Solutions Statistical Thermodynamics Tutorial 3

Exercise 6 Rotation partition functions

The expressions depend on the type of molecule. Here we assume that we can the high temperature approximation in all cases.

a) CO is a non-symmetric linear rotor: $\sigma = 1$

$$q^R = \frac{1}{hc\tilde{B}\beta}$$

b) CO_2 is a symmetric linear rotor: $\sigma = 2$

$$q^R = \frac{1}{hc2\tilde{B}\beta}$$

c) H_2O is a asymmetric non-linear rotor: $\sigma = 2$

$$q^R = \frac{1}{2}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}\tilde{C}}\right)^{1/2}$$

d) CH_4 is a spherical rotor: $\sigma = 12$ and $\tilde{A} = \tilde{B} = \tilde{C}$

$$q^R = \frac{1}{12}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}^3}\right)^{1/2} = \frac{1}{12}\left(\frac{kT}{hc\tilde{A}}\right)^{3/2}(\pi)^{1/2}$$

e) NH_3 is a symmetric rotor: $\sigma = 3$ and $\tilde{B} = \tilde{C}$

$$q^R = \frac{1}{3}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{\tilde{A}\tilde{B}^2}\right)^{1/2}$$

Exercise 7 A symmetric non-linear rotor

a) For high temperature, many J are occupied and we can use the approximation

$$q^R = \sum_{J=0}^{\infty}\sum_{K=-J}^{J}(2J+1)\exp\left[-\beta hc\tilde{B}J(J+1) - \beta hc(\tilde{A}-\tilde{B})K^2\right] \approx$$
$$\int_0^{\infty}\mathrm{d}J(2J+1)\exp(-NJ(J+1))\int_{-\infty}^{\infty}\mathrm{d}K\exp(-MK^2) \quad \text{with}$$
$$N = \beta hc\tilde{B} \quad \text{and} \quad M = \beta hc(\tilde{A}-\tilde{B}).$$

We substitute

$$x^2 = MK^2 \qquad \frac{\mathrm{d}K}{\mathrm{d}x} = \frac{1}{\sqrt{M}},$$

which gives

$$q^R = \int_0^{\infty}\mathrm{d}J(2J+1)\exp(-NJ(J+1))\int_{-\infty}^{\infty}\mathrm{d}x\frac{\mathrm{d}K}{\mathrm{d}x}\exp(-x^2) =$$
$$\int_0^{\infty}\mathrm{d}J(2J+1)\exp(-NJ(J+1))\frac{1}{\sqrt{M}}\int_{-\infty}^{\infty}\mathrm{d}x\exp(-x^2) =$$
$$\int_0^{\infty}\mathrm{d}J(2J+1)\exp(-NJ(J+1))\sqrt{\frac{\pi}{M}} = \sqrt{\frac{\pi}{M}}\frac{-1}{N}\int_0^{\infty}\mathrm{d}J\frac{\mathrm{d}\exp(-NJ(J+1))}{\mathrm{d}J} =$$
$$\sqrt{\frac{\pi}{M}}\frac{-1}{N}\left[\exp(-NJ(J+1))\right]_0^{\infty} = \sqrt{\frac{\pi}{M}}\frac{1}{N} = \sqrt{\frac{\pi}{\beta hc(\tilde{A}-\tilde{B})}}\frac{1}{\beta hc\tilde{B}} \quad \text{such that}$$
$$q^R = \left(\frac{1}{\beta hc}\right)^{\frac{3}{2}}\left(\frac{\pi}{\tilde{B}^2(\tilde{A}-\tilde{B})}\right)^{\frac{1}{2}}.$$

b) If $\tilde{A} >> \tilde{B}$ we recover the expression from Atkins.This corresponds to a relatively large rotational constant for rotations around the axis of symmetry. This we find for long molecules along this axis with a large mass at the extremes.

c) The characteristic rotational temperature θ^R is defined as the temperature for which holds $q^R(T = \theta^R) = 1$ in the high temperature approximation.

$$\left(\frac{k\theta^R}{hc}\right)^{\frac{3}{2}} \left(\frac{\pi}{\tilde{B}^2(\tilde{A} - \tilde{B})}\right)^{\frac{1}{2}} = 1,$$

$$\left(\frac{k\theta^R}{hc}\right)^{\frac{3}{2}} = \left(\frac{\tilde{B}^2(\tilde{A} - \tilde{B})}{\pi}\right)^{\frac{1}{2}},$$

$$\left(k\theta^R\right)^3 = \frac{(hc)^3\tilde{B}^2(\tilde{A} - \tilde{B})}{\pi}, \quad \text{and hence}$$

$$\theta^R = \frac{hc}{k}\sqrt[3]{\frac{\tilde{B}^2(\tilde{A} - \tilde{B})}{\pi}}$$

Exercise 8 Buckminster fullerene

a) The ideal gas law states $PV = nRT$, which gives

$$q^T = \frac{V}{\Lambda^3} = \frac{RT}{P\Lambda^3}$$

The mass of C_{60} is $m = 60 \cdot 12 \cdot u$ (*convert u into kg*), which gives

$$\Lambda = \sqrt{\frac{h^2}{2\pi mkT}} = \sqrt{\frac{(6.6 \cdot 10^{-34})^2}{2\pi \cdot 60 \cdot 12 \cdot 1.66 \cdot 10^{-27} \cdot 1.38 \cdot 10^{-23} \cdot 1000}} = 2.05 \text{ pm, and}$$

$$q^T = \frac{8.31451 \cdot 1000}{1 \cdot 10^5 \cdot (2.05 \cdot 10^{-12})^3} = 9.65 \cdot 10^{33}.$$

b) The total number of degrees of freedom is $3N = 3 \times 60 = 180$.
The translational and rotational degrees of freedom are both 3, which gives $N_V = 180 - 3 - 3 = 174$ vibrational degrees of freedom.

c) All vibration have the same frequency. The total vibration partition function is therefore:

$$q^V = \prod_{i=1}^{N_V} \frac{1}{1 - \exp(-\beta\epsilon_i)} = \left(\frac{1}{1 - \exp(-\beta\epsilon)}\right)^{174}, \quad \text{with}$$

$$\beta\epsilon = \frac{hc\nu}{kT} = \frac{6.6 \cdot 10^{-34} \cdot 3 \cdot 10^{10} \cdot 1000}{1.38 \cdot 10^{-23} \cdot 1000} = 1.434, \quad \text{and hence}$$

$$q^V = \left(\frac{1}{1 - \exp(-1.434)}\right)^{174} = 3.6 \cdot 10^{20}$$

d) C_{60} is a spherical rotor $\tilde{A} = \tilde{B} = \tilde{C}$.

e) The rotation point group of this molecule is $I = \{E,\ 12C_5,\ 12C_5^2,\ 20C_3\ en\ 15C_2\}$. [1]
The order of this group, the number of symmetry elements, is 60 and hence the symmetry number σ=60.

As an estimate for the characteristic rotational temperature θ^R, we use the expression for a linear rotor

$$\theta^R = \frac{hcB}{k} = \frac{6.63 \cdot 10^{-34} \cdot 3.00 \cdot 10^8 \cdot 2.8 \cdot 10^{-1}}{1.38 \cdot 10^{-23}} = 4.0 \cdot 10^{-3} \text{ K}.$$

We can safely use the high temperature approximation.

$$q^R = \frac{1}{\sigma}\left(\frac{1}{\beta hc}\right)^{\frac{3}{2}} \left(\frac{\pi}{\tilde{A}^3}\right)^{\frac{1}{2}} = \frac{1}{60}\left(\frac{1.38 \cdot 10^{-23} \cdot 1000}{6.63 \cdot 10^{-34} \cdot 3.00 \cdot 10^8}\right)^{\frac{3}{2}} \left(\frac{\pi}{(2.8 \cdot 10^{-1})^3}\right)^{\frac{1}{2}} = 3.64 \cdot 10^6.$$

[1] C_{60} consists of 12 regular pentagons surrounded by regular hexagons and 20 regular hexagons surrounded by three regular pentagons and 3 regular hexagons. This gives the following symmetry elements: the identity operator (E), 12 fivefold rotation axes ($12C_5$) and 12 fivefold rotation axes through the center of the pentagons ($12C_5^2$), 20 threefold rotation axes through the center of the hexagons ($20C_3$) and 15 twofold rotation axes through the center of the edges of the surrounding hexagons.

As a consequence of the small rotational constant, the rotational partition function is very large. The contribution by the vibrations is however even larger (see answer at (c)), despite the high vibrational wavenumber of 1000 cm^{-1}. The reason for this is the large number of vibrational degrees of freedom $N^V = 174$.