

Chemistry 21b
Problem set # 2

Out: 18 January 2008

Due: 25 January 2008

Problems are worth: 1a=5, 1b=10, 1c=10, 1d=5; 2a=10, 2b=15; 3=10.

1. At low temperatures, the rotational part of the partition function

$$Q(T) = \sum_{J=0}^{\infty} (2J + 1) \exp(-E_J/kT)$$

dominates the non-translational degrees of freedom, where $E_J = BJ(J + 1)$ cm⁻¹ for a simple diatomic or linear molecule in a ¹Σ (that is, closed shell) electronic state. Roughly, this function tells you over how many states the population is distributed, and is central to the Boltzmann distribution ($N_J/g_J = (N/Q)e^{-E_J/kT}$, where N_J =population in state J , g_J =degeneracy of state J , E_J =energy of state J , N =total population, and Q =the partition function) and statistical thermodynamics, as we'll see later in the class.

- (a.) Derive an alternative, approximate form of this partition function by replacing the summation with an integral and by taking J to be a continuous variable. This formula should depend only on the temperature T and the rotation constant B .
- (b.) Evaluate the values of $Q(T)$ at $T=20$ and $T=200$ K, both by the direct summation (truncated at some appropriate values of J , use a mathematical package for convenience!) and through use of your approximate formula for the HCCCN molecule. The rotational constant for this molecule is $B=4549.06$ MHz.
- (c.) Recall that the fractional population in level J is given by

$$p(J) = (2J + 1) \exp(-E_J/kT)/Q(T).$$

Derive a formula for the value of $J=J_{max}$ at which the maximum population occurs for any specified temperature, based upon your integral form of the partition function.

- (d.) Find J_{max} for $T=20$ and $T=200$ K for HCCCN.

2. Prove that the following relationships, asserted in class, are in fact true for a complete, orthonormal basis set:

$$(a) \quad \sum_f |f\rangle\langle f| = 1 \quad (\text{the closure relation})$$

$$(b) \quad \langle m | \frac{\partial}{\partial x} | k \rangle = -\frac{m}{\hbar^2} (E_m - E_k) \langle m | x | k \rangle .$$

(Hint: Do (b) for the one-dimensional case, and work with wavevector notation and not state-vector notation as it is written above for compactness.)

3. Adapted from Atkins, 10.14: In general, a diatomic molecule does not possess a zero-point rotational energy such as we will find is present in the vibrational degrees of freedom. However, in the case of H₂, there *is* an effective zero-point rotational energy. Explain why. What about the isotopologues HD and D₂?