Assignment #4

Due: Monday 10/6/03

1. (a) Calculate values of the translational, rotational, vibrational, and electronic partition functions of Cl₂ at 300, 1000, and 5000 K, assuming a volume of 1 dm³. The first excited electronic “state” of Cl₂ (actually a triplet of states) lies at an energy of about 17,440 cm⁻¹ and has a total degeneracy of 9.

(b) A useful interpretation of the value of a partition sum is that it measures the number of quantum states accessible to the system under a given set of conditions. However, this interpretation is only valid when energies are measured relative to the lowest energy state of a given type. How does this idea apply to the values you just calculated?

2. Starting with the definition of harmonic oscillator energy levels \( \varepsilon_n = (n + \frac{1}{2})h \nu \), derive expressions for the vibrational partition function, energy, and heat capacity appropriate in the high temperature limit \( k_B T >> \Delta \varepsilon_n = h \nu \). Express your results in terms of the vibrational temperature \( \Theta_{vib} = h \nu / k_B \).

3. Accurate semi-empirical values of the heat capacity of CO in the ideal gas state are given by the parameterization tabulated below, which I copied and pasted from the NIST web site: http://webbook.nist.gov/. (This web site is extremely handy source of data and I recommend that you look it over to see what it contains.)

**Gas Phase Heat Capacity (Shomate Equation)**

\[
C_p = A + Bt + Ct^2 + Dt^3 + E/t^2
\]
\[
H = A + Bt + C/t^2 + D/t^3 + E/t^4
\]
\[
S = A \ln(t) + Bt + C/t^2 + D/t^3 - E/t^2 + G
\]

where:
- \( C_p \) = heat capacity (J/mol*K)
- \( H \) = standard enthalpy (kJ/mol)
- \( S \) = standard entropy (J/mol*K)
- \( t = \) temperature (K) / 1000

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>298. - 1300.</th>
<th>1300. - 6000.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25.56759</td>
<td>35.15070</td>
</tr>
<tr>
<td>B</td>
<td>6.096130</td>
<td>1.30095</td>
</tr>
<tr>
<td>C</td>
<td>4.054656</td>
<td>-0.205921</td>
</tr>
<tr>
<td>D</td>
<td>-2.671301</td>
<td>0.013550</td>
</tr>
<tr>
<td>E</td>
<td>0.131021</td>
<td>-3.282780</td>
</tr>
</tbody>
</table>

Reference: Chase, 1998

Chase, 1998
(a) Calculate heat capacities of CO between 300-3000 K using the relations of Chapter 4 and plot your results together with values obtained from the NIST parameterization.

(b) Characterize the deviations observed between your calculations and the NIST values and discuss possible reasons for this deviation.

4. Consider the corrections to the classical value of $q_{rot}$ for a diatomic molecule provided by the Euler-Maclaurin expansion discussed in M&S problem 4-14.

   (a) Estimate at what reduced temperature ($T/\Theta_{rot}$) the error in using the classical value, $q_{rot} = T/\Theta_{rot}$, becomes less than 5%.

   (b) What temperature does this correspond to in H$_2$, HCl, and N$_2$?

5. M&S 4-23 (symmetry numbers)

6. M&S 4-39 (high temperature limits)