Electronic structure calculations and molecular mechanics both typically focus on the minima in the potential energy surface (PES) of a molecule. Nuclear motions affect the energies measured experimentally such that they differ from the energies of PES minima in two ways. First, the uncertainty principle requires that molecules are not localized to a single point on the PES but rather delocalized slightly, an effect that leads to vibrational zero-point energy. This effect is operative even at 0 K. In addition, a sample of molecules at non-zero temperatures will have a distribution of energies above the zero-point level as a result of nuclear motions. Both effects must be taken into account in order to make accurate comparisons to thermochemical data at finite temperatures.

I. Separability of Nuclear “Degrees of Freedom”:

The Born-Oppenheimer approximation enables us to separate nuclear and electronic motions. Nuclear motions are also separable to a reasonable approximation, so that the energy of a single molecule can be written:

\[ \mathcal{E} = \mathcal{E}_e + \mathcal{E}_{\text{nuc}} \]
\[ \mathcal{E}_{\text{nuc}} = \mathcal{E}_{\text{trans}} + \mathcal{E}_{\text{rot}} + \mathcal{E}_{\text{vib}} \]

\( \mathcal{E}_{\text{nuc}} \) is a function of the spatial coordinates and momenta of all of the nuclei. The potential energy depends on the spatial coordinates and the kinetic energy on the velocities or momenta. Each pair of a spatial coordinate and its associated momentum is counted as one “degree of freedom”.

Translational coordinates specify the position of the center of mass of a molecule relative to some laboratory coordinate system, rotational coordinates its orientation relative to this coordinate system. The vibrational coordinates are the “internal coordinates” specifying the relative positions of the nuclei with respect to one another.

1. How many nuclear degrees of freedom does a diatomic molecule possess?

2. Explain how these degrees of freedom partition into translational, rotational, and vibrational components.
3. Using the diagram below, indicate what coordinates you might use to describe the translational, rotational, and vibrational degrees of freedom of a diatomic molecule.

4. A PES depicts the potential energy of a molecule as a function of its vibrational coordinates only. Why aren’t translational and rotational coordinates also included in the PES?

5. How is the PES of a diatomic molecule determined in molecular mechanics calculations? In electronic structure calculations?
6. Enumerate the nuclear degrees of freedom present in the triatomic molecules H₂O and CO₂. (They should differ in the numbers of rotational and vibrational degrees of freedom.)

6. Why is there a difference between the H₂O and CO₂ cases, i.e. why is there a difference between linear and nonlinear molecules?

7. Fill out the following table, where $f_x$ denotes the number of degrees of freedom in nuclear motion $x$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$f_{trans}$</th>
<th>$f_{rot}$</th>
<th>$f_{vib}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>an atom</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>an $N$-atom linear molecule</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>an $N$-atom non-linear molecule</td>
<td></td>
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<td>acetylene (H-C≡C-H)</td>
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<td></td>
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<tr>
<td>dimethylacetylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
II. Molecular Vibrations:

The description of molecular vibrations usually assumes a harmonic picture in which displacements of atoms about a minimum in the PES result in a linear restoring force (Hooke’s Law) or a quadratic change in the energy. Using this harmonic approximation, nuclear motions involving the vibrational degrees of freedom of a molecule can be viewed in terms of $f_{vib}$ independent normal modes of vibration, each having a characteristic frequency, energy, and pattern of atomic motions.

1. At the right is a cartoon of a molecule in which all nuclear motion is frozen except for a single bond stretching coordinate “$x$”, and below it is a plot of how the PES might change as a function of $x$. Explain why the vertical axis of this plot labeled “$E_{el}$” and the meaning of this energy.

The general form of a Taylor expansion of a single variable $x$ is:

$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2!} f''(a)(x-a)^2 + \frac{1}{3!} f'''(a)(x-a)^3 + ...$$ (II-1)

where $f'(x) = df / dx$, $f''(x) = d^2 f / dx^2$, etc.

2. Express $E_{el}(x)$ as a Taylor expansion about the minimum in the PES at $x_e$.

3. The harmonic approximation keeps only terms up to order $x^2$ in such an expansion. Adopting the convention that the energy at the minimum of the PES is defined to be zero, and using the notation $k_x \equiv (d^2 E_{el} / dx^2)_{x=x_e}$, write an expression for the harmonic approximation to $E_{el}(x)$. 

4. Under what conditions would you expect the harmonic approximation to be inadequate?

The Classical Harmonic Oscillator: If nuclear motions could be treated classically, under the harmonic approximation, the atom under consideration would execute a trajectory \( x(t) \) consisting of sinusoidal motion of amplitude \( A \) about the equilibrium bond length \( x_e \):

\[
x(t) = x_e + A \cos(2\pi \nu t + \delta)
\]

The vibrational frequency is given by:

\[
\nu = \frac{1}{2\pi} \left( \frac{k}{m} \right)^{1/2}
\]

5. What is the repeat period of the vibration and what is the meaning of \( \delta \) in Eq. II-2?

6. The total energy (potential + kinetic) is a constant for such a system and it is determined by the amplitude \( A \). What is the potential energy at the classical turning points \( x = x_e \pm A \)?

Using the fact that at the classical turning points the velocity is zero, show that the total energy of the classical oscillator is given by

\[
E_{\text{vib}} = \frac{1}{2} k_A^2
\]
The Quantal Harmonic Oscillator: It is not usually appropriate to think of molecular vibrations classically. Instead of thinking of a trajectory \( x(t) \) of the atom as described by Eq. II-2 it is better to think of molecules existing in stationary energy eigenstates \( \psi_n \) of the vibrator, whose energies are which are:

\[
e_{\text{vib}} = h \nu(n + \frac{1}{2}) \quad n = 0, 1, 2, \ldots
\]  

(II-5)

where \( n \) is the vibrational quantum number. The frequency that determines the spacing between energy levels is identical to the classical vibrational frequency in Eq. II-3. A depiction of these energies and the probabilities of finding the bond with particular lengths as a function of \( n \) are shown below (from dePaula & Atkins, Ch. 12):

7. What is the magnitude of the zero point energy (ZPE) of a single oscillator of frequency \( \nu \)?

Normal Modes of Vibration: In a polyatomic molecule, the full PES depends on many internal coordinates \( \vec{R} \). For example, the vibrations of the molecule shown at the right could be described by the set of bond lengths and angles indicated, \( \vec{R} = \{r_1, r_2, r_3, \theta_1, \theta_2, \theta_3\} \). In the harmonic approximation, the PES can be written in terms of such internal coordinates as:

\[
E_{\text{el}}(\vec{R}) \equiv E_{\text{el}}(\vec{R}_c) + \frac{1}{2} \sum_{i=1}^{f_{\text{tot}}} \sum_{j=i}^{f_{\text{tot}}} k_{ij}(R_i - R_{i,c})(R_j - R_{j,c})
\]

(II-6)

where the force constants \( k_{ij} \) are the 2\textsuperscript{nd} derivatives:

\[
k_{ij} = \left( \frac{\partial^2 E_{\text{el}}}{\partial R_i \partial R_j} \right)_{\vec{R}_c}
\]

(II-7)

(The matrix comprised of these 2\textsuperscript{nd} derivatives is termed the Hessian matrix.)

The normal coordinates or normal modes \( \vec{Q} \) of a polyatomic molecule correspond to the particular set of coordinates formed by taking linear combinations of the \( \vec{R} \) coordinates so as to eliminate all of the cross terms in both the potential \( (\vec{R}_i \vec{R}_j \) terms in II-6) and the kinetic energy terms in the Hamiltonian. That is, the normal coordinates allow the vibrational Hamiltonian to be written as a sum of independent terms:

\[
\hat{H}_{\text{vib}} = \sum_{i=1}^{f_{\text{tot}}} \hbar \hat{h}(Q_i, P_i)
\]

(II-8)
What makes normal coordinates special is that this form of the Hamiltonian allows the energy to be written as a sum of independent harmonic oscillator energies:

\[ \varepsilon_{\text{vib}} = \sum_{i=1}^{\text{f}} \hbar \nu_i (n_i + \frac{1}{2}) \quad n_i = 0, 1, 2 \ldots \quad \nu_i = \frac{1}{2\pi} \left( \frac{k_i}{\mu_i} \right)^{1/2} \]  

(II-9)

and the vibrational wavefunction to be written as a simple product

\[ \Psi_{\text{vib}}(\vec{Q}) = \psi_{n_1}(Q_1)\psi_{n_2}(Q_2)\ldots\psi_{n_{\text{vib}}}(Q_{\text{vib}}) \]  

(II-10)

The normal mode frequencies \( \nu_i \) are determined by the effective force constants \( k_i \) and masses \( \mu_i \), which are related to the \( k_{ij} \) and atomic masses \( m \) through matrix manipulations of the sort described in the Leach 5.8 excerpt. The normal modes of water (also from this Leach excerpt) are illustrated below. The arrows indicate the extent and direction of motion of each atom in the normal modes (i.e. describe the linear combinations of the Cartesian coordinate set which make up each normal coordinate).

8. How would one specify the quantum-mechanical vibrational state of an \( N \)-atomic molecule?

9. Write a general expression for the zero point energy of a polyatomic molecule.
III. The Boltzmann Distribution

The Boltzmann distribution

\[ \frac{N_i}{N_j} = \frac{g_i e^{-\varepsilon_i / k_B T}}{g_j e^{-\varepsilon_j / k_B T}} \]  \hspace{1cm} (III-1)

thermal equilibrium at a temperature \( T \) in terms of the describes the relative numbers of molecules \( N \) being in an energy level with energy \( \varepsilon \) and degeneracy \( g \). The probability of a particular molecule being in a specific energy level \( i \) is given by:

\[ p_i = \frac{g_i e^{-\varepsilon_i / k_B T}}{q(T)} \quad \text{with} \quad q(T) = \sum_i g_i e^{-\varepsilon_i / k_B T} \]  \hspace{1cm} (III-2)

where the summation extends over all possible energy levels. The quantity \( q(T) \) in Eq. III-2 is termed the partition function and it plays a central role in statistical mechanics. In particular, it can be shown that the internal energy of a collection of \( N \) molecules in thermal equilibrium at a temperature \( T \) can be expressed:

\[ U(T) = N k_B T^2 \frac{1}{q} \frac{dq}{dT} \]  \hspace{1cm} (III-3)

If the energies in different degrees of freedom can be separated as in Eq. I-1, then one can think of the thermal distributions over these different types of energy (electronic, translational, rotational, and vibrational) separately. The total internal energy of a collection of \( N \) molecules is then given by:

\[ U(T) = U_{el}(T) + U_{trans}(T) + U_{rot}(T) + U_{vib}(T) \]  \hspace{1cm} (III-4)

CHEM ACTIVITY 19 from R. S. Moog, J. N. Spencer, and J. J. Farrell,

Physical Chemistry a Guided Inquiry (Houghton Mifflin, 2004)

Defining the zero of energy to be the minimum in the PES (of the lowest electronic state), at temperatures near 298 K the various thermal energies for one mole of molecules given approximately by:

\[ U_{el}(T) = 0 \]  \hspace{1cm} (III-5)

\[ U_{trans}(T) = \frac{1}{2} k_B T \]  \hspace{1cm} (III-6)

\[ U_{rot}(T) = \frac{1}{2} f \Delta_{rot} k_B T \]  \hspace{1cm} (III-7)

\[ U_{vib}(T) = U_{vib}(0) + R \sum_{i=1}^{\ell_{vib}} \frac{h \nu_i}{(1-e^{-h \nu_i / k_B T})} \]  \hspace{1cm} (III-8)

1. \( U_{vib}(0) \) is the zero point energy of a mole of molecules. What is the explicit expression for \( U_{vib}(0) \)?
Model 1: The Rotational Thermal Energy of Carbon Monoxide.

The rotational energy levels of a diatomic molecule are given by:

$$\varepsilon_J = J(J+1) \frac{\hbar^2}{8\pi^2 I} \quad J = 0, 1, 2, \ldots \quad m = 0, \pm1, \pm2, \ldots, \pm J$$ \hspace{1cm} (1)

The energy levels of carbon monoxide can be experimentally observed with microwave spectroscopy, and we find that

$$\varepsilon_J = J(J+1) \times 3.836 \times 10^{-23} \text{ Joules}$$ \hspace{1cm} (2)

$$g_J = 2J + 1$$ \hspace{1cm} (3)

Recall that

$$q = \sum_{i=0}^{i_{\text{max}}} g_i e^{-(\varepsilon_i-\varepsilon_0)/kT}$$

$$q = 1 + 3 e^{-\varepsilon_1/kT} + 5 e^{-\varepsilon_2/kT} + 7 e^{-\varepsilon_3/kT} + \ldots$$ \hspace{1cm} (4)

$$\frac{dq}{dT} = 3 \frac{\varepsilon_1}{kT^2} e^{-\varepsilon_1/kT} + 5 \frac{\varepsilon_2}{kT^2} e^{-\varepsilon_2/kT} + 7 \frac{\varepsilon_3}{kT^2} e^{-\varepsilon_3/kT} + \ldots$$ \hspace{1cm} (5)

$$\frac{dq}{dT} = \frac{1}{kT^2} \left( 3 \varepsilon_1 e^{-\varepsilon_1/kT} + 5 \varepsilon_2 e^{-\varepsilon_2/kT} + 7 \varepsilon_3 e^{-\varepsilon_3/kT} + \ldots \right)$$ \hspace{1cm} (6)

$$U_{\text{thermal,rot}} = \frac{N}{q} kT^2 \frac{dq}{dT}$$

$$= \frac{N}{\left(1 + 3e^{-\varepsilon_1/kT} + 5e^{-\varepsilon_2/kT} + 7e^{-\varepsilon_3/kT} + \ldots\right)} \left(3\varepsilon_1 e^{-\varepsilon_1/kT} + 5\varepsilon_2 e^{-\varepsilon_2/kT} + 7\varepsilon_3 e^{-\varepsilon_3/kT} + \ldots\right)$$ \hspace{1cm} (7)
Table 1. Various Quantities for the Determination of $q_{\text{rot}}$ and $dq/dT$ for CO at 300 K.

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<tr>
<th>J</th>
<th>gJ</th>
<th>$\varepsilon_J$</th>
<th>$g_J e^{-\varepsilon_J/kT}$</th>
<th>$\varepsilon_J g_J e^{-\varepsilon_J/kT}$</th>
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Sum ........................................ 1.08E+02 4.47E-19
Critical Thinking Questions

1. Verify that equation (3) is correct.

2. Verify that all of the entries for \( J = 1 \) in Table 1 are correct.

3. Use equation (7) and Table 1 to show that \( U_{\text{thermal,rot}} = 2.49 \text{ kJ/mole} \) for CO at 300 K.

4. The Boltzmann distribution for the ratio of the number of molecules in energy level \( J \) to the number of molecules in \( J = 0 \) is:

\[
\frac{N_i}{N_j} = \frac{g_i}{g_j} e^{-(\varepsilon_i - \varepsilon_j)/kT} = \frac{N_i}{N_0} = g_j e^{-\varepsilon_j kT}
\]

This ratio is identical to column four in Table 1. What is the ratio \( N_{10}/N_0 \) for CO at 300 K?
5. According to Table 1, which rotational energy level is most highly populated? What is the value of $N_j/N_0$ for this energy level?

6. What is the value of $N_{50}/N_0$?

7. Which molecules are more responsible for the thermal energy of 2.49 kJ/mole for CO at 300 K—the molecules in energy level $J = 50$ or the molecules in energy level $J = 10$?

8. Why was the summation stopped at $J = 50$? Could the summation have been stopped sooner? Explain.

Exercises

1. For CO, use the Boltzmann distribution equation along with equations (1), (2), and (3) to calculate the ratio of the number of molecules in rotational energy $\varepsilon_1$ to the number of molecules in $\varepsilon_0$ (that is, $N_1/N_0$) at 300 K. Calculate $N_{50}/N_0$ at 300 K.

2. It can be shown that for all linear molecules with unlike ends (HCl, HCN):

   \[ q_{\text{rot}} = \frac{8\pi^2I_k}{\hbar^2} \times T \]

   a) Use this equation to show that for one mole of molecules with unlike ends:

   \[ U_{\text{rot, thermal}} = RT \]

   b) Use the result from part a) to calculate the rotational thermal energy of one mole of CO at 300 K. How does this result compare to your result from CTQ 3?
Model 2: The Vibrational Thermal Energy of Carbon Monoxide.

The vibrational energy levels of a diatomic molecule are given by:

$$\varepsilon_\nu = (\nu + \frac{1}{2}) \frac{h}{2\pi} \sqrt{\frac{K}{\mu}} \quad \nu = 0, 1, 2, \ldots$$  \hspace{1cm} (8)

The energy levels of carbon monoxide can be experimentally observed with infrared spectroscopy, and we find that

$$\varepsilon_\nu = (\nu + \frac{1}{2}) \times 4.257 \times 10^{-20} \text{ Joules}$$  \hspace{1cm} (9)

$$g_\nu = 1$$  \hspace{1cm} (10)

$$q = 1 + e^{-(\varepsilon_1 - \varepsilon_0)/kT} + e^{-(\varepsilon_2 - \varepsilon_0)/kT} + \ldots$$  \hspace{1cm} (11)

$$\frac{dq}{dT} = \frac{(\varepsilon_1 - \varepsilon_0)}{kT^2} e^{-(\varepsilon_1 - \varepsilon_0)/kT} + \frac{(\varepsilon_2 - \varepsilon_0)}{kT^2} e^{-(\varepsilon_2 - \varepsilon_0)/kT} + \ldots$$  \hspace{1cm} (12)

$$U_{\text{thermal, vib}} = \frac{N}{q} kT^2 \frac{dq}{dT}$$

$$= \frac{N}{\left(1 + e^{-(\varepsilon_1 - \varepsilon_0)/kT} + e^{-(\varepsilon_2 - \varepsilon_0)/kT} + \ldots\right)} \left((\varepsilon_1 - \varepsilon_0)e^{-(\varepsilon_1 - \varepsilon_0)/kT} + (\varepsilon_2 - \varepsilon_0)e^{-(\varepsilon_2 - \varepsilon_0)/kT} + \ldots\right)$$  \hspace{1cm} (13)

<table>
<thead>
<tr>
<th>\nu</th>
<th>\varepsilon_\nu</th>
<th>\varepsilon_\nu - \varepsilon_0</th>
<th>e^{-(\varepsilon_\nu - \varepsilon_0)/kT}</th>
<th>(\varepsilon_\nu - \varepsilon_0) e^{-(\varepsilon_\nu - \varepsilon_0)/kT}</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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<td>0.00E+00</td>
<td>1.00E+00</td>
<td>1.00E+00</td>
</tr>
<tr>
<td>1</td>
<td>6.39E-20</td>
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<td>3.42E-05</td>
<td>1.46E-24</td>
</tr>
<tr>
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<td>8.51E-20</td>
<td>1.17E-09</td>
<td>9.97E-29</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td>1.00E+00</td>
<td>1.46E-24</td>
</tr>
</tbody>
</table>

Table 2. Various Quantities for the Determination of \( q_{\text{vib}} \) and \( dq/dT \) for CO at 300 K.

Critical Thinking Questions

9. Verify that all of the entries for \( \nu = 1 \) in Table 2 are correct.
10. Use equation (13) and Table 2 to show that at 300 K, $U_{\text{thermal, vib}} = 0.879 \text{ J/mole}$ for CO.

11. According to Table 2, which vibrational energy level is most populated?

12. About 50 energy levels were used to determine the rotational thermal energy. Only three energy levels were used to determine the vibrational thermal energy. Why?

13. The rotational thermal energy for CO is greater than the vibrational thermal energy. Why? [Hint: examine the Boltzmann distribution with regard to the value of $\varepsilon_i - \varepsilon_0$.]

**Exercises**

3. CO has a very strong bond (a triple bond), the separation between vibrational energy levels is quite large, and the thermal vibrational energy is quite small (0.877 J/mole). Find the thermal vibrational energy at 300 K for a diatomic molecule with a much weaker bond (a single bond), Cl₂. The vibrational energy levels of Cl₂ are given by:

$$\varepsilon_0 = \left(v + \frac{1}{2}\right) 1.11 \times 10^{-20} \text{ Joules}$$

4. Use the Boltzmann distribution equation along with equations (8), (9), and (10) to calculate $N_1/N_0$ (vibrational energy levels) for CO at 300 K. Is your result in agreement with the low thermal vibrational energy for CO at 300 K? Why or why not?

The lowest energy singlet state of the CO molecule is $1.286 \times 10^{-18}$ J above the ground electronic state.

Critical Thinking Questions

14. For CO, is the energy difference between the ground electronic state and the excited electronic state larger or smaller than the energy difference between the $v = 0$ vibrational state and the $v = 1$ excited vibrational state?

15. Assume the ground and first excited electronic energy states of CO are singly degenerate. Do you expect the thermal electronic energy to be higher or lower than the thermal vibrational energy?

Exercises

5. For one mole of CO molecules, use the Boltzmann distribution equation to calculate the number of molecules in the ground electronic state and the number of molecules in the first excited electronic state of CO at 300 K. [Hint: $N_{\text{ground}} + N_{\text{ex}} = N_A$.] Calculate the thermal electronic energy of CO at 300 K.

6. Comment on the following statement:

At normal temperatures the electronic thermal energy of any molecule is essentially zero.
Model 4: The Translational Thermal Energy of Carbon Monoxide.

The translational energy levels of a molecule in a container (particle-in-a-box) are given by:

\[ \varepsilon = \varepsilon(x) + \varepsilon(y) + \varepsilon(z) = \frac{n_x^2 \hbar^2}{8ma^2} + \frac{n_y^2 \hbar^2}{8mb^2} + \frac{n_z^2 \hbar^2}{8mc^2} \]  \hspace{1cm} (14)

where a, b, and c, are the dimensions of the container, and each \( n_i = 1, 2, 3, \ldots \).

It can be shown that the translational partition function is:

\[ q_{\text{trans}} = \left( \frac{2\pi mk}{\hbar^2} \right)^{3/2} V T^{3/2} \]  \hspace{1cm} (15)

where \( m \) is the mass of one molecule and \( V \) is the volume of the container.

Critical Thinking Questions

16. Use the translational partition function to show that \( U_{\text{trans, thermal}} = \frac{3}{2} RT \) for one mole of gas. Recall that:

\[ U_{\text{thermal}} = \frac{N}{q} kT^2 \frac{dq}{dT} \]

17. At 300 K, what is \( U_{\text{trans, thermal}} \) for one mole of CO(g)?
18. At 300 K, what is $U_{\text{rot, thermal}}$ for one mole of CO(g)?

19. At 300 K, what is $U_{\text{vib, thermal}}$ for one mole of CO(g)?

20. At 300 K, what is $U_{\text{elec, thermal}}$ for one mole of CO(g)?

21. At 300 K, what is $U_{\text{total, thermal}}$ for one mole of CO(g)?

22. At 300 K, which contributes more to the thermal energy of carbon monoxide—the translational thermal energy, the rotational thermal energy, the vibrational thermal energy or the electronic thermal energy?

Exercises

7. Estimate the total thermal energy (in kJ/mole) of Ne gas at 300.0 K. Estimate the total thermal energy of Ne gas at 301.0 K. The heat capacity of a substance is thermal energy change per mole per K. Estimate the heat capacity of Ne at 300 K, in J/(K mole) from your calculations above. Compare your value to the experimental heat capacity of Ne at 300 K, 12.47 J/K mole.

8. The translational thermal energy of a gas is given by $U_{\text{trans, thermal}} = \frac{3}{2} RT$ (CTQ 15). If the heat capacity is defined as $dU/dT$, what is the expression for the heat capacity of a gas with translational thermal energy only? Calculate a heat capacity for Ne based on this expression. Compare your value to the values in Exercise 7.