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Chemistry 562

Fall 2012

Problem Set 10

Due beginning of class on Wednesday, April 25th

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

2 1. Atkins *Problem 15.14.* (Part (a) means put each molecule in the same state.) How will the result be different if we have N_A (Avogadro's number) molecules?

3 2. Consider a two-level system that has an energy separation of ε between the two levels.

   (a) Write the partition function.

   (b) The total energy of the system as a function of temperature is $E(T) = \sum_i N_i \varepsilon_i$. Rewrite this equation in a form that contains the derivate of q with respect to β.

   (c) Plot E(T). What is the value at T=0, and why? What is the value at $T \to \infty$ and why?

3 3. The three normal modes of water are the symmetric stretch ($\tilde{\nu}_1 = 3652\ \text{cm}^{-1}$), the antisymmetric stretch ($\tilde{\nu}_3 = 3756\ \text{cm}^{-1}$), and the bend ($\tilde{\nu}_2 = 1595\ \text{cm}^{-1}$). Each normal mode has a harmonic oscillator potential.

   (a) Calculate the molecular vibrational partition function of water at 3000 K.

   (b) (All at 3000 K.) What fraction of water molecules have the bend excited to v_2=1. What fraction of water molecules have the symmetric stretch excited to v_1=1? Why do more molecules have the bend excited? What fraction of water molecules have both v_2=1 and v_1=1 excited?

   (c) Recalculate the fractions when the temperature is raised to 5000 K. Comment on the changes.

5 4. We will not cover the subject material in this question explicitly until lecture on Monday.

   (a) Determine the molecular rotational partition function for $H^{35}Cl$ at 300 K. Numerically sum the first 1, 10, 20, and 100 terms in the rotational partition function equation. (See Example 15.1 for an equation. Use $B = 10.591\ \text{cm}^{-1}$) To what value is the partition function converging? Give your answer to 5 significant figures.

   (b) What is the value of the rotational partition function in the high temperature limit? (See Eqn 16.15.) Is this a good approximation at 300 K?

   (c) Recall Problem Set 5, Question 4(e) where you were asked to sketch the pure rotational absorption spectrum of $H^{35}Cl$. In that problem, you were given the intensities. (Because those numbers were arbitrary, the results here may not match them.) Now we will calculate the relative intensities for the first seven transitions using the populations of the energy levels. (This approach omits some other factors). Make the intensities proportional to the probability of finding $H^{35}Cl$ in the initial rotational level. Draw the spectrum quantitatively. Make your x-axis wavenumbers.

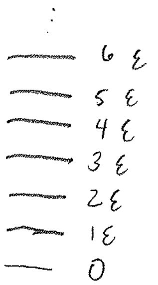
p 575
eqn 15.20 - 15.22

PS 10

(1)

1) Atkins 9.13

$$E = 5\varepsilon = \sum_{i=1}^{5} n_i \varepsilon_i$$



a) The only way to do this is put all molecules in the same state.

②

W = 1

④

b)

ε	0	1	2	3	4	5	W
n	4	0	0	0	0	1	5
	3	1	0	0	1	0	20
	3	0	1	1	0	0	20
	2	1	2	0	0	0	30
	2	2	0	1	0	0	30
	1	3	1	0	0	0	20
	0	5	0	0	0	0	1

$$W = \frac{N!}{\prod_i n_i!}$$

① {2, 1, 2, 0, 0 ...} and {2, 2, 0, 1, 0, 0 ...} are the most probable configurations

2) a) $q = 1 + e^{-\beta\epsilon}$

b) $E = \frac{N}{q} \sum \epsilon_i e^{-\beta\epsilon_i}$

$= -\frac{N}{q} \sum \frac{d}{d\beta}\left(e^{-\beta\epsilon_i}\right)$

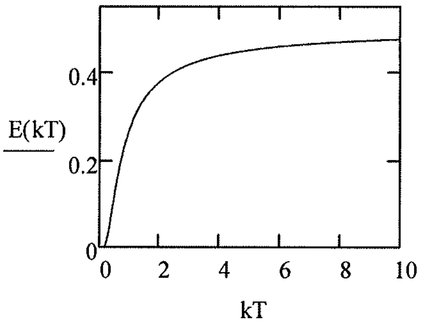
$= -\frac{N}{q} \frac{d}{d\beta}\left(\sum \epsilon_i \, e^{-\beta\epsilon_i}\right)$

$= -\frac{N}{q} \frac{dq}{d\beta}$

c)

2 c Set epsilon equal to 1, because it's not important in the plot

$$\varepsilon := 1 \quad E(kT) := \frac{\varepsilon}{1 + e^{\frac{\varepsilon}{kT}}}$$



3) $\tilde{\nu}_1 = 3652\ \text{cm}^{-1}$

$\tilde{\nu}_2 = 1595\ \text{cm}^{-1}$

$\tilde{\nu}_3 = 3756\ \text{cm}^{-1}$

$$q_{vib} = q_{\nu_1} q_{\nu_2} q_{\nu_3}$$

$$q_{HO} = \frac{1}{1 - e^{-\beta \varepsilon_{HO}}}$$

$$q_{vib} = (1 - e^{-\beta 3562\ \text{cm}^{-1}})^{-1}(1 - e^{-\beta 1595\ \text{cm}^{-1}})^{-1}(1 - e^{-\beta 3756\ \text{cm}^{-1}})^{-1}$$

$$k = 1.38 \times 10^{-23}\ \cancel{J}/K \ \frac{1}{6.626\times10^{-34}\ \cancel{J}\cdot \cancel{s}} \ \frac{1}{2.998\times10^{10}\ \text{cm}/\cancel{s}} = 0.695\ \text{cm}^{-1}/K$$

$\uparrow$ good number to remember!

$$\beta = \frac{1}{0.695\ \text{cm}^{-1}/K \cdot 3000\,K} = \frac{1}{2084.1\ \text{cm}^{-1}} = 4.798\times10^{-4}\ \text{cm}$$

$$q_{vib} = (1 - e^{-4.798\times10^{-4}\,\text{cm}\cdot 3562\,\text{cm}^{-1}})^{-1}(1 - e^{-4.798\times10^{-4}\,\text{cm}\cdot 1595\,\text{cm}^{-1}})^{-1}(1 - e^{-4.798\times10^{-4}\,\text{cm}\cdot 3756\,\text{cm}^{-1}})^{-1}$$

$q_{vib} = 2.734$ ③

b) $$p_i = \frac{e^{-\beta\varepsilon}}{q} = \frac{e^{(-4.798\times10^{-4}\,\text{cm}\cdot 1595\,\text{cm}^{-1})}}{2.734} = 0.1701 \quad ①$$

$$p_i = \frac{e^{(-4.798\times10^{-4}\,\text{cm}\cdot 3652\,\text{cm}^{-1})}}{2.734} = 0.06341 \quad ①$$

The bend is a lower frequency excitation. Thus at these modest temperatures (relative to these vib ν's), we would expect the lower energy excitation to be more populated ①

b) (cont.)

$$p_i = \frac{e^{(-4.798\times10^{-4}\,\mathrm{cm}\cdot 1595\,\mathrm{cm}^{-1})}\,e^{(-4.798\times10^{-4}\,\mathrm{cm}\cdot 3652\,\mathrm{cm}^{-1})}}{2.734}$$

$$= 0.02950$$ ①

c) $\beta = 2.878\times10^{-4}$ cm

$q = 6.413$ ②

$p_i = 0.0985\ (v_2 = 1)$

$p_i = 0.545\ (v_1 = 1)$

$p_i = 0.0344\ (v_2 = v_1 = 1)$

The first two are lower due ② to the maximum of the distribution shifting past the first excited state. However, the doubly excited oscillator has increased in population due to the shifted distribution.

4) $Q = q^N/N!$

⑦ $$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

all =1 for ideal gas

$$q_{\text{ideal gas}} = q_T\, q_V\, q_R\, q_E$$

$$q = q_T = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} V$$

$$p = kT\left(\frac{\partial \ln\left[\left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V\right\}^N / N!\right]}{\partial V}\right)_T = kT\left[\cancelto{0}{\frac{\partial \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2\cdot N}}{\partial V}} + \frac{\partial \ln V^{N}}{\partial V} - \cancelto{0}{\frac{\partial \ln N!}{\partial V}}\right]$$

$$p = kT\left(\frac{\partial N \ln V}{\partial V}\right)_T = kTN\frac{1}{V} \Rightarrow PV = NkT$$

#part → $N = nN_A$ ← # moles

$N_A \cdot k = R$

$$PV = nN_A kT = nRT; \quad \boxed{PV = nRT}$$

$k := 0.6950387\,\frac{\mathrm{cm}^{-1}}{\mathrm{K}}$ We found this in problem 2, I've added plenty of sig figs.

$T := 300\mathrm{K}$

$\beta := \frac{1}{k \cdot T}$

$B := 10.591\mathrm{cm}^{-1}$

$i := 0..100$

$\varepsilon_i := B \cdot i(i+1) \quad g_i := 2 \cdot i + 1$

$$q_i := \sum_{j=0}^{i} g_j \cdot e^{-\beta \cdot \varepsilon_j}$$

$q_0 = 1$ The first term is the zeroth level

$q_9 = 19.905$

$q_{19} = 20.024$

4/ $q_{99} = 20.024$ The sum converges to 20.024

The high temperature limit, as given by eq. 10.15b

$q_H := \frac{k \cdot T}{B}$ (my k is already in wavenumbers, so I don't need h, c)

$q_H = 19.688$

At 300 K, these values differ by

$\frac{q_{99} - q_H}{q_{99}} = 0.017$

2/ about one part in 60. T=300 K is reasonably high for rotations.

In order to calculate the probability of being in state j, we'll calculate the what fraction state j provides to the entire sum (and assuming that including 100 states will have a converged limit.)

4/ $j := 0..6 \qquad p_j := \frac{g_j \cdot e^{-\beta \cdot \varepsilon_j}}{q_{99}}$

$p_j =$

0.05
0.135
0.184
0.19
0.163
0.12
0.077

Stick spectra are cumbersome to plot in Mathcad. Here's a plot I made in gnuplot.