Chapter 6

The First Law of Thermodynamics and Heat Exchange Processes
Nature of Energy

Chemistry is the study of matter, its changes and the energy associated with these changes.

Energy is anything that has the capacity to do work.

Work is a force acting over a distance.

Energy = Work = Force x Distance

Heat is the flow of energy caused by a difference in temperature.
Energy, Heat, and Work

Energy is a quantity an object can possess.

Heat and work are the two different ways that an object can exchange energy with other objects.
Manifestations of Energy

Energy: Capacity to Do Work

- Kinetic Energy: Due to Motion
- Potential Energy: Due to Position or Composition
- Thermal Energy: Associated with Temperature
- Chemical Energy: Associated with Positions of Electrons and Nuclei
Some Forms of Energy

**Electrical**
kinetic energy associated with the flow of electrical charge

**Heat or thermal energy**
kinetic energy associated with molecular motion

**Light or radiant energy**
kinetic energy associated with energy transitions in an atom

**Nuclear**
potential energy in the nucleus of atoms

**Chemical**
potential energy due to the structure of the atoms, the attachment between atoms, the atoms' positions relative to each other
Conservation of Energy

The Law of Conservation of Energy states that "energy cannot be created or destroyed."

When energy is transferred between objects, or converted from one form to another, the total amount of energy present at the beginning must be present at the end.
System and Surroundings

What we study is the exchange of energy between the **system** and the **surroundings**.

We define the **system** as the material or process within which we are studying the energy changes.

We define the **surroundings** as everything else with which the system can exchange energy.

**Conservation of Energy** means that the amount of energy gained or lost by the system has to be equal to the amount of energy lost or gained by the surroundings.
Units of Energy

The amount of kinetic energy an object has is directly proportional to its mass and velocity.

\[ KE = \frac{1}{2}mv^2 \]

**joule** (J) is the amount of energy needed to move a 1-kg mass a distance of 1 meter

\[ 1 \text{ J} = 1 \text{ N} \cdot \text{m} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2. \]

**calorie** (cal) is the amount of energy needed to raise the temperature of one gram of water 1°C.

**kcal** = energy needed to raise 1000 g of water 1°C

1 Food Calorie = 1 kcal
Energy Conversion Factors

1 calorie (cal) = 4.184 joules (J)
1 Calorie (Cal) or kilocalorie (kcal) = 1000 cal = 4184 J
1 kilowatt-hour (kWh) = 3.60 × 10^6 J

<table>
<thead>
<tr>
<th>Unit</th>
<th>Amount Required to Raise Temperature of 1 g of Water by 1 °C</th>
<th>Amount Required to Light 100-W Bulb for 1 Hour</th>
<th>Amount Used by Human Body in Running 1 Mile (Approximate)</th>
<th>Amount Used by Average U.S. Citizen in 1 Day</th>
</tr>
</thead>
<tbody>
<tr>
<td>joule (J)</td>
<td>4.18</td>
<td>3.60 × 10^5</td>
<td>4.2 × 10^5</td>
<td>9.0 × 10^8</td>
</tr>
<tr>
<td>calorie (cal)</td>
<td>1.00</td>
<td>8.60 × 10^4</td>
<td>1.0 × 10^5</td>
<td>2.2 × 10^8</td>
</tr>
<tr>
<td>Calorie (Cal)</td>
<td>0.00100</td>
<td>86.0</td>
<td>100</td>
<td>2.2 × 10^5</td>
</tr>
<tr>
<td>kilowatt-hour (KWh)</td>
<td>1.16 × 10^-6</td>
<td>0.100</td>
<td>0.12</td>
<td>2.5 × 10^2</td>
</tr>
</tbody>
</table>
The First Law of Thermodynamics
Law of Conservation of Energy

“The total amount of energy in the universe is constant.”

Conservation of energy requires that the sum of the energy changes in the system and the surroundings must be zero.

\[ \Delta \text{Energy}_{\text{universe}} = 0 = \Delta \text{Energy}_{\text{system}} + \Delta \text{Energy}_{\text{surroundings}} \]
**Thermodynamics**
The study of heat and its transformations

**Thermochemistry**
A branch of thermodynamics that deals with the heat involved with chemical and physical change
**Fundamental Premise**
When energy is transferred from one object to another, it appears as work and/or as heat.

We must define a *system* to study; everything else then becomes the *surroundings.*
Internal Energy

The *internal energy* is the sum of the kinetic and potential energies of all of the particles that compose the system.

The *change in the internal energy* of a system only depends on the amount of energy in the system at the beginning and end.

\[ \Delta E = E_{\text{final}} - E_{\text{initial}} \]

\[ \Delta E_{\text{reaction}} = E_{\text{products}} - E_{\text{reactants}} \]
**Internal Energy**

*Internal energy* is a state function.

A *state function* is a mathematical function whose result only depends on the initial and final conditions, not on the process used.
If the final condition has a larger amount of internal energy than the initial condition, the change in the internal energy will be $\Delta E = +$.

If the final condition has a smaller amount of internal energy than the initial condition, the change in the internal energy will be $\Delta E = -$.
Energy Flow

When energy flows out of a system, it must all flow into the surroundings.

$\Delta E_{\text{system}}$ is $-$
$\Delta E_{\text{surroundings}}$ is $+$. 

Therefore:

$- \Delta E_{\text{system}} = \Delta E_{\text{surroundings}}$

When energy flows into a system, it must all come from the surroundings.

$\Delta E_{\text{system}}$ is $+$. 
$\Delta E_{\text{surroundings}}$ is $-$. 

Therefore:

$\Delta E_{\text{system}} = - \Delta E_{\text{surroundings}}$
Consider the reactions:

\[ \text{C(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \]
\[ \text{CO}_2(g) \rightarrow \text{C(s)} + \text{O}_2(g) \]

The total amount of internal energy in 1 mol of C(s) and 1 mole of O\(_2\)(g) is greater than the internal energy in 1 mole of CO\(_2\)(g).

In the reaction \( \text{C(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \), there will be a net release of energy into the surroundings.

\[ -\Delta E_{\text{reaction}} = \Delta E_{\text{surroundings}} \]

In the reaction \( \text{CO}_2(g) \rightarrow \text{C(s)} + \text{O}_2(g) \), there will be an absorption of energy from the surroundings into the reaction.

\[ \Delta E_{\text{reaction}} = -\Delta E_{\text{surroundings}} \]
Energy Exchange
Energy is exchanged between the system and surroundings through either heat exchange or work being done.
Energy is exchanged between the system and surroundings through **heat** and **work**.

\[ q = \text{heat (thermal) energy} \]
\[ w = \text{work energy} \]

\[ q \] and \[ w \] are NOT state functions, their value depends on the process.

\[ \Delta E = q + w \]

<table>
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<tr>
<th>( q ) (heat)</th>
<th>system gains heat energy</th>
<th>system releases heat energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( w ) (work)</td>
<td>system gains energy from work</td>
<td>system releases energy by doing work</td>
</tr>
<tr>
<td>( \Delta E )</td>
<td>system gains internal energy</td>
<td>system loses some of its internal energy</td>
</tr>
</tbody>
</table>
Energy Exchange

Symbols:

- $+w$: Energy input to the system
- $-w$: Energy output from the system
- $+q$: Energy gained from the surroundings
- $-q$: Energy lost to the surroundings

Diagram:

- System
- Surroundings

Arrows indicate energy exchange.
The white ball has an initial amount of 5.0 J of kinetic energy.

As it rolls on the table, some of the energy is converted to heat by friction.

The rest of the kinetic energy is transferred to the purple ball by collision.
On a smooth table, most of the kinetic energy is transferred from the white ball to the purple – with a small amount lost through friction.

Energy change for the white ball,
\[ \Delta E = KE_{\text{final}} - KE_{\text{initial}} = 0 \text{ J} - 5.0 \text{ J} = -5.0 \text{ J} \]

Kinetic energy transferred to purple ball, \[ w = -4.5 \text{ J} \]
Kinetic energy lost as heat, \[ q = -0.5 \text{ J} \]

\[ q + w = (-0.5 \text{ J}) + (-4.5 \text{ J}) = -5.0 \text{ J} = \Delta E \]
On a rough table, most of the kinetic energy of the white ball is lost through friction – less than half is transferred to the purple ball.

Energy change for the white ball,
\[ \Delta E = KE_{\text{final}} - KE_{\text{initial}} = 0 \text{ J} - 5.0 \text{ J} = -5.0 \text{ J} \]

Kinetic energy transferred to purple ball, \( w = -2.0 \text{ J} \)

Kinetic energy lost as heat, \( q = -3.0 \text{ J} \)

\[ q + w = (-3.0 \text{ J}) + (-2.0 \text{ J}) = -5.0 \text{ J} = \Delta E \]
Heat, Work, and Internal Energy

In the previous example, the $\Delta E$ of the white ball is the same for both cases, but $q$ and $w$ are not.

**On the rougher table**, the heat loss, $q$, is greater; $q$ is a more negative number.

**On the rougher table**, less kinetic energy is transferred to the purple ball, so the work done by the white ball, $w$, is less; $w$ is a less negative number.

$q + w$ is the same for both tables, even though the values of $q$ and $w$ are different.

$\Delta E$ is a state function and depends only on the velocity of the white ball before and after the collision.
If the burning of the fuel in a potato cannon performs 855 J of work on the potato and produces 1422 J of heat, what is $\Delta E$ for the burning of the fuel?

$q_{\text{potato}} = 1422 \text{ J}, \quad w_{\text{potato}} = 855 \text{ J} \quad \Delta E_{\text{fuel}} = ?$

$q_{\text{system}} = -q_{\text{surroundings}} \quad w_{\text{system}} = -w_{\text{surroundings}} \quad \Delta E = q + w$

$q_{\text{fuel}} = -q_{\text{cannon}} \quad w_{\text{fuel}} = -w_{\text{potato}}$

$q_{\text{fuel}} = -1422 \text{ J} \quad w_{\text{fuel}} = -855 \text{ J}$

$\Delta E = q + w$

$= (-(1422 \text{ J}) + (-855 \text{ J}))$

$= -2277 \text{ J}$
Reacting 50 mL of H\(_2\)(g) with 50 mL of C\(_2\)H\(_4\)(g) produces 50 mL of C\(_2\)H\(_6\)(g); THE VOLUME OF THE GASES DECREASES. If the reaction produces 3.1 \(\times\) 10\(^2\) J of heat and the decrease in volume requires the surroundings do 7.6 J of work on the gases, what is the change in internal energy of the gases?

\[
\text{H}_2(\text{g}) + \text{C}_2\text{H}_4(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})
\]

\[
q_{\text{reaction}} = -310 \text{ J}, \quad w_{\text{surroundings}} = -7.6 \text{ J} \quad \Delta E_{\text{gases}} = ?
\]

\[
q_{\text{system}} = -q_{\text{surroundings}} \quad W_{\text{system}} = -W_{\text{surroundings}} \quad \Delta E = q + w
\]

\[
w_{\text{surroundings}} = -w_{\text{gases}}
\]

\[
w_{\text{reaction}} = +7.6 \text{ J}
\]

\[
\Delta E = q + w
\]

\[
= ((-310 \text{ J}) + (+7.6 \text{ J}))
\]

\[
= -302.4 \text{ J} = -3.0 \times 10^2 \text{ J}
\]
Heat is the exchange of thermal energy between the system and surroundings.

Heat exchange occurs when system and surroundings have a difference in temperature.

Temperature is the measure of the amount of thermal energy within a sample of matter.

Heat flows from matter with high temperature to matter with low temperature until both objects reach the same temperature.
Heat Capacity

Quantity of Heat Energy Absorbed

When a system absorbs heat, its temperature increases.

The increase in temperature is directly proportional to the amount of heat absorbed.

The proportionality constant is called the heat capacity, \( C \).

Units of \( C \) are J/°C or J/K:

\[
q = C \times \Delta T
\]

\[
q/C = \Delta T
\]

The larger the heat capacity of the object being studied, the smaller the temperature rise will be for a given amount of heat.
Factors Affecting Heat Capacity

The heat capacity of an object depends on its quantity.

200 g of water requires twice as much heat to raise its temperature by 1°C as does 100 g of water.

The heat capacity of an object depends on the type of material.

1000 J of heat raises the temperature of 100 g of sand 12 °C, but raises the temperature of 100 g of water by only 2.4 °C.
Specific Heat Capacity

Measure of a substance’s *intrinsic* ability to absorb heat.

The **specific heat capacity** is the amount of heat energy required to raise the temperature of one gram of a substance 1°C. (We can compare $C_s$.

$C_s$ units are J/(g·°C)

The **molar heat capacity** is the amount of heat energy required to raise the temperature of one mole of a substance 1°C.

$C_{mol}$ units are J/(mol·°C)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$C_s$ (J/g · °C)*</th>
</tr>
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<tbody>
<tr>
<td>Elements</td>
<td></td>
</tr>
<tr>
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*At 298 K.
Specific Heat of Water

4.18 J/(g·°C)

The rather high specific heat of water allows water to absorb a large quantity of heat energy without a large increase in its temperature.

Without water, the Earth’s temperature would be about the same as the moon’s temperature on the side that is facing the sun (average 107 °C or 225 °F).

*Water is commonly used as a coolant* because it can absorb a large quantity of heat and removes it from important mechanical parts to keep them from overheating or even melting.
Quantifying Heat Energy

The heat capacity of an object is proportional to its mass and the specific heat of the material.

So we can calculate the quantity of heat absorbed by an object if we know the mass, the specific heat (for the particular type of matter), and the temperature change of the object.

Heat = (mass) x (specific heat) x (temp. change)

\[ q = (m) \times (C_s) \times (\Delta T) \]

\[ J = g \times \frac{J}{g \degree C} \times \degree C \]
How much heat is absorbed by a copper penny with mass 3.10 g whose temperature rises from −8.0 °C to 37.0 °C?

\[ T_1 = -8.0 \, ^\circ C, \quad T_2 = 37.0 \, ^\circ C, \quad m = 3.10 \, g, \quad C_s = 0.385 \, \text{J/g}^\circ \text{C} \]

\[ q = m \cdot C_s \cdot \Delta T \]

\[ \Delta T = T_2 - T_1 \]
\[ \Delta T = 37.0 \, ^\circ C - (-8.0 \, ^\circ C) \]
\[ = 45.0 \, ^\circ C \]

\[ q = (3.10 \, g) \cdot \left(0.385 \, \frac{\text{J}}{\text{g}^\circ \text{C}}\right) \cdot (45.0 \, ^\circ \text{C}) \]
\[ = 53.7 \, \text{J} \]
Calculate the amount of heat released when 7.40 g of water cools from 49° to 29 °C (water’s specific heat is 4.18 J/g°C).

\[ T_1 = 49 \, ^\circ C, \quad T_2 = 29 \, ^\circ C, \quad m = 7.40 \, g \quad q = ? \]

\[ q = m \cdot C_s \cdot \Delta T \]

\[ \Delta T = T_2 - T_1 \]
\[ \Delta T = 29 \, ^\circ C - (49 \, ^\circ C) \]
\[ = -20 \, ^\circ C \]

\[ q = m \cdot C_s \cdot \Delta T \]
\[ = (7.40 \, g) \cdot \left( 4.18 \, \frac{J}{g \cdot ^\circ C} \right) \cdot (-20 \, ^\circ C) \]
\[ = -618.64 \, J = -6.2 \times 10^2 \, J \]
Heat Transfer & Final Temperature

When two objects at different temperatures are placed in contact, heat flows from the material at the higher temperature to the material at the lower temperature.

Heat flows until both materials reach the same final temperature.

The amount of heat energy lost by the hot material equals the amount of heat gained by the cold material.

\[ q_{\text{hot}} = -q_{\text{cold}} \]

\[ (m_{\text{hot}})(C_{s,\text{hot}})(\Delta T_{\text{hot}}) = -(m_{\text{cold}})(C_{s,\text{cold}})(\Delta T_{\text{cold}}) \]
A hot piece of metal weighing 350.0 g is heated to 100.0 °C. It is then placed into a coffee cup calorimeter containing 160.0 g of water at 22.4 °C. The water warms and the metal cools until the final temperature is 35.2 °C. Calculate the specific heat of the metal and identify the metal.

**metal**: 350.0 g, $T_1 = 100.0$ °C, $T_2 = 35.2$ °C  
**H$_2$O**: 160.0 g, $T_1 = 22.4$ °C, $T_2 = 35.2$ °C, $C_s = 4.18$ J/g °C

$$C_s, \text{ metal} = ?$$

$$m, C_s, \Delta T \rightarrow q$$

$$q = m \cdot C_s \cdot \Delta T$$

$$q_{\text{metal}} = -q_{\text{H}_2\text{O}}$$

$$\Delta T_{\text{H}_2\text{O}} = 35.2^\circ\text{C} - 22.4^\circ\text{C}$$

$$\Delta T_{\text{H}_2\text{O}} = 12.8^\circ\text{C}$$

$$\Delta T_{\text{metal}} = 35.2^\circ\text{C} - 100.0^\circ\text{C}$$

$$\Delta T_{\text{metal}} = -64.8^\circ\text{C}$$
A hot piece of metal weighing 350.0 g is heated to 100.0 °C. It is then placed into a coffee cup calorimeter containing 160.0 g of water at 22.4 °C. The water warms and the metal cools until the final temperature is 35.2 °C. Calculate the specific heat of the metal.

\[ q = m \cdot C_s \cdot \Delta T \]

\[ q_{metal} = - q_{H_2O} \]

\[ m_{metal} \times C_{s,metal} \times \Delta T_{metal} = -(m_{H_2O} \times C_{s,H_2O} \times \Delta T_{H_2O}) \]

\[ 350 \text{ g} \times C_{s,metal} \times (-64.8^\circ\text{C}) = -(160.0 \text{ g} \times 4.18 \frac{\text{J}}{\text{g}^\circ\text{C}} \times 12.8^\circ\text{C}) \]

\[ C_{s,metal} = 0.378 \frac{\text{J}}{\text{g}^\circ\text{C}} \]
Identify the metal.

\[ C_s = 0.378 \text{ J/g } ^\circ \text{C} \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat Capacity, ( C_s ) (J/g ( \cdot ) ^\circ \text{C})*</th>
</tr>
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