Exercise 10

NAME:	MATRICULATION NUMBER:
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The exercise is due on Wednesday, July 4, 8 am.

10.1 Text book

Read sections 6.1 and 6.4 in G.H. Findenegg, T. Hellweg „Statistische Thermodynamik"

10.2 Occupation of the vibrational states of I_2

From the Raman spectrum of the diatomic Iodine at room temperature, the vibrational wave number is $\tilde{\nu_0} = 21460\text{m}^{-1}$.
Determine:

(a) the oscillation frequency.

(b) the characteristic temperature Θ_{vib}.

(c) the ratio $\frac{\Theta_{vib}}{T}$.

(d) the partition function z_{vib}.

(e) the occupation probability N_v/N of the first 4 vibrational states.

10.3 Vibrational contribution to the entropy

Plot the contribution to the entropy from a given vibrational mode as function of the quantity

$$x = \frac{hv}{k_B T}$$

for $T = 298K$ and $T = 1000K$.

10.4 Relative populations of the rotational energy levels

The relative populations of the rotational energy levels of an unsymmetric diatomic molecule are given as

$$p_J = \frac{N_J}{N} \quad \sim \quad (2J+1)\exp\left[-J(J+1)\frac{\Theta_{\text{rot}}}{T}\right]. \tag{1}$$

(a) Show that the level with the highest relative population is

$$J_{\text{max}} = \sqrt{\frac{T}{2\Theta_{\text{rot}}}} - \frac{1}{2}$$

(b) Plot J_{max} as a function of the temperature for

- $^1\text{H}^{19}\text{F}$: $\Theta_{\text{rot}} = 60.875$ K
- $^1\text{H}^{35}\text{Cl}$: $\Theta_{\text{rot}} = 15.021$ K
- $^1\text{H}^{81}\text{Br}$: $\Theta_{\text{rot}} = 12.012$ K
- $^1\text{H}^{127}\text{I}$: $\Theta_{\text{rot}} = 9.246$ K

10.5 Rotational-vibrational spectrum of CO

In this exercise, you will calculate the rotational vibrational spectrum of $^{12}C^{16}O$ for the vibrational transition $\nu = 0 \rightarrow \nu' = 1$. The characteristic temperatures for vibration and rotation are

$$\begin{aligned} \Theta_{\text{vib}} &= 3112 \text{ K} \\ \Theta_{\text{rot}} &= 2.766 \text{ K} \end{aligned} \tag{2}$$

(a) Calculate the frequency of the fundamental vibrational transition $(\nu = 0, J = 0) \rightarrow (\nu' = 1, J' = 0)$. Is this transition observed in the spectrum? Why?

(b) Calculate and plot the relative populations of the rotational states in the vibrational ground state.

(c) Calculate the frequencies in the R-Branch.

(d) Calculate the frequencies in the P-Branch .

(e) Sketch the spectrum.

(f) Do you expect a different line pattern in a spectrum of natural CO? Why?

10.6 Entropy of mixing

Calculate $\Delta_{mix}S$ for the mixing of two ideal gases A and B with molecule numbers N_A and N_B and volumes V_A and V_B into a total volume of $V = V_A + V_B$. Consider:

(a) indistinguishable particles of different species.

(b) distinguishable particles of different species.

(c) indistinguishable particles of only one species $(A = B)$.

(d) distinguishable particles of only one species.

How consistent is your result?