Chemistry 4000/5000/7001, Fall 2012, Assignment 3

Due: Friday, September 28, 4:00 p.m.
Total marks: 22

1. (a) Vibrational frequencies are often given as a wavenumber $\tilde{\nu}_0$, in units of cm^{-1}. The wavenumber is the inverse of the wavelength. From elementary quantum mechanics, recall that for photons $E = hc/\lambda$, so we have $E = hc\tilde{\nu}$. Correspondingly, for a harmonic oscillator, we could write $E_v = hc\tilde{\nu}_0\left(v + \frac{1}{2}\right)$. Obtain an equation relating $\tilde{\nu}_0$ to ω_0. [1 mark]

   (b) For $^1\mathrm{H}^{35}\mathrm{Cl}$, $\tilde{\nu}_0 = 2990.95\,\mathrm{cm}^{-1}$. What is ω_0? [2 mark]

   (c) What is the probability that a molecule of HCl is in the ground vibrational state at 20 °C? [4 marks]

   (d) Plot the vibrational partition function vs temperature. Around what temperature would the excited states become significantly populated? [4 marks]

2. In the lectures, I said that the equation for the classical partition function

$$Q = \int_{\mathcal{A}} g(\epsilon)\, \exp\left(-\frac{\epsilon}{k_B T}\right)\, d\epsilon$$

   could be obtained "using very similar reasoning to that used to obtain the quantum partition function". Provide the derivation of this equation. [3 marks]

3. Roughly how many translational states are accessible to a $^1\mathrm{H}_2$ molecule at 20 °C in a 1.050 L container? [6 marks]

   Isotopic mass of ^{1}H: 1.007 825 032 07 u

4. Without doing detailed calculations, estimate the number of translational states available to a molecule of $^2\mathrm{H}_2$ under the conditions of question 3. [2 marks]