mixing.

(c) Calculate the partial pressures of ^{16}O-^{16}O and of ^{12}C-^{16}O after mixing.

(d) Calculate the chemical potential of ^{16}O-^{16}O and of ^{12}C-^{16}O in the mixture (*Hint: Treat it as a monoatomic ideal gas*).

11.4 Entropy of mixing II

Sketch the entropy of mixing of two ideal gases A and B with respect to the molar fraction of A χ_A. Calculate the slope of $d\Delta_{mix}S/d\chi_A$ at $\chi_A = 0,\ 0.5$ and 1.

11.5 Equilibrium constant

For the reaction $N_2 + O_2 \rightleftharpoons 2\ NO$ calculate all terms of the equilibrium constant K

$$K = f_{trans} \cdot f_{rot} \cdot f_{vib} \cdot f_{elec} \cdot f_{nuc} \cdot \exp(-\Delta E_0/k_B T) \tag{1}$$

at $T = 298$ K, 500 K and 1000 K. The electronic ground state of NO is 2-fold of O_2 3-fold degenerated. The molecule specific constants can be obtained from Table 5.1 in G.H. Findenegg, T. Hellweg „Statistische Thermodynamik".