

Problem Set 11

P6

- a) 1 b) 2 c) 2 d) 12 e) 2

P12

- a) First, solving for the rotational constant (B):

$$B = \frac{h}{8\pi^2 c I} = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 (3.00 \times 10^{10} \text{ cm s}^{-1})(2.65 \times 10^{-47} \text{ kg m}^2)} = 10.57 \text{ cm}^{-1}$$

with B, the temperature (T) at which the spectrum was obtained can be determined as follows:

$$T = \frac{(2J+1)^2 hcB}{2k} = \frac{(9)^2 (6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(10.57 \text{ cm}^{-1})}{2(1.38 \times 10^{-23} \text{ J K}^{-1})} = 616 \text{ K}$$

- b) Using the first expression provided in part (a) to isolate the rotational level J:

$$T = \frac{(2J+1)^2 hcB}{2k}$$

$$\left(\frac{2kT}{hcB}\right) = (2J+1)^2$$

$$\frac{\left(\frac{2kT}{hcB}\right)^{\frac{1}{2}} - 1}{2} = J$$

$$\frac{\left(\frac{2(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(10.57 \text{ cm}^{-1})}\right)^{\frac{1}{2}} - 1}{2} \cong 5 = J$$

c) For the heavier Cl isotope, the moment of inertia will increase leading to a decrease in the rotational constant. Quantitatively:

$$\frac{B_{37}}{B_{35}} = \frac{\left(\frac{h}{8\pi^2 c \mu_{37} r^2}\right)}{\left(\frac{h}{8\pi^2 c \mu_{35} r^2}\right)} = \frac{\mu_{35}}{\mu_{37}} = \frac{\frac{m_H m_{35}}{m_H + m_{35}}}{\frac{m_H m_{37}}{m_H + m_{37}}} \cong \frac{35}{37} = 0.998$$

$$B_{37} = 0.998 B_{35} = 0.998(10.57 \text{ cm}^{-1}) = 10.55 \text{ cm}^{-1}$$

With this rotational constant, the temperature at which the $J = 4$ state is most populated becomes:

$$T = \frac{(2J+1)^2 hcB}{2k} = \frac{(9)^2 (6.626 \times 10^{-34} \text{ J s}) (3.00 \times 10^{10} \text{ cm s}^{-1}) (10.55 \text{ cm}^{-1})}{2(1.38 \times 10^{-23} \text{ J K}^{-1})} = 615 \text{ K}$$

This result is essentially identical to the result for the lighter Cl isotope. Therefore, at 1000 K we expect the $J = 5$ level to also be the most populated.

P15

- a) Using the moment of inertia, the rotational constants can be determined. Since all three moments of inertia are equal, the rotational constants will be equal as well. Paying careful attention to units, the rotational constants are:

$$B_a = B_b = B_c = \frac{h}{8\pi^2 c I} = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 (3.00 \times 10^8 \text{ m s}^{-1}) (5.31 \times 10^{-47} \text{ kg m}^2)} = 5.27 \text{ cm}^{-1}$$

- b) If the high-temperature limit is valid $T > \Theta_R$. Determining Θ_R :

$$\Theta_R = \frac{B}{k} = \frac{5.27 \text{ cm}^{-1}}{0.695 \text{ cm}^{-1} \text{ K}^{-1}} = 7.58 \text{ K}$$

The boiling temperature of CH₄ (112 K) is much greater than the rotational temperature; therefore, the high-temperature limit is appropriate.

P17

At 300 K for IF:

$$q = \frac{1}{1 - e^{-\beta hc \tilde{\nu}}} = \frac{1}{1 - e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s})(610 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}}} \cong 1.06$$

$$p_n = \frac{e^{-\beta hc n \tilde{\nu}}}{q}$$

$$p_0 = \frac{1}{q} = 0.943$$

$$p_1 = \frac{e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s})(610 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}}}{q} = 0.051$$

$$p_2 = \frac{e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s})(2)(610 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}}}{q} = 0.003$$

Repeating the above calculations for $T = 3000 \text{ K}$:

$$q = 3.94$$

$$p_0 = 0.254$$

$$p_1 = 0.189$$

$$p_2 = 0.141$$

Repeating the above calculations for IBr at 300 and 3000 K:

300 K		3000 K	
q	1.38	q	8.26
p_0	0.725	p_0	0.121
p_1	0.199	p_1	0.106
p_2	0.054	p_2	0.094

The probability of occupying a specific energy level is greater for IBr relative to IF for a given temperature since the energy-level spacings are smaller for IBr.

P19

The total vibrational partition function is the product of partition functions for each vibrational degree of freedom:

$$\begin{aligned}
 q_{V,\text{total}} &= (q_{V,1})(q_{V,2})(q_{V,3}) \\
 &= \left(\frac{1}{1 - e^{-\beta h c \tilde{\nu}_1}} \right) \left(\frac{1}{1 - e^{-\beta h c \tilde{\nu}_2}} \right) \left(\frac{1}{1 - e^{-\beta h c \tilde{\nu}_3}} \right) \\
 &= \left(\frac{1}{1 - e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(519 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}}} \right) \left(\frac{1}{1 - e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(1151 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}}} \right) \\
 &\quad \times \left(\frac{1}{1 - e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(1361 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}}} \right) \\
 &= 1.09
 \end{aligned}$$

P21

Under what conditions would you expect the resulting expression for q_V to be applicable?

$$\begin{aligned}
 q_V &\approx \int_0^{\infty} e^{-\beta h c n \tilde{\nu}} dn = \int_0^{\infty} e^{-\alpha n} dn \quad \{\alpha = \beta h c \tilde{\nu}\} \\
 &= \frac{-e^{-\alpha n}}{\alpha} \Big|_0^{\infty} = \frac{1}{\alpha} = \frac{1}{\beta h c \tilde{\nu}}
 \end{aligned}$$

This expression for q_V is expected to be valid in the high-temperature limit where many vibrational states will be populated thereby justifying evaluation of the partition function by integration over n .

P23

a)

$$q = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta(\hbar\omega^0 n - \hbar c \tilde{\chi} \tilde{\nu} n^2)} = \sum_n e^{-\beta \hbar \omega^0 n} e^{\beta \hbar c \tilde{\chi} \tilde{\nu} n^2}$$

Performing a series expansion for the second exponential term, and keeping only the first two terms since the exponent will be small for limited anharmonicity:

$$\begin{aligned} q &= \sum_n e^{-\beta \hbar \omega^0 n} e^{\beta \hbar c \tilde{\chi} \tilde{\nu} n^2} = \sum_n e^{-\beta \hbar \omega^0 n} (1 + \beta \hbar c \tilde{\chi} \tilde{\nu} n^2) \\ &= \sum_n e^{-\beta \hbar \omega^0 n} + \sum_n (\beta \hbar c \tilde{\chi} \tilde{\nu} n^2) e^{-\beta \hbar \omega^0 n} \\ &= q_{\text{harm}} + \beta \hbar c \tilde{\chi} \tilde{\nu} \sum_n n^2 e^{-\beta \hbar \omega^0 n} \\ &= q_{\text{harm}} + \beta \hbar c \tilde{\chi} \tilde{\nu} \sum_n n^2 (e^{-\beta \hbar \omega^0})^n \end{aligned}$$

Using series expression provided in the problem to evaluate the second term in the preceding expression:

$$\begin{aligned} q &= q_{\text{harm}} + \beta \hbar c \tilde{\chi} \tilde{\nu} \sum_n n^2 (e^{-\beta \hbar \omega^0})^n = q_{\text{harm}} + (\beta \hbar c \tilde{\chi} \tilde{\nu}) \left[\frac{e^{-2\beta \hbar \omega^0} + e^{-\beta \hbar \omega^0}}{(1 - e^{-\beta \hbar \omega^0})^3} \right] \\ &= q_{\text{harm}} + (\beta \hbar c \tilde{\chi} \tilde{\nu}) (q_{\text{harm}}^3) (e^{-2\beta \hbar \omega^0} + e^{-\beta \hbar \omega^0}) \\ &= q_{\text{harm}} (1 + (\beta \hbar c \tilde{\chi} \tilde{\nu}) (q_{\text{harm}}^2) (e^{-2\beta \hbar \omega^0} + e^{-\beta \hbar \omega^0})) \end{aligned}$$

b) First, the partition function in the harmonic-oscillator limit is:

$$q_{\text{harm}} = \frac{1}{1 - e^{-\beta \hbar \omega^0}} = \frac{1}{1 - e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(4401.2 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}}} = 1.0018$$

Next, evaluating the expression for the anharmonic oscillator:

$$\begin{aligned} q_{\text{anharm}} &= q_{\text{harm}} (1 + (\beta \hbar c \tilde{\chi} \tilde{\nu}) (q_{\text{harm}}^2) (e^{-2\beta \hbar \omega^0} + e^{-\beta \hbar \omega^0})) \\ &= (1.0018) \left(1 + \left(\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(121.3 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})} \right) \right. \\ &\quad \left. \times \left(e^{-\frac{2(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(4401.2 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}} + e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(4401.2 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}} \right) \right) \\ &= (1.0018) (1 + (0.175) (3.12 \times 10^{-6} + 1.76 \times 10^{-3})) \\ &= 1.0021 \end{aligned}$$

The percent error is :

$$\% \text{error} = \frac{q_{\text{anharm}} - q_{\text{harm}}}{q_{\text{anharm}}} \times 100\% = 0.03\%$$

P25

$$\begin{aligned}q_{\text{z}} &= \sum_{\text{n}} g_{\text{n}} e^{-\beta \epsilon_{\text{n}}} = 9e^{-0} + 7e^{-\beta(415.9 \text{ cm}^{-1})} + 5e^{-\beta(704.0 \text{ cm}^{-1})} + 3e^{-\beta(881.1 \text{ cm}^{-1})} + e^{-\beta(978.1 \text{ cm}^{-1})} \\&= 9 + 7e^{-\frac{415.9 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 5e^{-\frac{704.0 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + 3e^{-\frac{881.1 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} + e^{-\frac{978.1 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} \\&= 9 + 7(0.134) + 5(0.033) + 3(0.014) + 0.009 \\q_{\text{z}} &= 10.2\end{aligned}$$

P27

a)

$$\begin{aligned}q_{\text{z}} &= \sum_{\text{n}} g_{\text{n}} e^{-\beta \epsilon_{\text{n}}} = 2e^{-\beta 0} + 2e^{-\beta(121 \text{ cm}^{-1})} \\&= 2 + 2e^{-\frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298 \text{ K})}} \\&= 3.12\end{aligned}$$

b)

$$\begin{aligned}q_{\text{z}} &= 3 = 2e^{-\beta 0} + 2e^{-\beta(121 \text{ cm}^{-1})} \\3 &= 2 + 2e^{-\frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})T}} \\0.5 &= e^{-\frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})T}} \\0.693 &= \frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})T} \\T &= \frac{121 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(0.693)} \\T &= 251 \text{ K}\end{aligned}$$

P30

- a) To ensure that the wavefunction remain symmetric with exchange, the rotational part of the wavefunction must be even; therefore, only even J states (0, 2, 4, 6, ...) are allowed.
- b) Since $T \gg \Theta_R$ (i.e., 298 K \gg 0.56 K) the high-temperature approximation can be applied in evaluating the rotational partition function:

$$\begin{aligned}q_R &= \frac{1}{\sigma \beta \hbar c B} = \frac{kT}{\sigma \hbar c B} \\ &= \frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{2(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s}^{-1})(0.390 \text{ cm}^{-1})} \\ &= 265\end{aligned}$$

This calculation illustrates that there are roughly 265 rotational states available to CO_2 at 298 K; therefore, the high-temperature expression for the rotational partition function is more than reasonable.