Newtonian mechanics accurately describes the behavior of relatively large, slowly-moving objects. For molecular systems, care must be taken since the motion of electrons cannot be treated with this approach. However, other aspects of molecular motion can be described with classical mechanics. This chapter explores the energies of chemical systems. The starting point is classical, Newtonian mechanics. However, the final goal is a description of chemical systems consistent with the principles of quantum mechanics - the rules which describe the behavior and properties of electromagnetic radiation, atomic particles and the interaction of these two phenomena.

1. Kinetic Energy - Energy of Motion

The kinetic energy of a particle of mass, \( m \), travelling at a velocity \( v \) is given by:

\[
E_{\text{kin}} = \frac{1}{2}mv^2
\]

The kinetic energy of "slow-moving", "large" molecular-particles can be treated using this relationship. If the velocity approaches the speed of light, \( c \), relativistic mass corrections must be added to the energy expression.

1.1 Kinetic theory of gases

The kinetic-molecular theory of gases is a classical treatment of the energy, velocity and motion of molecules in the gas phase. The assumptions of this model are:

*1. A gas is composed of a large number of particles. The size of the gas atoms/molecules is much smaller than the volume of the system.
*2. Gas particles are in constant, random (three-dimensional) motion.
*3. The particles are independent and only interact with the walls of the container, or with each other, during short elastic collisions. Elastic collisions are characterized by conservation of energy and momentum.
*4. Classical (Newtonian) mechanics accurately described the motion of the particles.

Gas pressure, \( P \), arises from the collisions of gas particles with the walls of the container. This theoretical treatment predicts that the pressure exerted on a wall by \( N \) particles, each of mass \( m \), occupying a volume \( V \), moving at an average velocity of \( v \), is given by:

\[
P = \frac{1}{3} \frac{Nm v^2}{V}
\]

Since the kinetic energy, \( e_{\text{kin}} \), is given by \( \frac{1}{2}mv^2 \), this equation can also be written as

\[
P = \frac{2}{3} \frac{Ne_{\text{kin}}}{V}
\]

\[
PV = \frac{2}{3} Ne_{\text{kin}}
\]

If this equation is compared with the ideal gas equation, \( PV = nRT \), an expression is obtained for the kinetic energy of an ideal gas molecule in terms of temperature.
\[ PV = NRT \]

\[ PV = \frac{2}{3} N e_{kin} \]

\[ \therefore e_{kin} = \frac{3}{2} RT \]

A mole of an ideal gas has a kinetic energy of \( \frac{3}{2} RT \). Since each particle is moving in three-dimensions (x, y, and z), each of these degrees of freedom contributes \( \frac{1}{2}RT \) to the kinetic energy of a mole of gas particles. One can also state that each molecule has \( \frac{1}{2}kT \) of kinetic energy for each translation degree of freedom.

The derivation of the kinetic energy formula is based on average velocities. A more rigorous analysis predicts that a range of \( v \) and \( e_{kin} \) should be observed for gas behavior. The energy distribution, termed the Maxwell-Boltzmann, is given by

\[ f(e_{kin}) = 2\pi \left( \frac{1}{\pi kT} \right)^{\frac{3}{2}} \frac{1}{e_{kin}} \exp \left( -\frac{e_{kin}}{kT} \right) \]

and the velocity distribution is given by

\[ f(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \frac{1}{v^2} \exp \left( -\frac{\frac{1}{2}mv^2}{kT} \right) \]

However, many aspects of molecular behavior can be treated with the model based on average energy and velocity.

1.2 Degrees of Freedom and Molecular Motion:

A single particle moving in three-dimensions has \( \frac{3}{2} kT \) of kinetic energy (or \( \frac{3}{2} RT \) per mole). Therefore, each of the three degrees of freedom of a molecule can be associated with \( \frac{1}{2} kT \) of energy.

This principle is generalized to define the **equipartition theorem**: \( \frac{1}{2} kT \) of energy is associated with each degree of freedom in a molecule. A degree of freedom is any type of molecular motion: translation of the molecule, internal vibration or rotation about the center of mass.

Each atom in a molecule is free to move in three directions (regardless of the bonding assignments). Therefore, a single molecule made up of \( N \) atoms must have \( 3N \) degrees of freedom. Assigning chemical bonds does not diminish the total number of degrees of freedom for a group of atoms.

Chemical bonds transform a group of atoms into a molecule, thus introducing correlations between the \( 3N \) degrees of freedom. Instead of \( 3N \) independent atoms translating in space, the molecule translates as a unit, vibrates about defined equilibrium geometries and rotates about specific axis passing through the center of mass of the molecule. Therefore the \( 3N \) degrees of freedom must be redistributed among translational, vibrational and rotational modes of motion in the molecule.

*** Translation

The translational of a molecule is always assigned 3 degrees-of-freedom. The motion is characterized by:

- Movement in the x, y and z directions
- Motion of the molecular unit as a whole.
- Molecular position or location is attributed to the center of mass.

*** Rotation

For a linear molecule, 2 degrees of freedom correspond to the two axes of rotation.
For a non-linear system, 3 degrees of freedom correspond to the three axes of rotation. The actual rotation is about axes passing through the center of mass. A linear molecule has two such axes, a non-linear has three rotational axes.

### Vibration
The number of vibrational modes or degrees of freedom is determined by difference:

$$3N - \text{(Sum of translational and rotational degrees of freedom)}$$

For linear molecule there are 3 translational and 2 rotational degrees of freedom. Therefore, the molecule has $3N-5$ vibrational modes or degrees of freedom. For non-linear molecule (the more common case) there are 3 translational and 3 rotational degrees of freedom. Therefore, the molecule has $3N-6$ vibrational modes.

**Examples:**

a. For the diatomic O$_2$, $N=2$, therefore there are 6 (3*2) total degrees of freedom. 3 of these are translational. The molecule is linear therefore it has two rotational degrees of freedom. This leaves 1 $(3N-5=6-5=1)$ vibrational mode for O$_2$, corresponding to the vibration of the O-O bond. All diatomic molecules would have this distribution of degrees of freedom.

b. For methane, CH$_4$, $N=5$, thus there are 15 total degrees of freedom. As for the previous case, 3 are translational, but since this molecule is non-linear, it has 3 rotational degrees of freedom. This leaves 9 vibrational modes for CH$_4$.

The partitioning of degrees of freedom is a straightforward process. These modes are associated with bond stretch and bond-angle bending motions. However, the exact assignments require a rigorous analysis for each type of molecule. For diatomics, the single vibrational mode is easily assigned to the compression and stretching of the bond. For polyatomics, the assignments of vibrational modes is a bit more challenging.

For a bent triatomic, such as H$_2$O, the 9 degrees of freedom are partitioned as follows: 3 translational, 3 rotational and 3 vibrational. The vibrations are assigned to the 3 modes - or distinct shifts of atomic positions corresponding to natural vibrations.

**Exercises:**

a. Analyze the degrees of freedom for the linear CO$_2$ molecule.

b. Diagram the vibrational modes for CO$_2$.

### 1.3 Velocities of Ideal Gas Molecules

The kinetic energy of a gas molecule of mass "$m$" moving at velocity "$v$" is given by $\frac{1}{2}mv^2$. For a particle moving in three dimensions the kinetic energy is also equal to $\frac{3}{2}kT$.

Therefore, these two kinetic energy expressions can be equated to derive an expression for the velocity of a gas molecule, of mass "$m$", at a specific temperature.

$$\frac{1}{2}mv^2 = \frac{3}{2}kT$$

$$v^2 = \frac{3kT}{m}$$

$$v = \sqrt{\frac{3kT}{m}}$$

This velocity is called the $v_{rms}$, "root mean square" velocity, and is directly proportional to square-root of $T$ and inversely proportional to the square-root of the molecular mass.
Example: Determine the \( v_{rms} \) for a nitrogen molecule at 25ºC.

\[
T = 25 + 273.15 = 298.15 \text{ K}
\]

\[
m = 28 \text{ amu} = 28 \times (1.67 \times 10^{-27} \text{ kg}) = 4.7 \times 10^{-26} \text{ kg}
\]

\[
k = 1.38 \times 10^{-23} \text{ J K}^{-1} \quad \text{and} \quad 1 \text{ J} = \text{kg m}^2 \text{ s}^{-2}
\]

Substitution in the equation yields: \( v^2 = 2.626 \times 105 \text{ m}^2 \text{ s}^{-2} \) \( v_{rms} = 512 \text{ m s}^{-1} \)

This simple formula provides an estimate of the average velocities of gas molecules. However, no allowance is made for molecular geometry/size, internal degrees of freedom or collisions of molecules. Collisions of molecules, as they relate to chemical reactions, are discussed briefly in Chapter 13.

A more useful application of this relationship is the derivation of an equation for the relative velocity or speed of two molecules at the same temperature. For two molecules, with masses \( m_1 \) and \( m_2 \), the relative velocity is given by:

\[
\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}
\]

This result arises from the fact that for ideal gas particles the kinetic energy depends only on the temperature. Therefore, for two particles with the same kinetic energy, the larger molecule must move more slowly than the smaller molecule. Calculations of relative velocity are quite simple since they only require the mass ratio \( m_2/m_1 \).

Exercises:

a. Determine the velocity of Ar atoms at room temperature and 1000ºC. What are the relative velocities of Ar and He under these conditions?

b. Based on \( v_{rms} \), at what temperature will a He atom velocity match the speed of light? (Ignore relativistic effects)

c. Plot a graph of the speed of the Ar atoms as a function of temperature - from 0. to 2000. K.

2. Potential Energy - Energy of position

The potential energy arises from the interaction an object with an external potential. The potential usually depends on distance and possibly molecular orientation. The type of interaction reflects some characteristic of the atom or molecule, for example: ionic charge, mass, magnetic moment, dipole moment.

2.1 Electrostatic energy

In a vacuum, a particle of charge \( q_1 \) interacts with the electric potential, \( \phi_2(r) \), established by a second charged particle, \( q_2 \).

\[
\phi_2(r) = \frac{1}{4\pi\varepsilon_0} \frac{q_2}{r}
\]

where \( \varepsilon_0 \) is the vacuum permittivity.

The electrostatic (or Coulombic) energy, \( E_{\text{Coul}} \), of particle 1 interacting with the potential generated by particle 2 is given by \( q_1 \phi_2(r_{12}) \) or

\[
E_{\text{Coul}} = \frac{1}{4\pi\varepsilon_0} q_1 q_2 / r_{12}
\]

where \( r_{12} \) is the distance between the particles.

For electrons, \( q_i = -e \), for protons \( q_i = +e \) and for ions of charge \( n \), \( q_i = ne \), (integral units of \( e \)). The constant factor common to all Coulombic interactions is

\[
e^2/(4\pi\varepsilon_0) = 2.307 \times 10^{-28} \text{ J m.}
\]

Therefore \( E_{\text{Coul}} \) is given in units of joules/molecule, for \( r_{12} \) in \( m \).

For particles in other media (such as ions in solvents, air, or solids), \( \varepsilon_0 \) is replaced by \( \varepsilon \), the permittivity of the medium. The \( E_{\text{Coul(solvent)}} \) is therefore diminished in proportion to the dielectric constant, \( \varepsilon/\varepsilon_0 \). (Often the symbol \( \varepsilon \) is used for this ratio, since it
is assumed that the permittivity is measured relative to the vacuum).

The dielectric constants for a number of solvents in given in Table 3-1. Solvents with high dielectric constants have a greater capacity for stabilizing charge particles (relative to the vacuum), and hence facilitate the ionization of molecular species. This is termed the dielectric effect. Charged species which would normally be unstable, are stabilized by solvent molecules. The Coulombic interaction in a solvent is given by the following equation:

\[ E_{\text{Coul}}(\text{solvent}) = \left( \frac{\varepsilon_0}{\varepsilon} \right) \cdot E_{\text{Coul}}(\text{vacuum}) \]

or simply

\[ E_{\text{Coul}}(\text{solvent}) = \left( \frac{1}{\varepsilon} \right) \cdot E_{\text{Coul}}(\text{vacuum}) \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dielectric Constant$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.00</td>
</tr>
<tr>
<td>Water</td>
<td>78.54</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.63</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
</tr>
<tr>
<td>Acetone</td>
<td>20.7</td>
</tr>
<tr>
<td>Ammonia</td>
<td>16.9</td>
</tr>
<tr>
<td>Pyridine</td>
<td>12.3</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.28</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.02</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.88</td>
</tr>
<tr>
<td>Pentane</td>
<td>1.84</td>
</tr>
</tbody>
</table>


### 2.2 Gravitational energy

The gravitational energy of an object of mass $m$ is given by:  
\[ E_{\text{grav}} = mg\Delta h \]
where $g$ is the acceleration due to earth's gravity and $\Delta h$ is the height relative to the zero of gravitational energy.

#### Exercises
1. Determine the kinetic energy of an electron traveling at 0.10 % of the speed of light.
2. Calculate the Coulombic energy of a pair of electrons separated by 2.5 Å. Consider electrons in a vacuum and in water.

### 3. Quantized Energies - Classical vs. Quantum Mechanics

In classical mechanics, an object may have any kinetic, rotational or vibrational energy. However, for real molecules, only certain values of kinetic, vibrational and rotational energy are permitted. The use of classical concepts is totally inadequate to explain the observed behavior. These systems must be described by quantum mechanics in order to correctly explain experimental behavior.
3.1 Wave-Particle Duality:

Electromagnetic radiation exhibit wave and particle properties. Radiation displays wave character in diffraction experiments. X-ray are diffracted by a crystalline lattice, resulting in a reflected wave of constructive and destructive interference patterns. However, the energy of electromagnetic radiation is quantized in photons, discrete bundles of radiant energy and momentum. The energy is found to be related to the frequency of radiation, \( \nu \), by

\[
e = h\nu
\]

where \( h \) is Planck constant. The energy of a photon is independent of radiation intensity, as evidenced by photoelectron experiments. If desired, the energy can also be expressed in terms of wavelength, \( \lambda \), using the relationship:

\[
\lambda = \frac{h}{mv}
\]

Paradoxical, dual behavior is not limited to electromagnetic radiation. Objects normally viewed as particles also display wave character under certain conditions. In fact all matter exhibits wave and particle behavior, resulting in a "duality of nature". For example, neutrons exhibit wave character in diffraction experiments (similar to X-rays), but appear as particles in particle-scattering experiments.

de Broglie proposed that the "wavelength" of a moving material object is inversely proportional to the momentum \( (p) \) of the object \( (p = \text{mass} \times \text{velocity} = mv) \).

\[
\lambda = \frac{h}{p} = \frac{h}{mv}, \quad h \text{ is Planck's constant.}
\]

This property is relevant for small particles moving at high velocities in microscopic regions of space. The wave character is only evident when the de Broglie wavelength is comparable in size to the particle system or scale of the measurement. For classical systems wave character is not relevant; \( \lambda \) is usually much smaller than the size of the object.

Examples:

a. Consider an electron moving at 10% of the speed of light (assume relativistic effects can be ignored).

\[
h = 6.626 \times 10^{-34} \text{ J s} \\
 m = 9.11 \times 10^{-31} \text{ kg} \\
 v = 2.998 \times 10^7 \text{ m s}^{-1}
\]

\[
mv = 2.73 \times 10^{-23} \text{ kg m s}^{-1}
\]

\[
\lambda = 6.626 \times 10^{-34}/(2.73 \times 10^{-23}) = 2.42 \times 10^{-11} \text{ m} = 0.24 \text{ Å}
\]

For this electron, the wavelength is comparable in size to atomic and molecular systems.

b. Consider an electron moving at 1 m/s.

\[
mv = 9.11 \times 10^{-31} \text{ kg m s}^{-1}
\]

\[
\lambda = 6.626 \times 10^{-34}/(9.11 \times 10^{-31}) = 2.42 \times 10^{-3} \text{ m}
\]

The wavelength is much larger than the scale of microscopic systems.

Exercises

1. Calculate the energy of a photon whose wavelength is 300 nm.
2. Determine the wavelength of a 1000 kg car traveling at 100 kph (kilometer/hour). Are quantum considerations valid for this system?

3.2 Confined Particle

Consider a particle moving along a line of fixed length \( a \). The particle exists in a defined, 1-dimensional region of space. Based on de Broglie's hypothesis, the particle exhibits wave character. Therefore, the wave corresponding to this particle must fit the line, i.e. integral-multiples of one-half the wavelength must be equal to the size of the box, \( a \).
This can be described with the mathematical relationship

\[ a = i \left( \lambda/2 \right) \text{ with } i=1,2,3,4... \]

The waves for to \( i=1 \) and \( i=2 \) are shown in Figures 3-1 and 3-2.

**Probability and wavefunctions**

The square of the amplitude of the wave denotes the probability of finding the particle at a given point. The particle density can thus be derived from the quantum mechanical wave or wavefunction. For electron systems, the square of the wavefunction is the theoretical analog of electron density.

The wavefunction is given the symbol \( \Psi \). The probability is then described by \( \Psi^* \Psi \). The wavefunction may have a negative sign, however, the probability is always non-negative; \( \Psi^* \Psi = -0.2 \) and \( \Psi^* \Psi = 0.2 \) yield the same probability: \( \Psi^* \Psi = 0.04 \).

**Boundary conditions**

The amplitude of the wave is zero at the edges of the box, denoting that the particle is confined inside the box, i.e. between 0.0 and \( a \) along the line. Outside the box the probability, \( \Psi^* \Psi \), is also zero.

**Quantized energy levels**

Substituting the de Broglie's relationship for wavelength of a particle \( (\lambda = h/mv) \):

\[ \frac{i}{2} \left( \frac{h}{mv} \right) = a \]

\[ \Rightarrow \quad \text{mv} = \frac{ih}{2a} \]

The expression for classical kinetic energy can be altered to yield an equation in terms of "mv":

\[ e_{kin} = \frac{1}{2} \text{mv}^2 = \frac{(mv)^2}{2m} \]

Inserting the deBroglie expression for "mv", the energy is given by:

\[ e_{kin} = \frac{(ih/2a)^2}{2m} \]

\[ e_{kin} = \frac{i^2 h^2}{8ma^2} \]
The following conclusions are evident from the 1-dimensional confined-particle problem:

1. The kinetic energy is quantized for particles confined in specified regions of space; only certain discrete energies are permitted for the system.
2. \( n \) is an integer quantum number defining the energy and wavelength of the confined particle.
3. For large boxes and/or macroscopic particles the level-spacing approaches zero - the classical limit. This occurs when \( \hbar^2 \) is small relative to \( am^2 \).

The energy levels of the confined-particle can be described as \( e_i \): where \( e_i = i^2 e_1 \), and \( e_1 = \frac{\hbar^2}{8ma^2} \). All energy levels are derived from the ground state or lowest energy level.

For example, the first 5 energy levels are:

\[ e_1, 4e_1, 9e_1, 16e_1, \text{and } 25e_1. \]

The spacing between adjacent energy levels increases dramatically as the quantum number \( n \) and the resulting energy increase.

Example:

Determine the kinetic energy levels for an electron confined in a 1.0 Å box.

\[
\begin{align*}
\text{m} &= 9.11 \times 10^{-31} \text{ kg} \\
\hbar &= 6.626 \times 10^{-34} \text{ J s} \\
a &= 1.0 \text{Å} = 1.0 \times 10^{-10} \text{m} \\
e_1 &= \frac{(6.626 \times 10^{-34})^2}{(8.0 \times 9.11 \times 10^{-32} \times 1.0 \times 10^{-10} \times 1.0 \times 10^{-10})} \\
&= 6.02 \times 10^{-18} \text{ J/molecule} \\
e_2 &= 4e_1 = 14,515 \text{ KJ/mole} \\
e_i &= i^2 * 3629 \text{ KJ/mole}
\end{align*}
\]

The energy spacings for this system are very large. In fact the spacing between levels is much larger than the magnitude of the ground state energy term. This indicates that for electrons confined in atomic-sized regions of space, quantum mechanical treatments are clearly required.

Exercises:

1. Determine the energy levels for a proton confined in a 5 Å line.
2. How do these levels compare to a 20 g ball confined on a 1 m line.

All chemical systems exhibit quantized behavior. The energy levels are quantized energy, no matter the type of interaction or energy encountered (kinetic, electronic, spin, vibrational or rotational). For each type of system/energy a mathematical description can be developed to describe the behavior. Quantum mechanics is the formalism for describing the wavefunction and energies for particle(s) under the quantum conditions.

4 Occupancies of energy levels: The Boltzmann distribution

Quantum mechanics can be used to calculate the positions of energy levels, but the relative populations of these levels is obtained using the Boltzmann distribution. The population of energy levels will depend on the amount of thermal energy available to the system, given by \( k*T \) (k is the Boltzmann constant and T is the temperature in Kelvin.).

The relative populations of two energy levels \( e_i \) and \( e_j \) at temperature "T" (in degrees K) is given by the following formula.

\[
\frac{n_j}{n_j} = \exp\left(-\frac{e_i - e_j}{kT}\right)
\]

k, the Boltzmann constant, is given by the gas constant "R", divided by Avogadro's Number, \( N_A \): \( k = R/N_A \). A comparable relationship is used to derived the distribution in kinetic energies and velocities for gas molecules.

Due to the presence of the exponential term, the relative population changes rapidly with increasing energy gap or decreasing tempera-
Molecular Energies

ture. The limiting cases are:

a. At T=0, all electrons are in the ground state, \( n_2/n_1 = 0.0 \).  
b. At extremely high temperature two adjacent levels will have roughly equal populations.

For "classical" kinetic energy, at normal temperatures, the energy gap is small, relative to \( kT \); therefore quantum effects are not observed (\( e^0 = 1.0 \)). Adjacent energy levels have comparable populations.

If state have degenerate energy state the population equation is altered to accommodate this system feature. The \( n_i \) and \( n_j \) are each divided by the number of degenerate states, \( g_i \) and \( g_j \), for the i and j levels.

**Example:**

a. For an electron confined on a 1.0 Å line determine the relative population of the first two confined-particle energy state at room temperature (300 K).

From the previous work:

\[
\Delta e = e_2 - e_1 = (4-1)\times6.02\times10^{-18} = 1.81 \times 10^{-17} \text{ J/molecule}
\]

\[
kT = 1.318\times10^{-23} \times 300.0 = 3.95 \times 10^{-21} \text{ J}
\]

\[
\frac{\Delta e}{kT} = 4572.
\]

Therefore \( n_2/n_1 = e^{-4572} = 0.0 \)

All of the electrons are in the ground state.

b. The temperature is increased to 10^6 K (solar temperatures), determine the new population.

\[
\Delta e = e_2 - e_1 = (4-1)\times6.02\times10^{-18} = 1.81 \times 10^{-17} \text{ J/molecule}
\]

\[
kT = 1.318\times10^{-23} \times 1x10^6 = 1.32 \times 10^{-17} \text{ J}
\]

\[
\Delta e/kT = 1.37
\]

Therefore \( n_2/n_1 = e^{-1.37} = 0.25 \)

One particle is in the second state for every four particles in the ground state.

The Boltzmann distribution allows the prediction of the relative populations, given the energy gap and temperature, for any system or type of energy. In addition, it allows the prediction of the temperature required to support a given relative population. With this application in mind, the Boltzmann distribution may also be written as

\[
\ln \left( \frac{n_i}{n_j} \right) = - \left( \frac{e_i - e_j}{kT} \right)
\]

**Exercises:**

a. Determine the relative populations of two levels separated by \( 3 \times 10^{-21} \text{ J/molecule} \) at room temperature and at 5 K.

b. At what temperature will 30% of the particles be in the upper state and 70% in the more stable ground state.