1. Thermodynamics is all about energies. The standard unit of energy in chemical problems is kJ/mol (not kcal/mol!). It is useful to be able to quickly convert this basic unit into other commonly used energy measures. Express 1 kJ/mol in terms of the other “energy” units: (a) eV, (b) kcal/mol, (c) cm⁻¹, and (d) K.

I used the Mathcad worksheet shown below for this problem.

\[
\begin{align*}
e & := 1.60217733 \times 10^{-19} \text{C} \quad N_A := 6.0221367 \times 10^{23} \text{mol}^{-1} \quad \text{kJ} := 10^3 \cdot \text{J} \\
\text{e} \cdot V \cdot N_A \quad \frac{\text{kJ}}{\text{mol}} &= 96.49 \\
\frac{k\cdot J}{\text{mol} \cdot \text{mol}^{-1}} &= 0.2388 \\
k\cdot \text{cal} &= 4.187 \text{J} \\
\frac{k\cdot \text{cal}}{\text{mol} \cdot \text{mol}^{-1}} &= 1.036 \times 10^{-2} \\
h := 6.6260755 \times 10^{-34} \text{J} \cdot \text{s} \\
c := 299792458 \text{m} \cdot \text{s}^{-1} \\
1 \text{cm} := 10^{-2} \text{m} \\
\frac{h \cdot c \cdot \text{cm}^{-1} \cdot N_A}{\text{kJ} \cdot \text{mol}^{-1}} &= 0.01196 \\
\frac{k\cdot J}{h \cdot c \cdot \text{cm}^{-1} \cdot N_A} &= 120.27 \\
k_B := 1.380658 \times 10^{-23} \text{J} \cdot \text{K}^{-1} \\
\frac{k_B \cdot K \cdot N_A}{\text{kJ} \cdot \text{mol}^{-1}} &= 8.315 \times 10^{-3} \\
\frac{k\cdot J}{k_B \cdot K \cdot N_A} &= \text{100 K}
\end{align*}
\]

Note that with the exception of kcal/mol, the remaining conversions required the use of fundamental constants. The unit eV is a true energy measure, but it is on a per molecule rather than a per mole basis, so that the conversion requires use of Avogadro’s number. The units cm⁻¹ and K are not energy units at all. Use of such quantities as measures of energy requires that one apply the basic relationships \( \varepsilon = h \nu = h c \nu \) and \( \varepsilon = k_B T \).

For purposes of memory 1 kJ/mol is roughly equivalent to:

- 0.01 eV
- ¼ kcal/mol
- 80 cm⁻¹
- 100 K
2. Use the formulas and data in Chapter 1 of M&S to calculate the energy differences between the two lowest translational, rotational, vibrational, and electronic states of Cl₂ and compare these energies to the "thermal energy" \( k_BT \) at 298 K. (The 1st electronically excited state of Cl₂ occurs at 17,160 cm⁻¹.)

I carried out the calculations using the Mathcad worksheet appended below. The final results are:

<table>
<thead>
<tr>
<th>Mode</th>
<th>( \Delta \varepsilon / J )</th>
<th>( \Delta \varepsilon / kJ \text{ mol}^{-1} )</th>
<th>( \Delta \varepsilon / k_BT )</th>
</tr>
</thead>
<tbody>
<tr>
<td>translation</td>
<td>( 1.4 \times 10^{-40} )</td>
<td>( 8.4 \times 10^{-20} )</td>
<td>( 3.4 \times 10^{-20} )</td>
</tr>
<tr>
<td>rotation</td>
<td>( 9.6 \times 10^{-24} )</td>
<td>( 5.8 \times 10^{-3} )</td>
<td>( 2.3 \times 10^{-3} )</td>
</tr>
<tr>
<td>vibration</td>
<td>( 1.1 \times 10^{-20} )</td>
<td>( 6.6 )</td>
<td>( 2.7 )</td>
</tr>
<tr>
<td>electronic</td>
<td>( 3.4 \times 10^{-19} )</td>
<td>( 205 )</td>
<td>( 83 )</td>
</tr>
</tbody>
</table>

In this example, one finds that energy spacings are much smaller than thermal energies at room temperature in the case of translational and rotational modes but greater than thermal energies in the case of vibrational and electronic states. (This observation is generally correct and enables use of classical approximations for translational and rotational energies in most thermodynamic applications as we will see in Chapter 3.)

**Fundamental Constants & Conversion Factors:**
\[ h := 6.6260755 \times 10^{-34} \text{ J s} \quad k_B := 1.380568 \times 10^{-23} \text{ J K}^{-1} \]
\[ N_A := 6.0221367 \times 10^{23} \text{ mol}^{-1} \quad c := 2.99792458 \times 10^8 \text{ m s}^{-1} \]
\[ \Lambda := 10^{-10} \text{ m} \quad \text{amu} := 10^{-2} N_A^{-1} \text{ kg mol}^{-1} \quad \text{cm} := 10^{-2} \text{ m} \quad \text{kJ} = 10^3 \text{ J} \]

**Molecular Constants:**
\( m_1 := 35.453 \text{ amu} \quad R = 1.988 \text{ A} \quad v_0 := 554 \text{ cm}^{-1} \)

The thermal energy "kT" at 298 K is:
\[ kT := k_B \times 298K \quad kT := 4.114 \times 10^{-21} \text{ J} \]

(a) **Translation:** Translational energies are given by the particle-in-a-box expression:
\[ \epsilon(n_x, n_y, n_z) = \frac{\hbar^2}{8M} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \]

where \( M \) is the particle mass and \( L \) the confining box lengths. Assuming a cubic box of length \( L = 1 \) dm (i.e. a 1 liter volume), the two lowest energy states will have quantum numbers \((n_x, n_y, n_z) = (1, 1, 1) \) and \((1, 1, 2) \) and the energy difference between these states is \( \Delta \varepsilon = \frac{3\hbar^2}{16m_1L^2} \):

\[ \Delta \varepsilon = \frac{3\hbar^2}{16m_1L^2} \]

Numerical evaluation yields:
\[ L := 10^{-1} \text{ m} \quad \Delta \varepsilon := \frac{3\hbar^2}{8\text{2m_1L}^2} \]

\[ \Delta \varepsilon_{\text{tr}} = 1.3983 \times 10^{-40} \text{ J} \]
\[ \Delta \varepsilon_{\text{tr}} \frac{N_A}{\text{kJ mol}^{-1}} = 8.421 \times 10^{-20} \]
\[ \frac{\Delta \varepsilon_{\text{tr}}}{kT} = 3.399 \times 10^{-21} \]
(b) **Rotation**: Rotational energies of a rigid diatomic molecule are:

\[ \varepsilon(J) = \frac{\hbar^2 J (J + 1)}{8\pi^2 I} \text{ with } J = 0, 1, 2, \ldots \]

where \( I = \mu R_e^2 \) and \( \mu = \frac{m_1 m_2}{(m_1 + m_2)} = m_1 \frac{1}{2} \) here. The two lowest energy states will be \( J = 0 \) and \( J = 1 \) whose difference is:

\[ \Delta \varepsilon = \frac{\hbar^2}{2\pi^2 m_1 R_e^2} \]

\[ \Delta \varepsilon_{\text{rot}} = \frac{\hbar^2}{2\pi^2 m_1 R_e^2} \]

Numerical evaluation yields:

\[ \Delta \varepsilon_{\text{rot}} = 9.56 \times 10^{-24} \text{ J} \]

\[ \frac{\Delta \varepsilon_{\text{rot}}}{\text{kJ mol}^{-1}} = 5.757 \times 10^{-3} \]

\[ \frac{\Delta \varepsilon_{\text{rot}}}{kT} = 2.324 \times 10^{-3} \]

(c) **Vibration**: Vibrational energies of a diatomic are:

\[ \varepsilon(n) = \hbar \nu (n + \frac{1}{2}) \text{ with } n = 0, 1, 2, \ldots \]

The two lowest levels are \( n = 0, 1 \) with a spacing of \( \hbar \nu \), i.e. \( \Delta \varepsilon = \hbar \nu = \hbar \nu \). Evaluating this expression gives:

\[ \Delta \varepsilon_{\text{vib}} = \hbar \cdot c \cdot \nu_e \]

\[ \Delta \varepsilon_{\text{vib}} = 1.1 \times 10^{-20} \text{ J} \]

\[ \frac{\Delta \varepsilon_{\text{vib}}}{\text{kJ mol}^{-1}} = 6.627 \]

\[ \frac{\Delta \varepsilon_{\text{vib}}}{kT} = 2.675 \]

(d) **Electronic**: The electronic energy spacing is

\[ \Delta \varepsilon_{\text{el}} = 17160 \cdot 10^2 \cdot \text{m}^{-1} \cdot \hbar \cdot c \]

\[ \Delta \varepsilon_{\text{el}} = 3.409 \times 10^{-19} \text{ J} \]

\[ \frac{\Delta \varepsilon_{\text{el}}}{\text{kJ mol}^{-1}} = 205.279 \]

\[ \frac{\Delta \varepsilon_{\text{el}}}{kT} = 82.855 \]

3. (a) Using the data in Table 7.2 of the Berry, Rice, & Ross reading, determine the vibrational quantum numbers at which the actual vibrational energy level spacings (i.e. those computed using Eq. 7.10 of BR&R) of \( F_2 \) and \( Cl_2 \) deviate by 10% from the harmonic spacings based on \( \nu_e \) alone.

(b) Compare the energies at which these deviations occur to the dissociation energies (\( D_e \)) of the molecules.

(c) What temperatures do these energies correspond to?

Vibrational energy levels are described by:

\[ \varepsilon_{\text{vib}}(n) = \hbar \nu_e \left\{ (n + \frac{1}{2}) - x_e (n + \frac{1}{2})^2 + y_e (n + \frac{1}{2})^3 + \ldots \right\} \]
The spacing between adjacent energy levels (i.e. the energy of the transition between states \( n \rightarrow n+1 \)) is given by:

\[
\Delta \varepsilon_{\text{vib}}(n) = \varepsilon_{\text{vib}}(n+1) - \varepsilon_{\text{vib}}(n) \\
= h \nu_v \{ 1 - 2x_v(n+1) + \ldots \} \tag{3-2}
\]

and the equilibrium dissociation energy is:

\[
D_e = D_0 - \varepsilon_{\text{vib}}(n = 0) = D_0 - h \nu_v \{ \frac{1}{2} - \frac{1}{4}x_v + \frac{1}{8}y_v + \ldots \} \tag{3-3}
\]

There are a number of ways that one could solve this problem. I chose to simply calculate energies for the first several vibrational states using the Excel spreadsheet shown below. I chose to work in units of the vibrational quantum \( h \nu_v \) and to throw in a calculation for \( \text{H}_2 \) for good measure. The columns in the lower part of the table are the vibrational quantum number \( n \), the anharmonic energy (“E vib”), the anharmonic energy spacings (“\( \Delta E \) vib”) and the anharmonic energy expressed in units of the dissociation energy \( D_e \) and as a temperature. In units of \( h \nu_v \) the harmonic spacing is unity, so that finding the vibrational quantum number where the anharmonic energy spacing deviates by 10% from the harmonic value amounts to looking for the lowest value of \( n \) for which \( \varepsilon_{\text{vib}}(n) / h \nu_v \leq 0.9 \). These values are highlighted in the table.

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>( \nu \text{vib} )</th>
<th>( \Delta \nu \text{vib} )</th>
<th>( \nu \text{vib} / k_B )</th>
<th>( \nu )</th>
<th>( \nu \text{vib} )</th>
<th>( \Delta \nu \text{vib} )</th>
<th>( \nu \text{vib} / k_B )</th>
<th>( \nu )</th>
<th>( \nu \text{vib} )</th>
<th>( \Delta \nu \text{vib} )</th>
<th>( \nu \text{vib} / k_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.50</td>
<td>0.97</td>
<td>0.04</td>
<td>656</td>
<td>0</td>
<td>0.50</td>
<td>0.99</td>
<td>0.01</td>
<td>402</td>
<td>1</td>
<td>1.49</td>
</tr>
<tr>
<td>1</td>
<td>1.47</td>
<td>0.94</td>
<td>0.11</td>
<td>1939</td>
<td>1</td>
<td>1.49</td>
<td>0.98</td>
<td>0.04</td>
<td>1199</td>
<td>2</td>
<td>2.47</td>
</tr>
<tr>
<td>2</td>
<td>2.41</td>
<td>0.91</td>
<td>0.18</td>
<td>3183</td>
<td>2</td>
<td>2.47</td>
<td>0.97</td>
<td>0.07</td>
<td>1989</td>
<td>3</td>
<td>3.44</td>
</tr>
<tr>
<td>3</td>
<td>3.32</td>
<td>0.88</td>
<td>0.24</td>
<td>4388</td>
<td>3</td>
<td>3.44</td>
<td>0.96</td>
<td>0.10</td>
<td>2771</td>
<td>4</td>
<td>4.40</td>
</tr>
<tr>
<td>4</td>
<td>4.20</td>
<td>0.85</td>
<td>0.31</td>
<td>5554</td>
<td>4</td>
<td>4.40</td>
<td>0.95</td>
<td>0.12</td>
<td>3545</td>
<td>5</td>
<td>5.35</td>
</tr>
<tr>
<td>5</td>
<td>5.05</td>
<td>0.82</td>
<td>0.37</td>
<td>6680</td>
<td>5</td>
<td>5.35</td>
<td>0.94</td>
<td>0.15</td>
<td>4312</td>
<td>6</td>
<td>6.30</td>
</tr>
<tr>
<td>6</td>
<td>5.87</td>
<td>0.79</td>
<td>0.43</td>
<td>7768</td>
<td>6</td>
<td>6.30</td>
<td>0.93</td>
<td>0.18</td>
<td>5070</td>
<td>7</td>
<td>7.23</td>
</tr>
<tr>
<td>7</td>
<td>6.67</td>
<td>0.49</td>
<td>0.88</td>
<td>8816</td>
<td>7</td>
<td>7.23</td>
<td>0.92</td>
<td>0.20</td>
<td>5821</td>
<td>8</td>
<td>8.15</td>
</tr>
<tr>
<td>8</td>
<td>9.06</td>
<td>0.90</td>
<td>0.26</td>
<td>7300</td>
<td>9</td>
<td>9.06</td>
<td>0.90</td>
<td>0.26</td>
<td>7300</td>
<td>10</td>
<td>9.97</td>
</tr>
<tr>
<td>10</td>
<td>9.86</td>
<td>0.31</td>
<td>8747</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These calculations show that 10% deviation from harmonic frequencies (highlighted) occurs near \( \nu = 3 \) for \( \text{F}_2 \), \( \nu = 9 \) in \( \text{Cl}_2 \) and \( \nu = 2 \) in \( \text{H}_2 \). The energies at these levels correspond to about 20-25% of the dissociation energy in all three cases. (This commonality reflects the similar shape of the vibrational potential surface for these and many other closed shell diatomic molecules.) Equating the energies of these levels to temperatures, 10% deviations are equivalent to temperatures in the thousands of degrees K.

Alternatively, one could have chosen to solve the problem algebraically. Letting \( f \) denote the fraction of the harmonic spacing we’re looking for \( \nu \) such that:

\[
f \to \frac{\varepsilon_{\text{vib}}(n)}{h \nu_v} = 0.9
\]
\[ \frac{|\Delta \varepsilon_{an} (n) - \Delta \varepsilon_{harm} (n)|}{\Delta \varepsilon_{harm} (n)} = f \]  \hspace{1cm} (3-4)

Using Eq. 3-2 for \( \Delta \varepsilon_{an} \) and \( \Delta \varepsilon_{harm} = h \nu_e \) this becomes, \( 2x_e (n+1) = f \) or \( n = f / 2x_e - 1 \). Solving this equation for \( \nu \) I find \( n = 2.4 \) in the case of F\(_2\) and \( n = 9.4 \) in the case of Cl\(_2\).

4. M&S 1-47: Express the energy both in units of cm\(^{-1}\) and kJ/mol.

The zero point energy of a molecule (in the harmonic approximation) is: \( \varepsilon_{zpe} = \frac{1}{2} \hbar \sum \nu_i \). In the case of CH\(_4\) \( f_{vib} = 3 \cdot 5 - 6 = 9 \), with many of modes being degenerate due to the molecule’s high symmetry. Degeneracies are indicated by the values in parentheses in Table 1.6. Using the information listed there:

\[ \varepsilon_{zpe} / hc / \text{cm}^{-1} = \frac{1}{2} \{2898 + 2 \cdot 1515 + 3 \cdot 3002 + 3 \cdot 1300\} = 9417 \]

or \( \varepsilon_{zpe} = 112.6 \text{ kJ mol}^{-1} \).

5. M&S 1-44: Determine the number of degrees of freedom of N\(_2\), C\(_2\)H\(_2\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), and C\(_6\)H\(_6\).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( N )</th>
<th>( f_{tot} )</th>
<th>type</th>
<th>( f_{tr} )</th>
<th>( f_{rot} )</th>
<th>( f_{vib} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>2</td>
<td>6</td>
<td>L</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>4</td>
<td>12</td>
<td>L</td>
<td>3</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>6</td>
<td>18</td>
<td>NL</td>
<td>3</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>8</td>
<td>24</td>
<td>NL</td>
<td>3</td>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td>C(_6)H(_6)</td>
<td>12</td>
<td>36</td>
<td>NL</td>
<td>3</td>
<td>3</td>
<td>30</td>
</tr>
</tbody>
</table>

where \( N \) is the number of atoms in the molecule, \( f_{tot} \) is the total number of degrees of freedom \( ( f_{tot} = 3N ) \), \( f_{tr} \) is the number of translational \( (3) \), \( f_{rot} \) the number of rotational \( (2 \text{ for a linear molecule or } 3 \text{ for a nonlinear molecule}) \), and \( f_{vib} \) the number of vibrational degrees of freedom \( ( f_{vib} = f_{tot} - f_{tr} - f_{rot} ) \).