6.1 The Nature of Energy

- **Definition of Energy:** *Energy* is defined as *the capacity to do work or produce heat*. In CHM 101 we will concentrate on *chemical energy*, the heat transfer that accompanies chemical reactions.

- **Conservation of Energy:** The *Law of Conservation of Energy* states that *energy can neither be created nor destroyed*, although it can be converted from one form to another. Another way of stating this is to say that *the energy of the universe is constant*; it neither increases nor decreases.

- **Types of Energy**
  - **Potential Energy:** Potential energy is energy due to *position* or composition. A skier poised at the top of a ski run by virtue of her position at the top of the hill. Water held behind a power dam has potential energy that can be converted to (electrical) work by allowing it to flow through a turbine. Gasoline has potential energy in its chemical bonds that can be released by combustion with oxygen.
  
  - **Kinetic Energy:** Kinetic energy is energy possessed by an object due to its motion. A skier hurtling down a ski run has lots of kinetic energy on account of his speed. The hot gases produced when gasoline is burned have kinetic energy by virtue of the rapid motion of their molecules. Quantitatively, the kinetic energy of an object with mass, \( m \), and velocity, \( v \), is given by the equation:

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

- **Energy Conversion:** Energy can be converted from one form to another. The energy in a swinging pendulum continually changes from 100% potential energy at one end of its path to 100% kinetic energy at its mid-path low point and back to 100%
potential energy at the other end of its path. Its kinetic energy is zero at either end when momentarily it is not moving and is maximized at the low point where its speed is maximized. Conversely, its potential energy is at its minimum at the low point and at its maximum at the two high points.

A hypothetical frictionless pendulum can swing forever, but a real pendulum will gradually slow down and eventually stop because of friction in the pivot point and because of air resistance. The energy of the pendulum is dissipated because of frictional heating of the pivot and of the air through which the bob moves. This dissipated energy is not lost; it has simply been converted from mechanical energy into a less useful form.

- **Heat and Temperature:** Heat and temperature are decidedly different concepts. We saw in Chapter 5 that *temperature* is a property reflecting *random molecular motion*. (The faster the motion, the higher the temperature.) *Heat*, on the other hand, involves the *transfer of* (thermal) *energy* from an object with a higher temperature to an object with a lower temperature. The temperature of an object does not depend on the size of the object, but the quantity of heat needed to raise the temperature of the object from the temperature, $T_1$, to the temperature, $T_2$, is directly proportional to the size of the object.

- **Work:** *Work* is defined as *force acting over a distance*. For example, work is involved in the transfer of mechanical energy from one ball to another in the situation pictured in Figure 6.1. Initially, Ball A is held in place on a hillside and possesses potential energy by virtue of its position above the bottom of the hill. When it is released, this potential energy is converted to
kinetic energy as Ball A rolls down the hill and gains speed. Then it strikes Ball B. The impact causes Ball A to transfer its kinetic energy to Ball B, whereupon Ball B rolls up the hill to its final position. Ball A has done work on Ball B, manifest now as potential energy inherent in the position of Ball B on the hillside above the foot of the hill.

It is important, however, to realize that not all the energy initially present as the potential energy of Ball A ends up as potential energy of Ball B. The picture clearly shows that the final position of Ball B is lower than the initial position of Ball A. So, where is the missing energy? The answer is some of it was dissipated in frictional heating of the hills, the valley, and the two balls. We will call this “Process 1,” and we will write for the change in energy for Ball A:

$$\Delta E_1 = q_1 + w_1$$

The Greek letter, Δ (delta), indicates the change in energy between the initial and final states of the system; q stands for
heat gained by the system, and \( w \) stands for the work done on Ball B.

Now suppose that the hillside down which Ball A rolls is so rough that it slows Ball A down so that it is hardly moving when it strikes Ball B. Then both balls end up at the bottom of the hill, and the system has no remaining potential energy, all of the initial potential energy having been dissipated as heat. The same amount of energy has been transferred, but this time no work was done on Ball B. We will call this “Process 2,” and this time the change in energy is:

\[
\Delta E_2 = q_2
\]

There is no term this time for work, since the work done in Process 2 is zero. But we observe:

\[
\Delta E_2 = \Delta E_1
\]

Since Ball A loses the same amount of energy in either process. However:

\[
q_1 \neq q_2 \quad \text{and} \quad w_1 \neq 0
\]

This tells us that the change in energy depends only on the initial and final states of Ball A, but that the work and heat transferred by Ball A to its surroundings (Ball B and the hills) depends on the pathway taken during the process.

- **State Functions** (also called State Properties): Properties like energy are considered state properties. They depend only on the state of the system but not on the pathway taken to get to that state. A good example is the net change in altitude for a trip from San Francisco to South Lake Tahoe. Since this net change in altitude depends only on the altitudes of San Francisco and of South Lake Tahoe. The distance travelled however, depends on the route. The trip via Truckee is longer than the trip via Placerville.

- **Chemical Energy**: Since we are interested in chemistry, we’ll leave the mechanical examples behind. We have used the combustion of methane in air several times already as an example, each time ignoring the principal reason why we burn methane. Now we write the reaction as:

\[
\text{CH}_4 (g) + 2\text{O}_2 (g) \rightarrow \text{CO}_2 (g) + \text{H}_2\text{O} (g) + \text{energy (heat)}
\]

We are not very interested in the \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) produced in the reaction; what we really want is the heat.
• **System and Surroundings, the Two Parts of the Universe:**

In order to do quantitative studies of the heat produced in this reaction, we must divide the universe into two pieces:

  o **System:** This is the part of the universe we focus upon. In the case of the methane combustion reaction, we consider the system to be the reactants and the products that are involved in the reaction.

  o **Surroundings:** This is the rest of the universe, especially including the reaction container (perhaps a furnace), the room, the building, and less importantly, everything else out to the farthest galaxies.

The system and surroundings for the methane combustion reaction are pictured in Figure 6.2 from your text:

![Figure 6.2](image)

**FIGURE 6.2**
The combustion of methane releases the quantity of energy \( \Delta(PE) \) to the surroundings via heat flow. This is an exothermic process.

• **Exothermic and Endothermic Processes:**

  o **Exothermic:** If a reaction produces heat and delivers it from the system to the surroundings, we call it exothermic (from the Greek words for "out of" and "heat"). Heat flows out of the system and into the surroundings, as in our methane combustion reaction.

  o **Endothermic:** If a reaction consumes heat and absorbs it from its surroundings, we call it endothermic (from the Greek words for "into" and "heat"). Heat flows from the...
surroundings into the system, as in the synthesis of nitrogen monoxide (the systematic name for nitric oxide that you learned in Section 2.8):

\[ \text{N}_2 (g) + \text{O}_2 (g) + \text{energy (heat)} \rightarrow 2\text{NO} (g) \]

The system and surroundings for this reaction are pictured in Figure 6.3 from your text:

---

**What Happens to the Energy?**

- **Exothermic Processes:** In an exothermic process it is easy to see that the energy flows into the surroundings and heats them. But where did the energy come from? The answer is that it came from the difference in potential energy (\(\Delta\text{PE}\)) between the reactants (\(\text{CH}_4 & \text{O}_2\)) and the products (\(\text{CO}_2 & \text{H}_2\text{O}\)). Looking back at Figure 6.2, we see that the reactants have a greater (chemical) potential energy than do the products. This difference is the source of the heat that flowed from the system to the surroundings. Quantitatively, the amount of energy delivered to the surroundings in the form of heat is the same as the loss in potential energy from the conversion of reactants into products.
Endothermic Processes: In this case we have a flow of energy from the surroundings into the system, as in the reaction that produces NO from O₂ and N₂. Here the product (NO) has a greater potential energy than do the reactants, as we see by looking back at Figure 6.3. Quantitatively, the amount of energy extracted from the surroundings is the same as the gain in potential energy from the conversion of the reactants to the product.

The First Law of Thermodynamics: Here we examine two questions: 1) What is Thermodynamics? and 2) What is its First Law?

Thermodynamics: Simply put, thermodynamics is the study of energy and its interconversions among its various forms. In CHM 101, we will be primarily interested in heat and (chemical) potential energy, but we will also examine mechanical energy in the form of pressure-volume work.

The First Law: This is another name for the law of conservation of energy, namely that the energy of the universe is constant.

Internal Energy: What is the energy of the system, as distinguished from the energy of the surroundings and the energy of the universe? We can define the internal energy of the system as the sum of the potential and kinetic energies of all the particles in the system. (Recall that the kinetic energy is closely related to the temperature of the system, whereas the potential energy represents energy stored in chemical bonds.) If the system undergoes some kind of process involving the flow of heat and/or work between the system and its surroundings, then the internal energy of the system changes by:

\[ \Delta E = q + w \]

Here, \( \Delta E \) is the change in the internal energy of the system, \( q \) is the heat, and \( w \) is the work. This equation is a quantitative statement of the First Law.

Signs and Magnitudes: Thermodynamic quantities (like \( \Delta E \), \( q \), and \( w \)) always have a number to show the magnitude of the change and a sign to show the direction of the flow. The sign reflects the system’s point of view. Thus if a process involves the flow of heat into the system (but there is no flow of work) and the magnitude of the...
heat flow is \( x \), then \( q \) and \( \Delta E \) are both positive quantities and:

\[
\Delta E = q = +x
\]

Since heat flows into the system, the process is endothermic. Conversely if heat flows out of the system and the magnitude of the flow is \( x \), then \( q \) and \( \Delta E \) are both negative quantities and:

\[
\Delta E = q = -x
\]

Since heat flows out of the system, the process is exothermic.

In General Chemistry, we will use the same convention for work. Whenever the system does work on the surroundings, the sign of the work will be negative. If, however, the surroundings do work on the system, the sign of \( w \) is positive. (Note that engineers define work, but not heat, from the surrounding’s point of view, as discussed on page 233 of your text.)

- **Sample Exercise 6.1** (p. 233): Calculate \( \Delta E \) for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system. We write the magnitudes and signs of the heat and the work as:

\[
q = +15.6 \text{ kJ} \quad \text{and} \quad w = +1.4 \text{ kJ}
\]

Both signs are positive because heat flows into the system and work is performed on the system. We then plug these quantities into the First Law to obtain the answer:

\[
\Delta E = +15.6 \text{ kJ} + 1.4 \text{ kJ} = 17.0 \text{ kJ}
\]
The system has gained energy, so $\Delta E$ is a positive quantity. This is consistent with the fact that the process is endothermic.

- **Pressure-Volume Work:** Returning to our methane combustion reaction, our original discussion pictured it as running in a furnace with the objective being to produce heat. What if, instead, we ran it inside an internal combustion engine so as to produce mechanical work? How do we measure that work? Suppose we picture the engine as a cylinder with a moveable piston, as shown in Figure 6.4. The reaction runs inside the cylinder and produces expanding gases that exert force on the piston. (The force shown in the diagram is the equal but opposite force opposing the force of the expanding gases.)

![Diagram of Pressure-Volume Work](image)

**FIGURE 6.4**
(a) The piston, moving a distance $\Delta h$ against a pressure $P$, does work on the surroundings. (b) Since the volume of a cylinder is the area of the base times its height, the change in volume of the gas is given by $\Delta h \times A = \Delta V$.

The pressure ($P$) of the gases is related to the force ($F$) and the area ($A$) of the piston by the following equation:

$$P = \frac{F}{A}$$

We can solve this for the force; it is simply:

$$F = P \cdot A$$
Work is defined as force exerted over a distance. In this case, the distance is represented as $\Delta h$, so we can write the work as:

$$\text{work} = F \cdot \Delta h$$

Substituting for the force, we obtain:

$$\text{work} = P \cdot A \cdot \Delta h = P \cdot \Delta V$$

Here $\Delta V$ is the difference between the final volume and the initial volume. What is the sign of this work? In this case, our system is expanding its volume against the surroundings, hence it is performing work on the surroundings. Thus the sign of the work should be negative, even though $P$ and $\Delta V$ are both positive quantities. This forces us to write:

$$w = - P \cdot \Delta V$$

for the work done against the surroundings by an expanding gas. Note that this same expression gives us the correct sign in the case of the surroundings doing work on the system to compress a gas. In this case, $\Delta V$ is a negative quantity, making $w$ a positive quantity.

- **Sample Exercise 6.2** (p. 234): Calculate the work associated with the expansion of a gas from 46 L to 64 L at a constant external pressure of 15 atm.
  - We start with our expression for work:
    $$w = - P \cdot \Delta V$$
  - Since $\Delta V$ is given by:
    $$\Delta V = V_{\text{final}} - V_{\text{initial}}$$
  - We obtain for $w$:
    $$w = - P \cdot (V_{\text{final}} - V_{\text{initial}}) = -15 \cdot (64 - 46) \text{ L} \cdot \text{atm} = -270 \text{ L} \cdot \text{atm}$$
  - The negative sign on this result is consistent with the fact that the system does work on the surroundings by its expansion.

- **Sample Exercise 6.3** (pp. 234-5): A balloon is being inflated by heating the air inside it. In the final states of the process, the volume of the balloon expands from $4.00 \times 10^6$ L to $4.50 \times 10^6$ L through the addition of $1.3 \times 10^8$ J of energy to the balloon in the form of heat. Assume that the external pressure remains at a constant 1.0 atm. You can use the following expression to convert between J and L·atm:

$$1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$$
We will start with the First Law:
\[ \Delta E = q + w \]

Since \(1.3 \times 10^8\) J of energy was added as heat, we can write that:
\[ q = +1.3 \times 10^8\] J

And we can calculate the work:
\[ w = -P \cdot \Delta V = -(1.0 \text{ atm}) \cdot (0.50 \times 10^6 \text{ L}) = -0.50 \times 10^6 \text{ L} \cdot \text{atm} \]

The sign is negative, since the gas is expanding and doing work on the surroundings.

Now we want to convert the work from L \cdot atm to J. We can use the unit factor:
\[ (101.3 \text{ J})/(1 \text{ L} \cdot \text{atm}) = 1 \]

Thus the work is:
\[ w = -(0.50 \times 10^6 \text{ L} \cdot \text{atm}) \cdot (101.3 \text{ J})/(1 \text{ L} \cdot \text{atm}) = -0.51 \times 10^8\] J

Now we are ready to plug the work and the heat into the First Law:
\[ \Delta E = +1.3 \times 10^8\] J \(- 0.51 \times 10^8\] J = +0.8 \times 10^8\] J

### 6.2 Enthalpy and Calorimetry:

We defined internal energy in the previous section. Now we define **enthalpy**. Enthalpy is a particularly useful concept to use in thermodynamics, because it automatically takes PV work into account for reactions run at constant pressure. We will see in a moment how this comes about.

- **Enthalpy**: The *enthalpy* \((H)\) of a system is defined in terms of the internal energy \((E)\), pressure \((P)\) and volume \((V)\) of the system:

\[ H = E + PV \]

Since internal energy, pressure, and volume are all state functions, enthalpy is also a state function. But what is enthalpy? Consider a process carried out at constant pressure and such that the only work is pressure-volume work. (Recall that \(w = -P \cdot \Delta V\) for pressure-volume work.) If we define \(q_P\) as the heat of a process run at constant pressure, we can write the First Law:
\[ \Delta E = q_P + w = q_P - P \cdot \Delta V \]

Solving for \(q_P\) we obtain:
\[ q_P = \Delta E + P \Delta V \]
Now we can relate $q_P$ to a change in enthalpy. Since we defined enthalpy as:

$$H = E + PV$$

We can write a change in enthalpy ($\Delta H$) as:

$$\Delta H = \Delta E + \Delta(PV)$$

We can write a change in enthalpy ($\Delta H$) as:

$$\Delta H = \Delta E + \Delta(PV)$$

Since our process runs at constant pressure, we can rewrite this as:

$$\Delta H = \Delta E + P\Delta V$$

But this is the same as our earlier expression for $q_p$, the heat of a process run at constant pressure such that the only work is PV work. Thus:

$$\Delta H = q_p$$

Thus at constant pressure (and where only PV work is allowed), the change in enthalpy ($\Delta H$) of the system is equal to the energy flow as heat. Because of this equality, we can say that in a reaction run at constant pressure, the change in enthalpy is the same as the heat of the reaction.

- **Sample Exercise 6.4** (p. 236): When 1 mole of methane (CH$_4$) is burned at constant pressure, 890 kJ of energy is released as heat. Calculate $\Delta H$ for a process in which 5.8 g of methane is burned at constant pressure:

  We can write the heat of reaction (at constant pressure) as:

  $$q_p = \Delta H = -890 \text{ kJ/mol}$$

  Since the number of moles of methane ($n_{\text{CH}_4}$) is:

  $$n_{\text{CH}_4} = \frac{m_{\text{CH}_4}}{MM_{\text{CH}_4}} = \frac{5.8 \text{ g}}{16.0 \text{ g/mol}} = \frac{5.8}{16.0} \text{ mol}$$

  The heat of the process where 5.8 g of methane burns at constant pressure thus is:

  $$\Delta H = n_{\text{CH}_4} \times q_p = \frac{5.8}{16.0} \text{ mol} \times (-890 \text{ kJ/mol}) = -320 \text{ kJ}$$
• **Calorimetry:** *Calorimetry* is an experimental process for *measuring heats of reaction*. The *device* used for these experiments is called a *calorimeter*.

• **Heat Measurements, Temperature, and Heat Capacity:** We do not have a way to make direct measurements of heat. What we actually measure is temperature, or, more specifically, the *change in temperature* resulting from a chemical reaction. Through knowledge of the *heat capacity* of the substance containing the heat generated by the process. We define the heat capacity (*C*) of a substance as:

\[
C = \frac{\text{heat absorbed}}{\text{increase in temperature}}
\]

• **Units of Heat Capacity:** If we heat a substance, the rise in temperature we obtain from adding a particular amount of heat depends on the amount of substance that is present.

  o **Specific Heat Capacity:** When we express a heat capacity in terms of the mass of substance that is heated, we use units of joules per °C per gram, or equivalently, joules per Kelvin per gram per Kelvin (J/K·g). Some specific heat capacities are given in Table 6.1:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat Capacity (J/°C · g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O(l)</td>
<td>4.18</td>
</tr>
<tr>
<td>H₂O(s)</td>
<td>2.03</td>
</tr>
<tr>
<td>Al(s)</td>
<td>0.89</td>
</tr>
<tr>
<td>Fe(s)</td>
<td>0.45</td>
</tr>
<tr>
<td>Hg(l)</td>
<td>0.14</td>
</tr>
<tr>
<td>C(s)</td>
<td>0.71</td>
</tr>
</tbody>
</table>

  o **Molar Heat Capacity:** When we express a heat capacity in terms of the number of moles of substance that is
heated, we use units of joules per C° per mole, or equivalently, joules per Kelvin per mole (J/K·mol).

- **Constant Pressure Calorimetry:** Constant pressure calorimetry is nothing more than calorimetry carried out under conditions of constant pressure. A simple device for doing calorimetric measurements at ambient pressure is illustrated in Figure 6.5. It is made from Styrofoam coffee cups (hence the name, coffee cup calorimeter), but it is accurate enough for a student to use in chemistry lab.

![Styrofoam coffee cups calorimeter](image)

**FIGURE 6.5**
A coffee-cup calorimeter made of two Styrofoam cups.

It is designed to study reactions that take place in aqueous solution. (Recall that the heat generated in an exothermic reaction run at constant pressure is the change in enthalpy of the system.) We’ll follow the example in the text on pages 237-9, where we take 50.0 mL of 1.0 M HCl at 25.0 °C and 50.0 mL of 1.0 M NaOH also at 25.0 °C and mix them in the calorimeter. After we stir the mixed solutions, we measure a temperature of 31.9 °C. From these data we wish to determine the heat of the reaction that has just taken place inside the calorimeter.
The reaction is the neutralization of a strong acid by a strong base, and we learned in Section 4.8 that the equation for the reaction is written:

\[ \text{H}^+ (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O} (l) + q_P \]

Since we observed an increase in temperature, we know that the reaction generated heat, and we include this heat \((q_P)\) on the right hand side.

At this point you might argue that the heat still remains in the system; that it has yet to flow to the surroundings. We can answer this argument two ways (They both yield the same result.):

1) We can define the system as consisting only of the ions that have reacted and the small amount of water that they generated in the reaction. Then the surroundings include the solvent water, and essentially all the heat produced by the reaction now resides in that portion of the surroundings that is inside the calorimeter.

2) Alternatively we could argue that the system includes the solvent, and the surroundings stop at the inside wall of the calorimeter. The heat that produced the rise in temperature has been temporarily captured within the system, and we can measure it before it flows out of the system into the surroundings.

Either way, the heat of the reaction was sufficient to raise the temperature of 100.0 mL of water by 6.9 Kelvins. But how much heat is this? If we consult Table 6.1, we see that the heat capacity of water \(C_{water}\) is 4.18 J/K·g. Thus:

\[ q = C_{water} \cdot m_{water} \cdot \Delta T = (4.18 \text{ J/K} \cdot \text{g})(100.0 \text{ g})(6.9 \text{ K}) = 2.9 \times 10^3 \text{ J} \]

Here \(q\) is the heat actually produced inside the calorimeter by the reaction of the HCl \((aq)\) with the NaOH \((aq)\). (We have assumed that the volume of the solution is exactly the combined volumes of the HCl \((aq)\) and the NaOH \((aq)\) and that the density of the solution is exactly 1.000 g/mL.) What if we had reacted twice as much acid with twice as much base? We would have obtained twice as much heat. What if we had reacted 1.00 mole of HCl \((aq)\) with 1.00 mole of NaOH \((aq)\)? We can calculate this from the number of moles that actually reacted and the heat \((q)\) that was produced:
\[ n_{\text{HCl}} = V_{\text{HCl}} \cdot M_{\text{HCl}} = (0.0500 \text{ L})(1.0 \text{ mol/L}) = 0.050 \text{ mol} \]

\[ \Delta H = \frac{-q}{n_{\text{HCl}}} = \frac{-2.9 \times 10^3 \text{ J}}{0.050 \text{ mol}} = -58 \text{ kJ/mol} \]

Here \( \Delta H \) represents the enthalpy of reaction for 1 mole of HCl (aq) reacting with 1.00 mole of NaOH (aq). The sign is negative because the reaction is exothermic.

- **Sample Exercise 6.5** (pp.239-40): 1.00 L of 1.00 \( M \) Ba(NO\(_3\))\(_2\) solution at 25.0 °C is reacted with 1.00 L of 1.00 \( M \) Na\(_2\)SO\(_4\) solution, also at 25.0 °C in a constant pressure calorimeter. A white, solid precipitate of BaSO\(_4\) forms and the temperature of the mixture rises to 28.1 °C. Calculate the enthalpy change per mole of BaSO\(_4\) that forms. You may assume that the calorimeter absorbs a negligible amount of heat, that the specific heat capacity of the solution is 4.18 J/K·g, and that the density of the solution is 1.0 g/mL.
  
  o First we write the net ionic reaction:
    \[ \text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq) \rightarrow \text{BaSO}_4 (s) \]
  
  o We observed a rise in temperature, indicating that the reaction generated heat. Thus the reaction is exothermic and the change in enthalpy (\( \Delta H \)) will be negative. The volume of the combined solution is 2.00x10\(^3\) mL, so the mass of the solution is 2.00x10\(^3\) g. The change in temperature is 3.1 K. Thus the heat evolved by the reaction is:
    \[ q = C_{\text{water}} \cdot m_{\text{water}} \cdot \Delta T = (4.18 \text{ J/K·g})(2.00 \times 10^3 \text{ g})(3.1 \text{ K}) = 2.6 \times 10^4 \text{ J} \]

  o Since the reaction produced 1 mole of BaSO\(_4\) (s), the molar enthalpy change is
    \[ \Delta H = -q = -2.6 \times 10^4 \text{ J/mol} = -26 \text{ kJ/mol} \]

- **Constant Volume Calorimetry**: This topic is discussed in your text in pp. 240-2, and you are welcome to read about it. There
are no homework problems based on constant volume calorimetry, so we will not discuss it in class.