

PS10 KEY

1. For N_2 at 77.3 K, 1 atm, in a 1-cm^3 container, calculate the one-molecule translational partition function and ratio of this partition function to the number of N_2 molecules present under these conditions.

$$q_T(N_2) = \frac{V}{\Lambda^3}$$

$$\Lambda = \left(\frac{h^2}{2\pi m k T} \right)^{1/2} = \left(\frac{(6.626 \times 10^{-34} \text{ J s})^2}{2\pi \left(\frac{0.028 \text{ kg mol}^{-1}}{N_A} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (77.3 \text{ K})} \right)^{1/2} = 3.75 \times 10^{-11} \text{ m}$$

$$q_T(N_2) = \frac{V}{(3.75 \times 10^{-11} \text{ m})^3} = \frac{(1 \text{ cm}^3)(10^{-6} \text{ m}^3 \text{ cm}^{-3})}{(3.75 \times 10^{-11} \text{ m})^3} = 1.90 \times 10^{25}$$

Next, the number of molecules (N) present at this temperature is determined using the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(1 \text{ atm})(1.00 \times 10^{-3} \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(77.3 \text{ K})} = 1.58 \times 10^{-4} \text{ mol}$$

$$N = n \times N_A = 9.49 \times 10^{19} \text{ molecules}$$

The ratio is:

$$\frac{q_T}{N} = \frac{1.90 \times 10^{25}}{9.49 \times 10^{19}} = 2.00 \times 10^5$$

2. Which species will have the largest rotational partition function: H_2 , HD , or D_2 ? Which of these species will have the largest translational partition function assuming that volume and temperature are identical? When evaluating the rotational partition functions, you can assume that the high-temperature limit is valid.

With the high-temperature limit, the rotational partition function (q_R) is equal to:

$$q_R = \frac{1}{\sigma \beta B}$$

Since $\beta = 1/k_B T$ will be the same for all three species (the comparison is done at a given temperature), and assuming that the bond length is the same for all species then the ratio of rotational partition functions for any two species can be reduced to:

$$\frac{q_R(1)}{q_R(2)} = \frac{\left(\frac{1}{\sigma_1 \beta B_1}\right)}{\left(\frac{1}{\sigma_2 \beta B_2}\right)} = \frac{\sigma_2 B_2}{\sigma_1 B_1} = \frac{\sigma_2 \left(\frac{h}{8\pi^2 c \mu_2 r^2}\right)}{\sigma_1 \left(\frac{h}{8\pi^2 c \mu_1 r^2}\right)} = \frac{\sigma_2 \mu_1}{\sigma_1 \mu_2}$$

The reduced masses and symmetry number for the three species of interest are:

molecule	σ	μ
H ₂	2	m _H /2
D ₂	2	m _H
HD	1	2 m _H /3

With these values, the ratio of rotational partition functions is readily calculated:

$$\frac{q_R(D_2)}{q_R(H_2)} = \frac{(\sigma_{H_2}) \mu_{D_2}}{(\sigma_{D_2}) \mu_{H_2}} = \frac{(2) m_H}{(2) m_H / 2} = 2$$

$$\frac{q_R(HD)}{q_R(H_2)} = \frac{(\sigma_{H_2}) \mu_{HD}}{(\sigma_{HD}) \mu_{H_2}} = \frac{(2)^2 m_H / 3}{(1) m_H / 2} = \frac{8}{3}$$

Therefore $q_R(HD) > q_R(D_2) > q_R(H_2)$.

Performing the same analysis for the translational partition function, we begin by reducing the ratio of translational partition functions for two species:

$$\frac{q_T(1)}{q_T(2)} = \frac{\frac{V}{\Lambda^3(1)}}{\frac{V}{\Lambda^3(2)}} = \frac{\Lambda^3(2)}{\Lambda^3(1)} = \left[\frac{\left(\frac{h^2}{2\pi m_2 kT}\right)}{\left(\frac{h^2}{2\pi m_1 kT}\right)} \right]^{3/2} = \left(\frac{m_1}{m_2} \right)^{3/2}$$

The species with the largest mass will have the largest translational partition function at equivalent temperature and volume. Therefore $q_T(D_2) > q_T(HD) > q_T(H_2)$.

3. For IF ($\tilde{\nu} = 610 \text{ cm}^{-1}$) calculate the vibrational partition function and populations in the first three vibrational energy levels for $T = 300$ and 3000 K . Repeat this calculation for IBr ($\tilde{\nu} = 269 \text{ cm}^{-1}$). Compare the probabilities for IF and IBr. Can you explain the differences between the probabilities of these molecules? For convenience, since it is really the probabilities that matter, you can ignore the zero point energy contribution in the partition functions.

At 300 K for IF:

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

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

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

$$p_1 = \frac{e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s})(2)(610 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}}}{q} = 0.051$$

$$p_2 = \frac{e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm}^{-1} \text{ s})(3)(610 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}}}{q} = 0.003$$

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.

4. a) In the rotational spectrum of H^{35}Cl ($I = 2.65 \times 10^{-47} \text{ kg m}^2$), the transition corresponding to the $J = 4$ to $J = 5$ transition is the most intense. At what temperature was the spectrum obtained?

b) At 1000 K, which rotational transition of H^{35}Cl would you expect to demonstrate the greatest intensity?

a) First, solve 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:

Differentiate the probability expression and set to zero to get the maximum.

$$\begin{aligned} \frac{d}{dJ} ((2J+1) \exp(-J(J+1)\Theta_R/T)) \\ = (2 - (2J+1)(2J+1)\Theta_R/T) ((\Theta_R/T) \exp(-J(J+1)T/\Theta_R)) = 0 \end{aligned}$$

where $\Theta_R \equiv hcB/k$ to then find

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

Evaluating this for the given data:

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

b) Using the above expression for T rearranged to isolate the rotational level J :

$$\begin{aligned} T &= \frac{(2J_{\max} + 1)^2 hcB}{2k} \\ \left(\frac{2kT}{hcB} \right) &= (2J_{\max} + 1)^2 \\ J_{\max} &= \frac{\left(\frac{2kT}{hcB} \right)^{1/2} - 1}{2} \\ &= \frac{\left(\frac{2(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(10.57 \text{ cm}^{-1})} \right)^{1/2} - 1}{2} \cong 5 \end{aligned}$$

The maximum intensity level has shifted to $J_{\max} = 5$. So the 5-6 transition would have maximum intensity.