An Introduction to Chemistry
by Mark Bishop
Some Chemical Changes Release Energy

- For example, the methane in natural gas reacts with oxygen gas to form carbon dioxide, water, and energy.
Some Chemical Changes Absorb Energy

Some reactions absorb energy.

$O_2(g) + \text{energy} \rightarrow 2O(g)$
Energy Terms

- **Energy** = the capacity to do work
- **Work**, in this context, may be defined as what is done to move an object against some sort of resistance.
Kinetic energy, momentum, force of collisions, and work

- **Kinetic Energy** = the energy of motion = \( \frac{1}{2} m \mu^2 \).
  
  \( m = \text{mass}, \mu = \text{velocity} \)

- The force of collisions is proportional to the momentum (mass \( \times \) velocity, \( m\mu \)) of the objects colliding.

- Therefore, if two objects are moving at the same velocity, the more massive object will have greater momentum, so it will collide with more force, giving it a greater capacity to do work, and a greater kinetic energy.

- If two objects have the same mass but are moving at different velocities, the faster moving object will have greater momentum, so it will collide with more force, giving it a greater capacity to do work, and a greater kinetic energy.
Coin and Potential Energy

- **Potential Energy** = energy by virtue of position or state

  - More stable
  - Lesser capacity to do work
  - Lower potential energy

  - Less stable
  - Greater capacity to do work
  - Higher potential energy
Law of Conservation of Energy

- Energy can be neither created nor destroyed, but it can be transferred from one system to another and changed from one form to another.

When a coin is flipped, some of the kinetic energy of the moving thumb is transferred to kinetic energy of the moving coin.

As the coin falls, potential energy is converted to kinetic energy.

The kinetic energy associated with the coin's upward movement is converted to potential energy as the coin slows and eventually stops.
Endergonic Change

coin in hand $\rightarrow$ coin in air above hand
more stable $\rightarrow$ less stable system
lesser capacity to do work $\rightarrow$ greater capacity to do work
lower PE $\rightarrow$ energy $\rightarrow$ higher PE
Bond Breaking and Potential Energy

\[ \text{O}_2(g) + \text{energy} \rightarrow 2\text{O}(g) \]

- atoms in bond + Energy → separate atoms
- greater force of attraction + Energy → lesser force of attraction
- more stable + Energy → less stable
- lower PE + Energy → higher PE
Exergonic Change

coin in air above hand $\rightarrow$ coin on ground

less stable system $\rightarrow$ more stable

greater capacity to do work $\rightarrow$ lesser capacity to do work

higher PE $\rightarrow$ lower PE + energy
Bond Making and Potential Energy

\[ O(g) + O_2(g) \rightarrow O_3(g) + \text{energy} \]

- separate atoms → atoms in bond
- lesser force of attraction → greater force of attraction
- less stable → more stable
- higher PE → lower PE

Energy + Energy + Energy
Incandescent light bulbs burn out because their tungsten filament gradually evaporates, weakening until it breaks. Argon gas is added to these bulbs to reduce the rate of evaporation. Collisions between the argon atoms and the higher-temperature wire leads to KE being transferred to the argon atoms, cooling the wire. Which has greater energy, (1) an argon atom, Ar, with a velocity of 428 m/s or (2) the same atom moving with a velocity of 456 m/s? (These are the average velocities of argon atoms at 20 ºC and 60 ºC.)
Which higher energy? Is it kinetic or potential?

• Because krypton, Kr, atoms have a greater mass than argon atoms, krypton gas does a better job than argon of reducing the rate of evaporation of the tungsten filament in an incandescent light bulb. Because of krypton’s higher cost, however, krypton is only used when longer life is worth the extra cost. Which has higher energy, (1) an argon atom with a velocity of 428 m/s or (2) a krypton atom moving at the same velocity?
According to our model for ionic solids, the ions at the surface of an ionic crystal are constantly moving out and away from the other ions and then being attracted back to the surface. Which has more energy, (1) a stationary sodium ion well separated from the chloride ions at the surface of a sodium chloride crystal or (2) a stationary sodium ion located quite close to the chloride ions on the surface of the crystal?
Sodium Chloride, NaCl

Each chloride anion is surrounded by six cations.

Each sodium cation is surrounded by six anions.

Salt (sodium chloride)
What we know about charge.

- It’s the characteristic of matter that gives rise to electromagnetic forces.
- Some particles have charge and some do not.
- There are two types of charge, plus and minus.
- Like charges repel each other.
- Opposite charges attract each other.
- The closer the charged particles are, the stronger the repulsion or attraction.
Sodium Chloride, NaCl
Potential energy for the Na\(^+\) and Cl\(^-\) attraction

- Na\(^+\) cations and Cl\(^-\) anions attract each other.
- The closer the Na\(^+\) and Cl\(^-\) ions are, the stronger the attraction is between them. This makes the Na\(^+\) cation that is closer to the Cl\(^-\) ions in the system on the right less likely to change, more stable, and lower PE.
Potential energy for the Na\(^{+}\) and Cl\(^{-}\) attraction

- Energy is required to pull the Na\(^{+}\) cation and Cl\(^{-}\) anions apart in the system on the right, and this energy goes to increased PE of the less stable, higher PE ions that are less attracted to each other in the system on the left.
Which higher energy? Is it kinetic or potential?

• The chemical reactions that lead to the formation of polyvinyl chloride (PVC), which is used to make rigid plastic pipes, are initiated by the decomposition of peroxides. The simplest peroxide is hydrogen peroxide, $\text{H}_2\text{O}_2$ or HOOH. Which has more energy, (1) a hydrogen peroxide molecule or (2) two separate HO molecules that form when the relatively weak O–O bond in an HOOH molecule is broken?

$\text{HOOH} \rightarrow 2\text{HO}$
• Hydrogen atoms react with oxygen molecules in the earth’s upper atmosphere to form HO$_2$ molecules. Which has higher energy, (1) a separate H atom and O$_2$ molecule or (2) an HO2 molecule?

\[ \text{H(g)} + \text{O}_2 \text{(g)} \rightarrow \text{HO}_2 \text{(g)} \]
Units of Energy

- Joule (J) = \( \frac{\text{kg m}^2}{\text{s}^2} \)

- 4.184 J = 1 cal
- 4.184 kJ = 1 kcal
- 4184 J = 1 Cal (dietary calorie)
- 4.184 kJ = 1 Cal
Approximate Energy of Various Events

- Average KE of room temperature air molecule, about $10^{-24}$ J
- Hopping Flea, about $10^{-10}$ J
- Burning match, about 1 J
- Burning one gallon of gasoline, about $10^3$ J
- Severe earthquake, about $10^5$ J
- Yearly solar emission, about $10^{31}$ J
- Creation of the universe, about $10^{65}$ J

- Electron in atom, about $10^{-21}$ J
- Human heartbeat, about $10^{-3}$ J
- Lightning Bolt, about $10^{-7}$ J
- Human running for one hour, about $10^{-4}$ J

[joules]
External KE is the energy associated with the overall motion of an object.

Internal KE is the energy associated with the random motion of particles within an object.
External and Internal Kinetic Energy

- **External Kinetic Energy** = Kinetic energy associated with the overall movement of a body

- **Internal Kinetic Energy** = Kinetic energy associated with the random motion of the particles within a body
Temperature and heat transfer

- Temperature reflects the average internal KE ($\frac{1}{2}m\mu^2$) of the particles.
- Higher temperature means greater average internal KE for the particles.
- The force of collisions is proportional to the momentum ($mass \times velocity$, $m\mu$) of the objects colliding.
- Therefore, the higher the temperature, the greater the average internal KE of the particles, the greater their average momentum, and the greater the average force of collisions.
Heat Transfer

Lower-temperature object
↓
Lower average force of collisions
↓
Particles speed up when they collide with particles of the higher-temperature object.
↓
Increased energy

Higher-temperature object
↓
Higher average force of collisions
↓
Particles slow down when they collide with particles of the lower-temperature object.
↓
Decreased energy
Heat

• **Heat** = the process by which internal kinetic energy is transferred from a region of higher temperature to a region of lower temperature due to collisions of particles.
Radiant Energy

- **Radiant Energy** is electromagnetic energy that behaves like a stream of particles.
- It has both particle and wave character.
  - Particle
    - photons = tiny packets of radiant energy
    - $10^{17}$ photons/second from a flashlight bulb
  - Wave
    - oscillating electric and magnetic fields
    - describes effect on space, not true nature of radiant energy
A Light Wave’s Electric and Magnetic Fields

Source

Electric field, perpendicular to magnetic field

Magnetic field, perpendicular to electric field

Radiant energy
A Light Wave’s Electric Field

Before turning on light

After turning on light
A Light Wave’s Electric and Magnetic Fields

Source

Wavelength, $\lambda$, the distance between two peaks

Electric field, perpendicular to magnetic field

Magnetic field, perpendicular to electric field

Radiant energy
Wavelength and Photon Energy

- The shorter the wavelength is, the higher the energy of the photon.
- The longer the wavelength is, the lower the energy of the photon.
- There is a huge range of wavelengths and energies for radiant energy.
- We divide the complete radiant energy spectrum into categories based on how they are formed and how they effect us.
Radiant Energy Spectrum

- **Gamma Rays**: From radioactive decay
- **X-rays**: Used for medical and dental x-rays
- **UV (Ultraviolet)**: Causes tanning, skin cancer
- **Visible**: Released when bodies cool
- **Infrared (IR)**: Used for microwave ovens, radar, and space vehicle communication
- **Microwaves**: Used for communication and entertainment
- **Television and Radiowaves**: Used for communication and entertainment

Photon energy (J) vs. Wavelength (m)
Atomic Theory

- To see a World in a Grain of Sand
  And a Heaven in a Wild Flower
  Hold Infinity in the palm of your hand
  And Eternity in an hour

  William Blake   Auguries of Innocence

- Thus, the task is not so much to see what
  no one has yet seen, but to think what
  nobody has yet thought, about that which
  everybody sees.

  Erwin Schrödinger
Particle and Wave Nature

• All matter has both particle and wave character.
• The less massive the particle, the more important its wave character.
• The electron has a very low mass, low enough to have significant wave character.
A Problem

- **Problem**: We have a barrier to our understanding, and things with significant wave character are to some degree outside that barrier. This means that the behavior of electrons is non-intuitive.
How We Solve the Problem

- One way we have been able to “describe” things outside our barrier of understanding is through mathematics.
- We describe things outside our barrier of understanding with mathematical equations, we solve the equations, we drag the results back under our barrier, and we apply them to things we do understand.
- If this helps us explain things or predict things, we assume we are on the right track.
Strangenessness of Tiny Particles

• Things become very strange in the realm of the very, very small.

• One element of this strangeness is that we lose the possibility of being able to predict with certainty where small particles are going to be and how they are moving.

• Thus we shift from talking about where tiny things will be to where they will probably be.
Ways to deal with Complexity and Uncertainty

• **Analogies**  In order to communicate something of the nature of the electron, scientists often use analogies. For example, in some ways, electrons are *like* vibrating guitar strings.

• **Probabilities**  In order to accommodate the uncertainty of the electron’s position and motion, we refer to where the electron *probably is* within the atom instead of where it definitely is.
Guitar String Waveform

7 possible configurations for the vibration of a guitar string

Superimposing the configurations produces the waveform of the guitar string's standing wave.
Allowed Vibrations for a Guitar String
Equation for Guitar String

\[ A_x = A_0 \sin \left( \frac{n\pi x}{a} \right) \]

- \( A_x \) = the amplitude at position \( x \)
- \( A_0 \) = the maximum amplitude at any point on the string
- \( n = 1, 2, 3, \ldots \)
- \( x = \) the position along the string
- \( a = \) the total length of the string
Guitar String
Amplitudes

A_1

A_0

A_2
Guitar String Waveform 1

\[ A_x = A_0 \sin \frac{n\pi x}{a} \]

\[ A_x = A_0 \sin \frac{\pi x}{a} \]
Guitar String
Waveform 2

\[ A_x = A_0 \sin \left( \frac{2\pi x}{a} \right) \]
Guitar String
Waveform 3

\[ A_x = A_0 \sin \frac{3\pi x}{a} \]
Dimensions

Guitar String

Dimensions:
- x-axis
- y-axis

Drumhead

Electron for hydrogen

Nucleus

Axes:
- x-axis
- y-axis
- z-axis
Step 1: Set up the general form of the wave equation that describes the electron in a hydrogen atom. We call this equation the wave function and the values calculated from the wave equation are represented by $\Psi$.

$\Psi_{x,y,z} = f(x,y,z)$
Determination of the Allowed Electron Waveforms

- **Step 2:** Determine the forms of the general equation that fit the boundary conditions. Each equation has its own set of three quantum numbers. For example,

\[
\Psi_{1s} = f_{1s}(x,y,z) \text{ with } 1,0,0 \text{ for quantum numbers}
\]

\[
\Psi_{2s} = f_{2s}(x,y,z) \text{ with } 2,0,0 \text{ for quantum numbers}
\]

\[
\Psi_{2p} = f_{2p}(x,y,z) \text{ with } 2,1,1 \text{ or } 2,1,0 \text{ or } 2,1,-1 \text{ for quantum numbers}
\]
• **Step 3:** Use the specific form of the wave equation to do a series of repetitive calculations to get values for many different positions outside the nucleus. Each position is represented in the equation by different $x$, $y$, and $z$ coordinates.

• **Step 4:** We ask our computer to summarize the values calculated in two ways.
Graph for the 1,0,0 Equation

Relationship between the value for the wave function and distance from the nucleus for the 1s orbital of a hydrogen atom
Waveform for 1s Electron (1,0,0)

Nucleus, about 0.00001 the diameter of the atom

The electron-wave character is most intense at the nucleus and decreases in intensity with distance outward.
Particle Interpretation of 1s Orbital

A multiple exposure picture of the electron in a 1s orbital of a hydrogen atom might look like this.
“Just give up approach”

Nucleus, about 0.00001 the diameter of the atom

The negative charge is most intense at the nucleus and decreases in intensity with distance outward.
Almost all of the electron's charge lies within a spherical shell with the diameter of this circle.

Sphere enclosing almost all of the electron's negative charge
Wave Character of the Electron

• Just as the intensity of the movement of a guitar string can vary along the length of the string, so can the intensity of the negative charge of the electron vary at different positions outside the nucleus.

• We can calculate these variations by using a one-dimensional wave equation for the guitar string and a three-dimensional wave equation for the electron.
Guitar and Electron Waveforms

• The calculated variation in the intensity of the movement of the guitar string and the calculated variation in the intensity of the electron charge can be described in terms of three-dimensional standing waves.
• Although both the electron and the guitar string can have an infinite number of possible waveforms, only certain waveforms are possible.

• We can focus our attention on the waveforms of varying motion of the guitar string or the varying electron charge intensity without having to think about the actual physical nature of the string or electron.
Cutaway of 1s and 2s (2,0,0) Orbitals

1s

The 2s orbital is larger and has a node.
An electron in 2s is less stable and higher PE than an electron in 1s

- Electron in 2s is a greater average distance from the positive nucleus than an electron in the 1s.
- 2s electron less attracted.
- 2s electron is less stable (more likely to change).
- 2s electron is higher potential energy.
- The one electron of hydrogen is more likely to be in the smaller, more stable, and lower PE 1s orbital where it is most strongly attracted to the nucleus.
Ground State and Excited State

• Hydrogen atoms with their electron in the 1s orbital are said to be in their \textit{ground state}.

\[
\begin{align*}
2s & \quad \underline{\text{__}} \\
1s & \quad \underline{\text{\textarrow{up}}}
\end{align*}
\]

• A hydrogen atom with its electron in the 2s orbital is in an \textit{excited state}.

\[
\begin{align*}
2s & \quad \underline{\text{\textarrow{up}}} \\
1s & \quad \underline{\text{__}}
\end{align*}
\]
Realistic and Stylized $2p_y$ Orbital (2,1,1)
$2p_x (2,1,1)$, $2p_y (2,1,0)$, and $2p_z (2,1,-1)$ Orbitals
• Orbitals that have the same potential energy, the same size, and the same shape are in the same sublevel.

• The sublevels are sometimes called subshells.
Other Allowed Waveforms

- $3d_{z^2}$
- $3d_{xz}$
- $3d_{yz}$
- $3d_{xy}$
- $3d_{x^2 - y^2}$
- $3s$
- $3p_x$
- $3p_y$
- $3p_z$
- $2s$
- $2p_x$
- $2p_y$
- $2p_z$
- $1s$
Orbitals for Ground States of Known Elements

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No other orbitals are necessary for describing the electrons of the known elements in their ground states.
No two electrons in an atom can be the same in all ways.

There are four ways that electrons can be the same:

- Electrons can be in the same principal energy level.
- They can be in the same sublevel.
- They can be in the same orbital.
- They can have the same spin.
Ways to Describe Electrons in Atoms

• Arrows are added to an orbital diagram to show the distribution of electrons in the possible orbitals and the relative spin of each electron. The following is an orbital diagram for a nitrogen atom.

\[
\begin{align*}
2s & \quad \uparrow \! \! \! \! \! \! \! \downarrow \\
1s & \quad \uparrow \! \! \! \! \! \! \! \downarrow \\
2p & \quad \uparrow \quad \uparrow \quad \uparrow 
\end{align*}
\]

• The information in orbital diagrams is often described in a shorthand notation called an electron configuration.

\[1s^2 \ 2s^2 \ 2p^3\]
Electron Configurations

- The sublevels are filled in such a way as to yield the lowest overall potential energy for the atom.
- No two electrons in an atom can be the same in all ways. This is one statement of the **Pauli Exclusion Principle**.
- When electrons are filling orbitals of the same energy, they prefer to enter empty orbitals first, and all electrons in half-filled orbitals have the same spin. This is called **Hund’s Rule**.
Electron Configurations (cont.)

- Represents the principal energy level
- Shows the number of electrons in the orbital
- Indicates the shape of the orbital

$1s^2$
Order of Orbital Filling

Start here and move along the arrows one by one.

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p
## Second Period Electron Configurations

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Writing Electron Configurations

• Determine the number of electrons in the atom from its atomic number.
• Add electrons to the sublevels in the correct order of filling.
• Add two electrons to each $s$ sublevel, 6 to each $p$ sublevel, 10 to each $d$ sublevel, and 14 to each $f$ sublevel.
• To check your complete electron configuration, look to see whether the location of the last electron added corresponds to the element’s position on the periodic table.
Order of Filling from the Periodic Table

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| 5d      | 23 |
| 6d      | 24 |
| 7d      | 25 |
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| 9d      | 27 |
| 10d     | 28 |
| 11d     | 29 |
| 12d     | 30 |

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| 17f     | 102|
### Long Periodic Table

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#### p block

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<td>5A</td>
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#### 1s

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#### 5d

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#### 6d

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Drawing Orbital Diagrams

- Draw a line for each orbital of each sublevel mentioned in the complete electron configuration. Draw one line for each s sublevel, three lines for each p sublevel, five lines for each d sublevel, and seven lines for each f sublevel.

- Label each sublevel.

- For orbitals containing two electrons, draw one arrow up and one arrow down to indicate the electrons’ opposite spin.

- For unfilled sublevels, follow Hund’s Rule.
Abbreviated Electron Configurations

• The highest energy electron are most important for chemical bonding.
• The noble gas configurations of electrons are especially stable and, therefore, not important for chemical bonding.
• We often describe electron configurations to reflect this representing the noble gas electrons with a noble gas symbol in brackets.
• For example, for sodium
  \[1s^2 2s^2 2p^6 3s^1\] goes to \[[\text{Ne}]\ 3s^1\]
Writing Abbreviated Electron Configurations

- Find the symbol for the element on a periodic table.
- Write the symbol in brackets for the noble gas located at the far right of the preceding horizontal row on the table.
- Move back down a row (to the row containing the element you wish to describe) and to the far left. Following the elements in the row from left to right, write the outer-electron configuration associated with each column until you reach the element you are describing.
Abbreviated Electron Configurations – Optional Step

- Rewrite the abbreviated electron configuration, listing the sublevels in the order of increasing principal energy level (all of the 3’s before the 4’s, all of the 4’s before the 5’s, etc.)
Group 1 Abbreviated Electron Configurations

Li: [He] 2s¹
Na: [Ne] 3s¹
K: [Ar] 4s¹
Rb: [Kr] 5s¹
Cs: [Xe] 6s¹
### Abbreviated Electron Configuration Steps for Zinc

**Step 1** Find the symbol for the element (zinc).

**Step 2** Write the symbol in brackets for the nearest, smaller noble gas.

**Step 3** Write the outer electron configuration for the remaining electrons.
Common Mistakes

• Complete electron configurations – miscounting electrons (Use the periodic table to determine order of filling.)
• Orbital diagrams – forgetting to leave electrons unpaired with the same spin when adding electrons to the $p$, $d$, or $f$ sublevels (Hund’s Rule)
• Abbreviated electron configurations
  – Forgetting to put $4f^{14}$ after $[Xe]$
  – Forgetting to list sublevels in the order of increasing principal energy level