Unit 5 includes the following OpenStax sections

- 5.1 Energy Basics
- 5.2 Calorimetry
- 5.3 Enthalpy

Figure 5.1

Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. (credit: modification of work by Laszlo Ilyes)

- Chemical changes and their accompanying changes in energy are important parts of our everyday world.
    - The reactions involved in the metabolism of food.
    - The burning of fossil fuels (gasoline, natural gas, coal).
    - The production of useful products from raw materials.

- **Thermochemistry:** The study of the heat absorbed or released during chemical and physical changes.
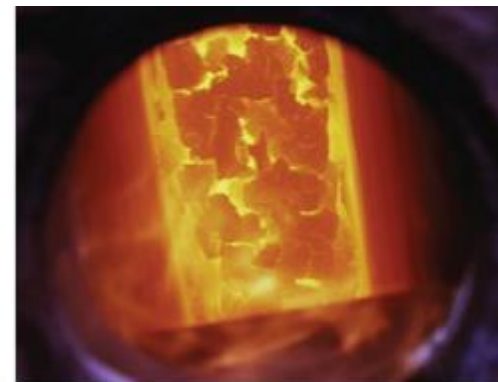
Figure 5.2

The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner)

- **Energy:** The capacity to supply heat or do work.

- Two main types of energy:
  - **Potential energy:** the energy an object has because of its relative position, composition, or condition

  - **Kinetic energy:** the energy that an object possesses because of its motion

Figure 5.3

(a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons)

Law of Conservation of Energy

- **Law of conservation of energy:** During a chemical or physical change, energy can be neither created nor destroyed, although its form can change.
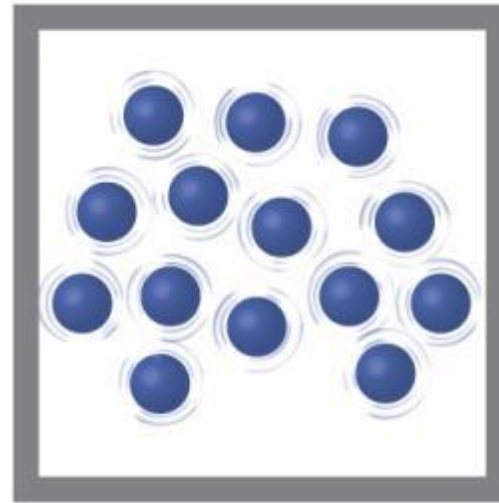
Thermal Energy and Temperature

- **Thermal energy** is a type of kinetic energy (KE) associated with the random motion of atoms and molecules.

- **Temperature** is a quantitative measure of "hot" or "cold."

- *Fast* moving molecules → High thermal energy → "Hot"

- *Slow* moving molecules → Low thermal energy → "Cold"
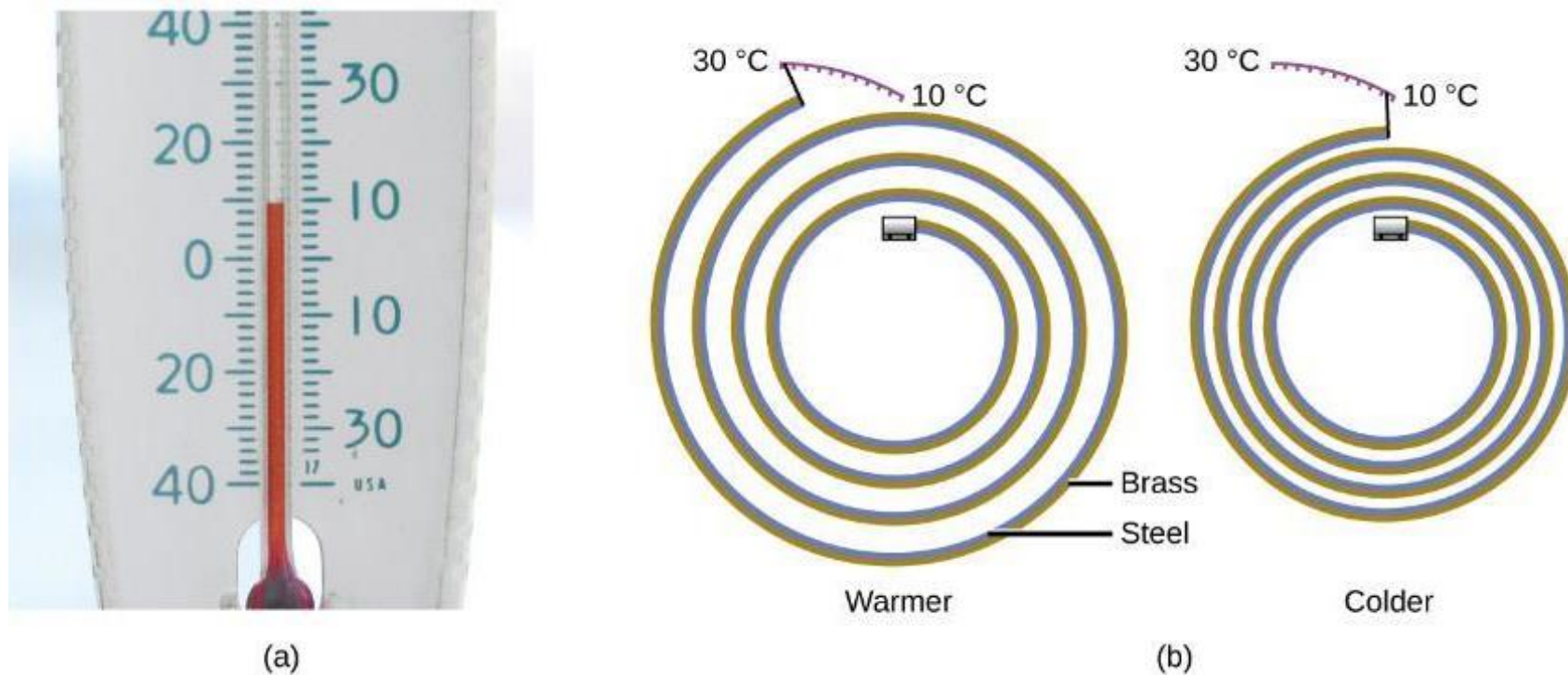
Figure 5.4
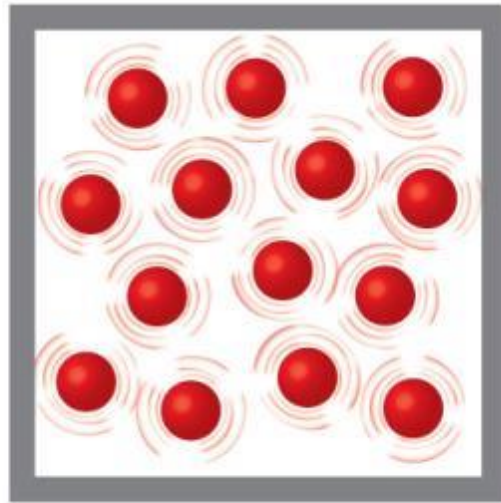
Hot liquid

(a)

Cold liquid

(b)

(a) The molecules in a sample of hot liquid move more rapidly than (b) those in a sample of cold liquid.

Figure 5.5

(a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by "dwstucke"/Flickr)

Heat

- **Heat (q)** is the transfer of thermal energy between two bodies at different temperatures.

- **Heat flow** (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other.

- When two substances are placed in contact, thermal energy will always flow from the high temperature substance to the low temperature substance.
  - Heat flow will continue until both substances are at the same temperature.

Figure 5.6
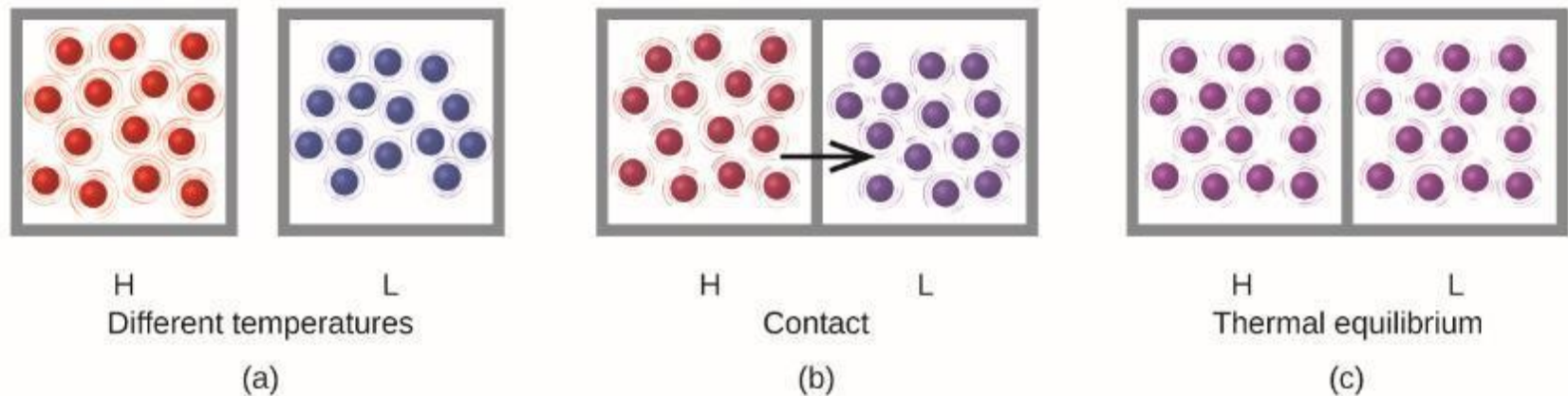
(a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Exothermic and Endothermic Processes

- Matter undergoing chemical reactions and physical changes can release or absorb heat.

- A change that *releases heat* is called an **exothermic process**.
  - Example: the combustion reaction that occurs when using an oxyacetylene torch.

- A change that *absorbs heat* is an **endothermic process**.
  - Example: the reaction in a cold pack used to treat muscle strains

Figure 5.7

(a)

(b)

(a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons)

- Historically, energy was measured in units of **calories (cal)**.

- A **calorie** is the amount of energy required to raise one gram of water by 1 °C (or 1 kelvin).

- The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a **kilocalorie**.

Heat Units

- The SI unit of heat, work, and energy is the joule.

- A **joule (J)** is defined as the amount of energy used when a force of 1 newton moves an object 1 meter.
  - It is named in honor of the English physicist James Prescott Joule.

- 1 calorie = 4.184 joules

Heat Capacity

- The **heat capacity (C)** of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 °C (or 1 kelvin):

$$C = \frac{q}{\Delta T}$$

- Heat capacity is an extensive property.

- For example, the heat capacity of a large cast iron pan is greater than the heat capacity of a small cast iron pan.

Specific Heat Capacity

- The **specific heat capacity (*c*)** of a substance, commonly called its "specific heat," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 °C (or 1 kelvin):

$$c = \frac{q}{m\Delta T}$$

- Specific heat capacity is an intensive property—it only depends on the identity of the substance, not the amount.

- For example, the specific heat capacity of a large and small cast iron pan are identical.

Figure 5.8

Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

Table 5.1 Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	He(g)	5.193
water	H_2O(l)	4.184
ethanol	C_2H_6O(l)	2.376
ice	H_2O(s)	2.093 (at −10 °C)
water vapor	H_2O(g)	1.864
nitrogen	N_2(g)	1.040
air		1.007
oxygen	O_2(g)	0.918
aluminum	Al(s)	0.897
carbon dioxide	CO_2(g)	0.853
argon	Ar(g)	0.522
iron	Fe(s)	0.449
copper	Cu(s)	0.385
lead	Pb(s)	0.130
gold	Au(s)	0.129
silicon	Si(s)	0.712

Calculating Heat

- The amount of heat, *q*, entering or leaving a substance can be calculated:

$$q = c \times m \times \Delta T$$

$$q = c \times m \times \left(T_f - T_i \right)$$

- If a substance *gains* thermal energy, $T_{final} > T_{initial}$, then the **value of *q* is positive**.

- If a substance *loses* thermal energy, $T_{final} < T_{initial}$, then the **value of *q* is negative**.

Example 5.1

- A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

$$q = c \times m \times \Delta T$$
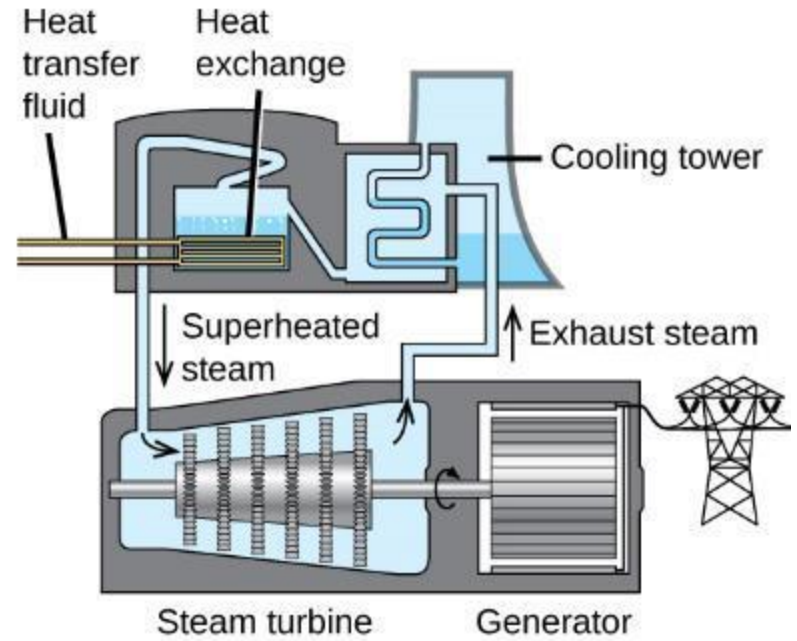
$$q = c \times m \times \left(T_f - T_i\right)$$

$$q = \left(4.184 \text{ J/g} \times °\text{C}\right) \times \left(8.0 \times 10^2 \text{ g}\right) \times \left(85°\text{C} - 21°\text{C}\right)$$

$$q = 2.1 \times 10^5 \text{ J}$$

Figure 5.9

This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

Figure 5.10

(a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by "USFWS Pacific Southwest Region"/Flickr)

- 5.2 Calorimetry
  - Explain the technique of calorimetry
  - Calculate and interpret heat and related properties using typical calorimetry data

Calorimetry

- One technique that can be used to measure the amount of heat involved in a chemical or physical process is known as calorimetry.

- **Calorimetry** is used to measure the amount of heat transferred to or from a substance.

- The heat is exchanged with a calibrated object (calorimeter).

- The change in temperature of the measuring part of the calorimeter is converted into the amount of heat.
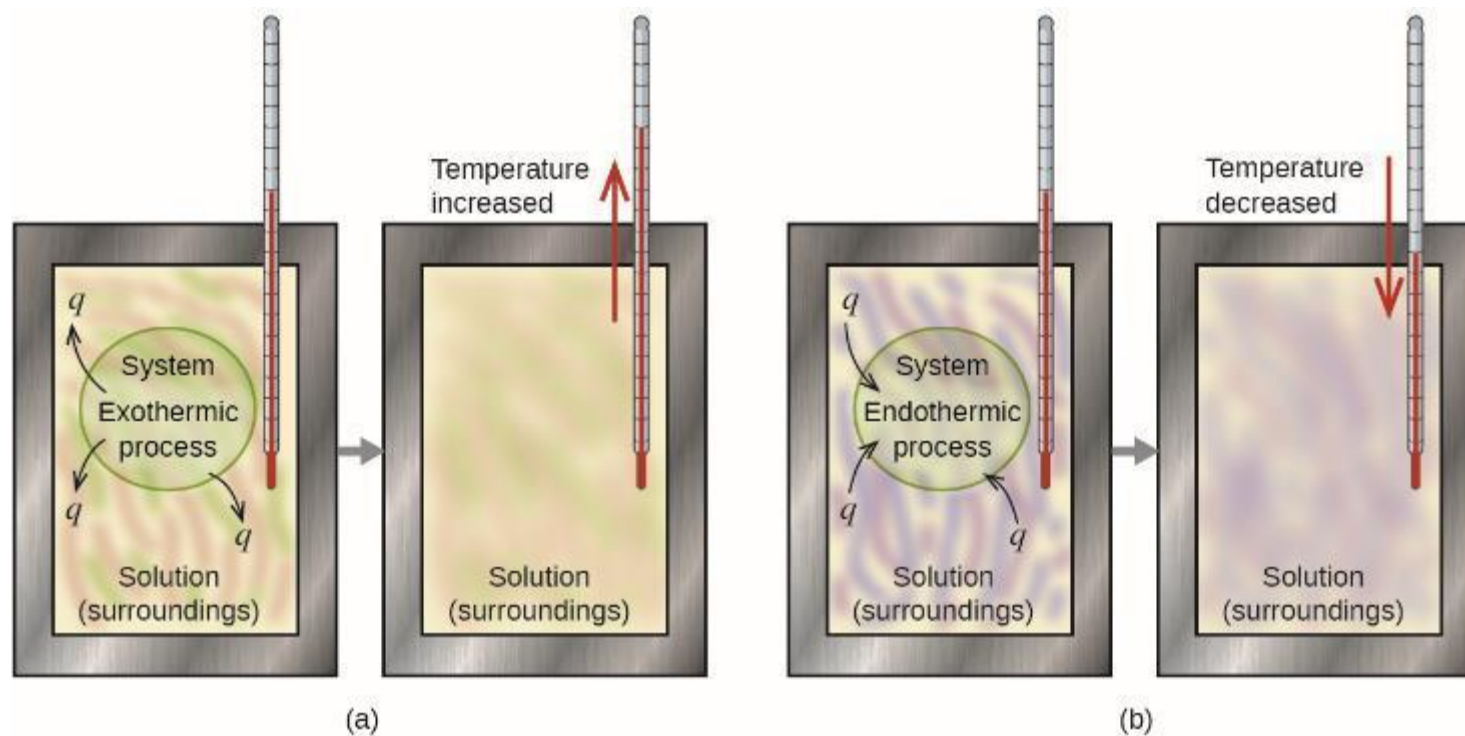
System and Surroundings

- **System:** the substance or substances undergoing the chemical or physical change

- **Surroundings:** all other matter, including components of the measurement apparatus, that serve to either provide heat to the system or absorb heat from the system

- A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process.

- Many processes measured in a calorimeter occur in solution.

- If the reaction is **exothermic**, the heat produced by the reaction is absorbed by the solution.

- If the reaction is **endothermic**, the heat required for the reaction to occur is provided by the solution.
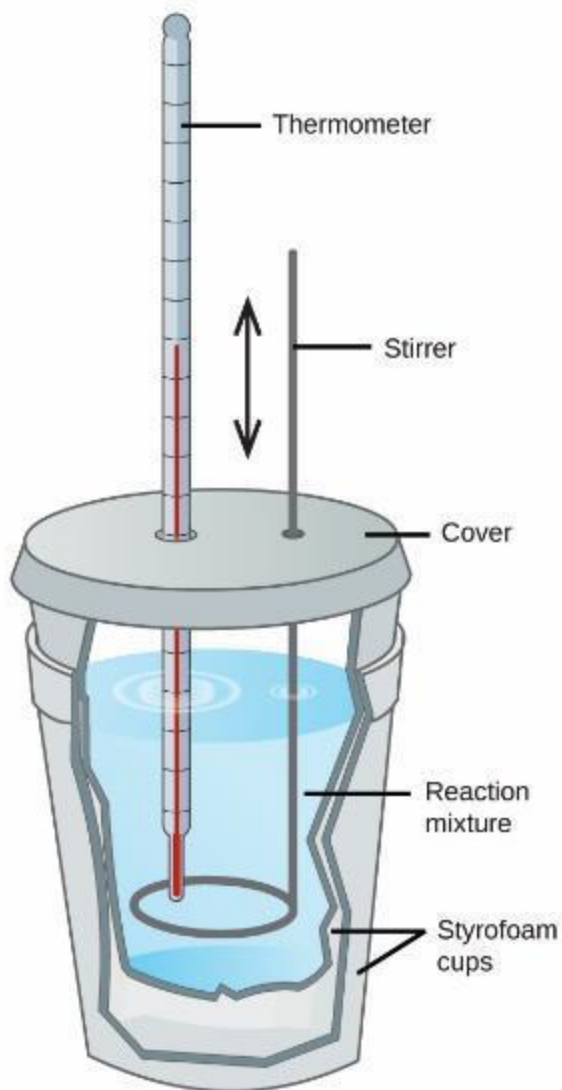
Figure 5.11

In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.
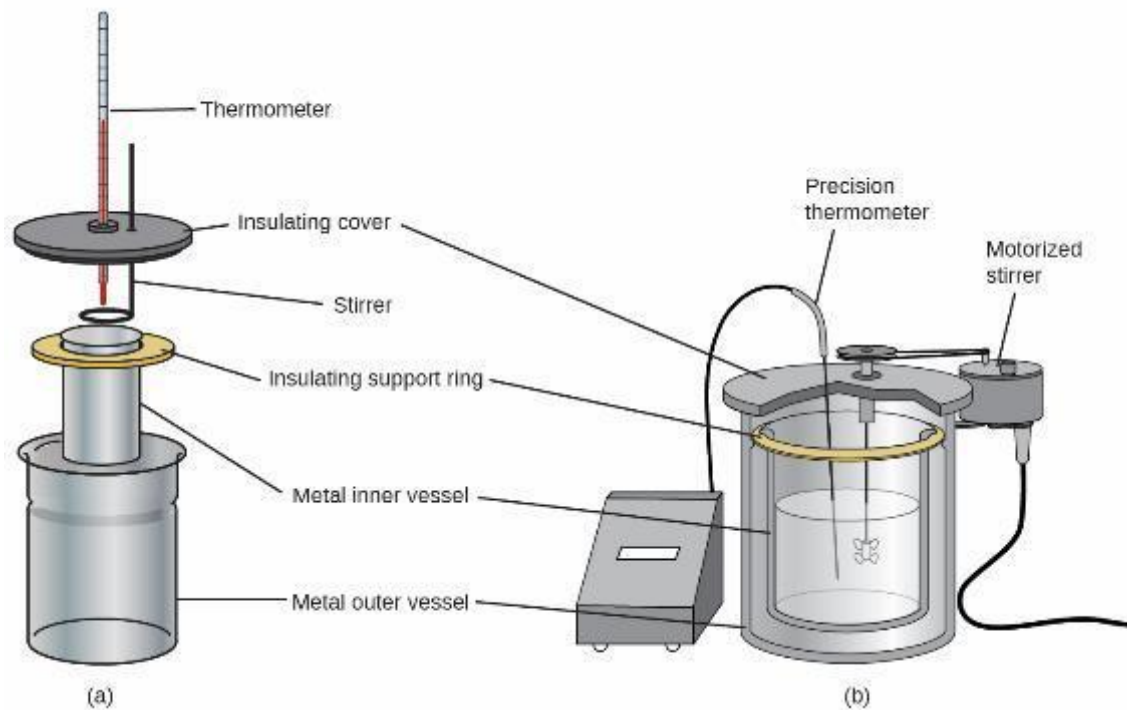
Calorimeter

- The calorimeter must be well insulated in order to prevent the transfer of heat with the outside environment.

- To obtain accurate results, all heat exchange must take place only between the system and the surroundings.

- **Coffee-cup calorimeters** (constructed of polystyrene cups) are often used in general chemistry labs.

- Commercial calorimeters of better design are used in industry and for research.

Figure 5.12

A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Figure 5.13

Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Calorimetry Principles

- Consider a hot piece of metal (M) and cool water (W).

- If the metal is placed in the water within a calorimeter, heat will transfer from M to W.

- The temperature of M will decrease.

- The temperature of W will increase.

- Eventually, thermal equilibrium will be reached and both objects will have the same temperature.

Calorimetry Principles

- Since this is done in a calorimeter, the heat exchange is only between M and W.
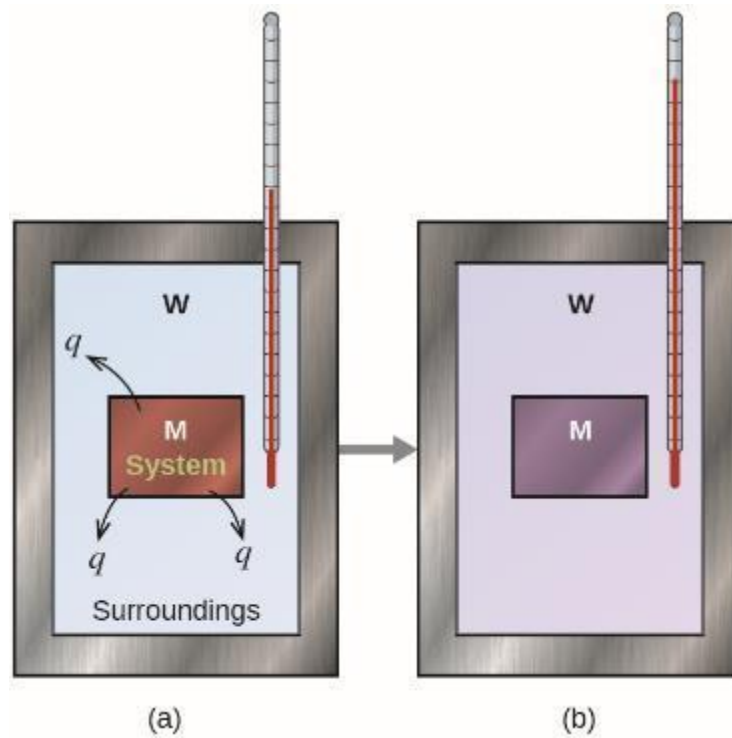
- The net change in heat is zero.

$$q_M + q_W = 0$$

- Rearranging shows that the heat gained by M is equal to the heat lost by W.

$$q_M = -q_W$$

- The heat of both substances is equal in magnitude but opposite in sign.

Figure 5.14

In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 5.3

- A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured to be 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table 5.1) and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the outside environment).

Example 5.3

- The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which must of been initially at some higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the outside environment, then *heat given off by rebar = –heat taken in by water*, or:

$$q_{rebar} = -q_{Water}$$

Example 5.3

- Since we know how heat is related to other measurable quantities, we have:

$$\left(c_{rebar} \times m_{rebar} \times \Delta T_{rebar} \right) = -\left(c_{water} \times m_{water} \times \Delta T_{water} \right)$$

- Letting f = final and i = initial, in expanded form, this becomes:

$$c_{rebar} \times m_{rebar} \times \left(T_{f,rebar} - T_{i,rebar} \right) = -c_{water} \times m_{water} \times \left(T_{f,water} - T_{i,water} \right)$$

Example 5.3

- The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$\left(0.449\ J/g\cdot{}^{\circ}C\right)\left(360\ g\right)\left(42.7\ {}^{\circ}C - T_{i,\,rebar}\right) = -\left(4.184\ J/g\cdot{}^{\circ}C\right)\left(425\ g\right)\left(42.7\ {}^{\circ}C - 24.0\ {}^{\circ}C\right)$$

- Solving this equation gives $T_{i,rebar}$= 248 °C, so the initial temperature of the rebar was 248 °C.

Calorimetry Principles

- When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply.

- Because energy is neither created nor destroyed during a chemical reaction, the heat produced or consumed by the reaction (the "system"), $q_{reaction}$, plus the heat absorbed or lost by the solution (the "surroundings"), $q_{solution}$, must add up to zero.

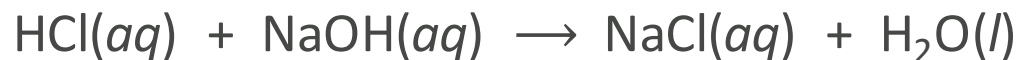$$q_{\text{reaction}} + q_{\text{solution}} = 0$$

- This means that the amount of heat produced or consumed by the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

- This concept lies at the heart of all calorimetry problems and calculations.

Example 5.5

- When 50.0 mL of 1.00 M HCl(*aq*) and 50.0 mL of 1.00 M NaOH(*aq*), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$$HCl(aq) \ + \ NaOH(aq) \ \longrightarrow \ NaCl(aq) \ + \ H_2O(l)$$

Example 5.5

- To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

- The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

Example 5.5

- Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{\text{solution}} = c_{\text{solution}} \times m_{\text{solution}} \times \Delta T_{\text{solution}}$$

Example 5.5

- To proceed with this calculation, we need to make a few reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and density values.

- The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is 4.184 J/g °C, so we use this value for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = \left(4.184 \text{ J/g} \times {}^{\circ}\text{C}\right)\left(1.0 \times 10^2 \text{ g}\right)\left(28.9\,{}^{\circ}\text{C} - 22.0\,{}^{\circ}\text{C}\right)$$

$$= 2.9 \times 10^3 \text{ J}$$

Example 5.5

- Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.9 \times 10^3 \text{ J}$$

- The negative sign indicates that the reaction is exothermic. The reaction produces 2.9 kJ of heat.

Figure 5.15

Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Figure 5.16

An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.
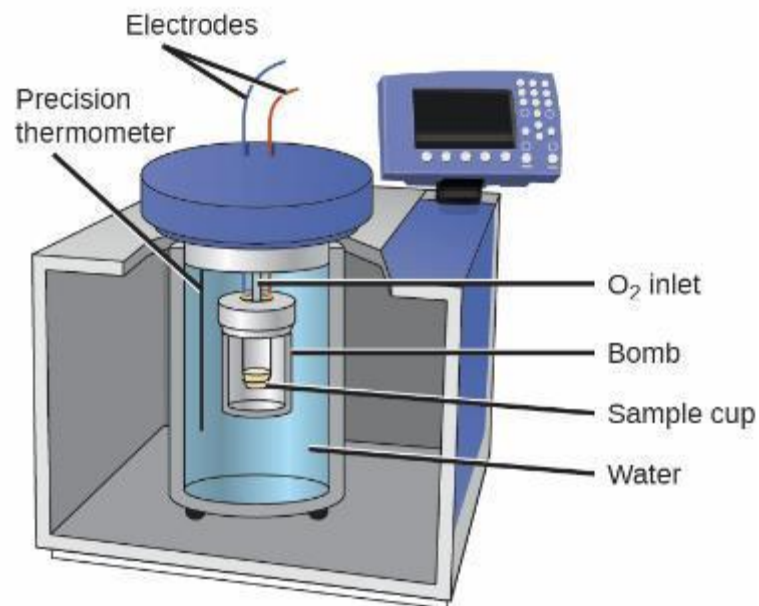
Bomb Calorimeter

- A **bomb calorimeter** is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions.

- This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water.

- The energy produced by the reaction is trapped in the steel bomb and the surrounding water.

Figure 5.17

(a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by "Harbor1"/Wikimedia commons)

Whole-Body Calorimeter

- **Whole-body calorimeters** of various designs are large enough to hold a human being.

- These calorimeters are used to measure the metabolism of individuals under different conditions:
  - environmental conditions
  - dietary regimes
  - health conditions, such as diabetes

- A **nutritional calorie (Calorie)** is the energy unit used to quantify the amount of energy derived from the metabolism of foods.

Figure 5.18

(a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

- 5.3 Enthalpy
  - State the first law of thermodynamics
  - Define enthalpy and explain its classification as a state function
  - Write and balance thermochemical equations
  - Calculate enthalpy changes for various chemical reactions
  - Explain Hess's law and use it to compute reaction enthalpies

Enthalpy

- **Thermochemistry** is a branch of chemical thermodynamics, the science that deals with the relationships between heat, work, and other forms of energy.

- Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them.

- Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised.

Internal Energy

- The total of all possible kinds of energy present in a substance is called the internal energy (U), sometimes symbolized as E.

- The relationship between the change in internal energy (ΔU), heat (q), and work (w) is summarized in the **First Law of Thermodynamics**:

$$\Delta U = q + w$$

Internal Energy

- Energy can be transported into a system, resulting in an *increase* in internal energy.
    - The system absorbs heat from the surroundings: $+q$.
    - Or the surroundings do work on the system: $+w$.

- Energy can also be transferred out of a system, resulting in a *decrease* in internal energy.
    - The system releases heat to the surroundings: $-q$.
    - Or the system does work on the surroundings: $-w$.

Figure 5.19
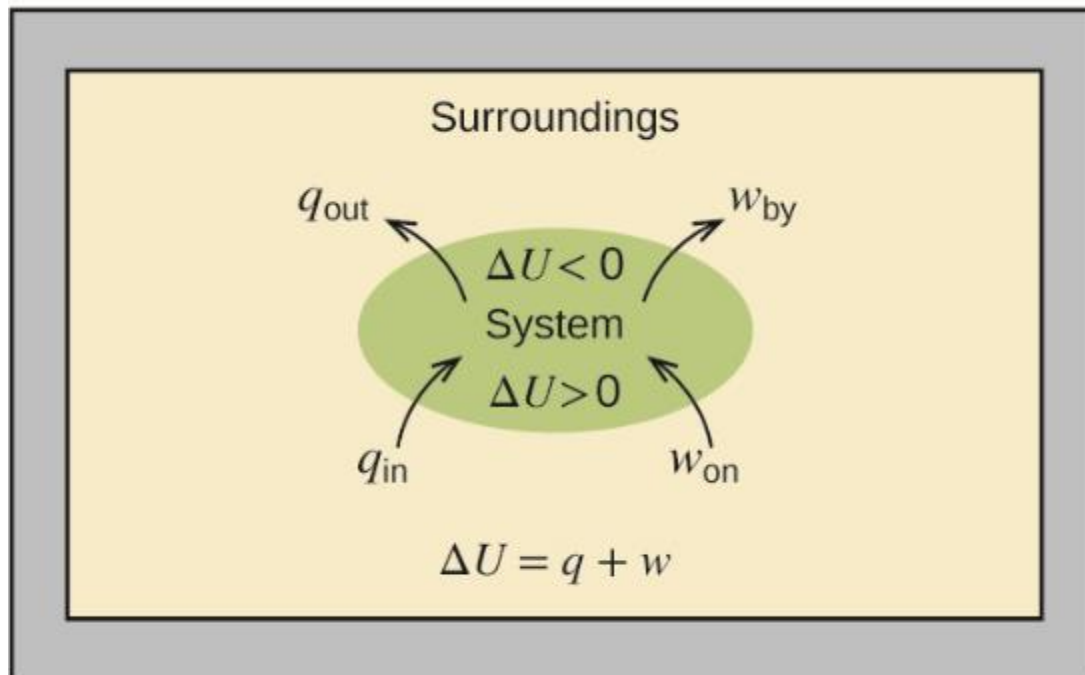
The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

Work

- A type of work called **expansion work** (or pressure-volume work) occurs when:
  - A system pushes back the surroundings against a restraining pressure.
  - The surroundings compress the system.

Internal Energy, Work, and Heat Example

- Consider an internal combustion engine.
    - System = gasoline and oxygen
    - Surroundings = rest of the universe, including the engine.
    - The reaction is **exothermic**, so heat is given off to the surroundings: $-q$
    - The reaction pushes the pistons out, so *work is done on the surroundings*: $-w$

$$\Delta U = q + w$$

- Internal energy of the system decreases: $-\Delta U$

Work

- Internal energy is an example of a **state function** (or state variable).

- The value of a state function depends only on the state that a system is in, and not on how that state is reached.

- Altitude or elevation is also a state function.

- If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5,895 m. It does not matter whether you hiked there or parachuted there.

Figure 5.20
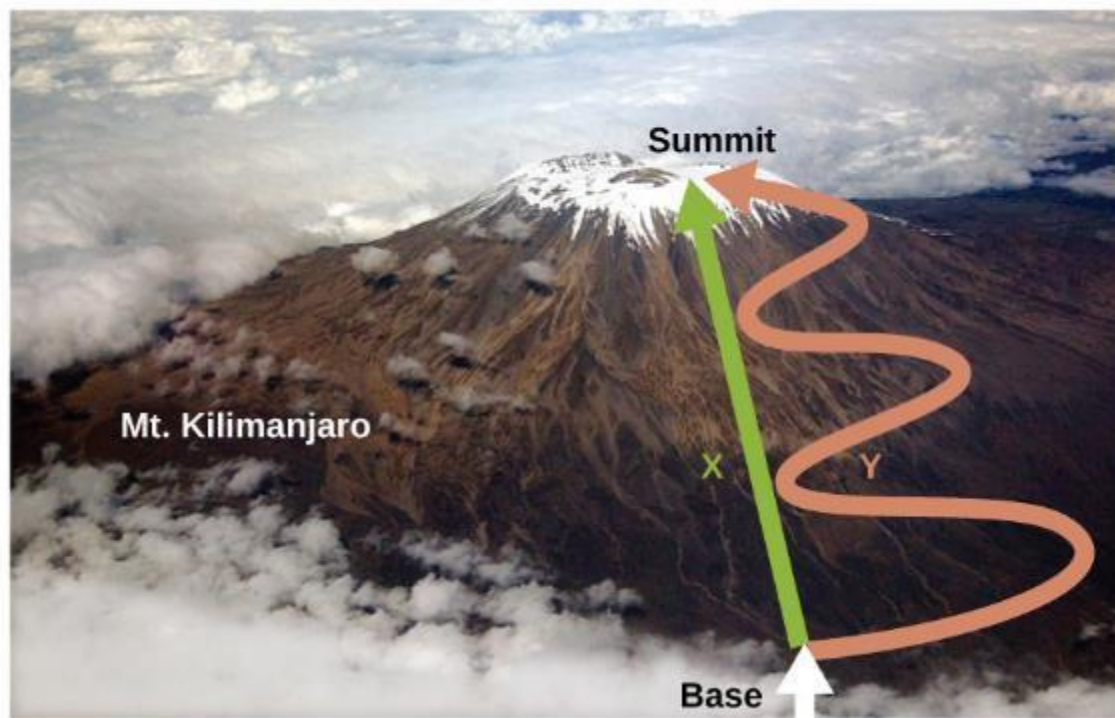
Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

- **Enthalpy (*H*)** is defined as the sum of a system's internal energy (*U*) and the mathematical product of its pressure (*P*) and volume (*V*):

$$H = U + PV$$

- Enthalpy is also a state function.

- Enthalpy values for specific substances cannot be measured directly; only **enthalpy changes (ΔH)** for chemical or physical processes can be determined.

- Commonly, chemical and physical processes occur at constant pressure.

- At constant pressure, the **enthalpy change** (Δ*H*) is:

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

- The mathematical product $P\Delta V$ represents pressure-volume work (*w*). By definition, the arithmetic signs of ΔV and w will always be opposite:

$$P \Delta V = -w$$

Enthalpy Change (ΔH)

- At constant pressure *q = q_p and*

$$\Delta U = q_p + w$$

- Substituting into the enthalpy-change equation yields:

$$\Delta H = q_p + w - w$$

$$\Delta H = q_p$$

- q_p is the heat of reaction at constant pressure.

Enthalpy Change (ΔH)

- Chemists usually perform experiments in open containers under normal atmospheric conditions so the external pressure is constant.

- At these conditions, if the only work done is caused by expansion or contraction, then the heat flow (q_p) and the enthalpy change (ΔH) for the process are equal.

- This makes enthalpy the most convenient choice for determining heat.

Thermochemical Equations

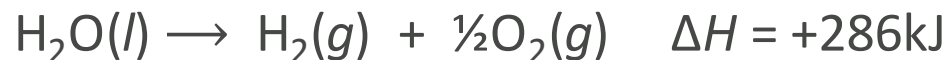- Chemists use a **thermochemical equation** to represent the changes in both matter and energy.

- In a thermochemical equation, the enthalpy change (ΔH) of a reaction is written to the right of the balanced equation.

- Example:

$$H_2(g) \ + \ \tfrac{1}{2}O_2(g) \ \longrightarrow \ H_2O(l) \quad \Delta H = -286\text{kJ}$$

- This ΔH value indicates the amount of heat associated with the reaction as written.

Conventions of Thermochemical Equations

- If the direction of a chemical equation is reversed, the arithmetic sign of ΔH is also reversed.
  - $\Delta H < 0$ indicates an **exothermic reaction**.
  - $\Delta H > 0$ indicates an **endothermic reaction**.

- A process that is exothermic in one direction is endothermic in the opposite direction and vice-versa.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -286\text{kJ}$$

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g) \quad \Delta H = +286\text{kJ}$$
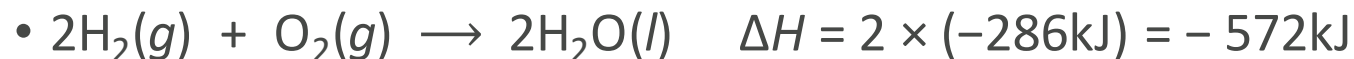
Conventions of Thermochemical Equations

- If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must also be multiplied by that same factor *(ΔH is an extensive property)*.

$$H_2(g) \ + \ \tfrac{1}{2}O_2(g) \ \longrightarrow \ H_2O(l) \quad \Delta H = -286 \text{kJ}$$

- Multiply by a factor of two:
    - $2H_2(g) \ + \ O_2(g) \ \longrightarrow \ 2H_2O(l) \quad \Delta H = 2 \times (-286\text{kJ}) = -572\text{kJ}$

- Multiply by a factor of one-half:
    - $\tfrac{1}{2}H_2(g) \ + \ \tfrac{1}{4}O_2(g) \ \longrightarrow \ \tfrac{1}{2}H_2O(l) \quad \Delta H = \tfrac{1}{2} \times (-286\text{kJ}) = -143\text{kJ}$

- The ΔH of a reaction depends on the physical state of the reactants and products, so these must be shown.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -286\text{kJ}$$

- For example, if gaseous water was formed instead of liquid water:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \quad \Delta H = -242\text{kJ}$$

Example 5.9

- A gummy bear contains 2.67 g of sucrose, $C_{12}H_{22}O_{11}$. When the gummy bear reacts with 7.19 g of potassium chlorate, $KClO_3$, 43.7 kJ of heat is produced.

- Write a thermochemical equation for the reaction of one mole of sucrose:

$$C_{12}H_{22}O_{11}(aq) + 8KClO_3(aq) \longrightarrow 12CO_2(g) + 11H_2O(l) + 8KCl(aq)$$

Example 5.9

$$2.67 \text{ g} \times \frac{1 \text{ mol}}{342.3 \text{ g}} = 0.00780 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}$$

$$7.19 \text{ g} \times \frac{1 \text{ mol}}{122.5 \text{ g}} = 0.0587 \text{ mol KClO}_3$$

$$\frac{0.0587 \text{ mol KClO}_3}{0.00780 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} = 7.52$$

Example 5.9

- The balanced equation indicates 8 mol $KClO_3$ are required for reaction with 1 mol $C_{12}H_{22}O_{11}$. Since the provided amount of $KClO_3$ is less than the stoichiometric amount, it is the limiting reactant and may be used to compute the enthalpy change:

$$\Delta H = \frac{-\ 43.7 \text{ kJ}}{0.0587 \text{ mol } KClO_3} = 744 \text{ kJ/mol } KClO_3$$

- Because the equation, as written, represents the reaction of 8 mol $KClO_3$, the enthalpy change is:

$$(744 \text{ kJ/mol } KClO_3)(8 \text{ mol } KClO_3) = 5960 \text{ kJ}$$

- Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions.

- A **standard state** is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions.

- The IUPAC standard state conditions:
    - Pressure of 1 bar (or 1 atm; 1 bar = 0.987 atm)
    - Solutions at 1 M concentration

Standard State Change in Enthalpy

- We will include a superscript "o" in the enthalpy change symbol to designate standard state conditions.

- The usual (but not technically standard) temperature is 298.15 K.

- The symbol, ΔH^{o}, is used to indicate an enthalpy change for a process occurring under these conditions.

Standard State Change in Enthalpy

- The enthalpy changes for many types of chemical and physical processes are available in the reference literature.

- Recall ΔH is an extensive property—it is proportional to the amount of substances involved.

- Often ΔH is normalized to a per-mole basis.

- **Standard enthalpy of combustion ($\Delta H°_C$)** is the enthalpy change when *exactly 1 mole* of a substance burns (combines vigorously with oxygen) under standard state conditions.

- Sometimes called the "heat of combustion."

Standard Enthalpy of Combustion

- For example, the enthalpy of combustion of ethanol is −1366.8 kJ/mol

- This is the amount of heat produced when *1 mole* of ethanol undergoes complete combustion at 25 °C and 1 atm pressure, yielding products also at 25 °C and 1 atm.

$$C_2H_5OH(l) \ + \ 3O_2(g) \ \longrightarrow \ 2CO_2 \ + \ 3H_2O(l)$$
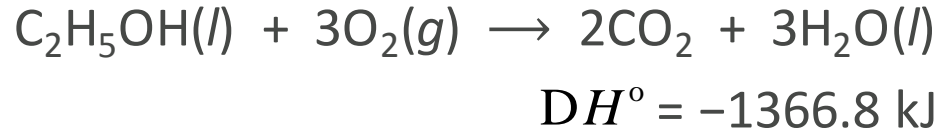
$$\Delta H° = -1366.8 \text{ kJ}$$

Table 5.2 Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion, $\Delta H°_c$ (kJ/mol at 25 °C)
carbon	$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5
hydrogen	$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$	−285.8
magnesium	$Mg(s) + \frac{1}{2} O_2(g) \longrightarrow MgO(s)$	−601.6
sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$	−296.8
carbon monoxide	$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$	−283.0
methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−890.8
acetylene	$C_2H_2(g) + 5/2\ O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$	−1301.1
ethanol	$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	−1366.8
methanol	$CH_3OH(l) + 3/2\ O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−726.1
isooctane	$C_8H_{18}(l) + 25/2\ O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$	−5461

Figure 5.21

The combustion of gasoline is very exothermic. (credit: modification of work by "AlexEagle"/Flickr)

Example 5.10

- As Figure 5.21 suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.

Example 5.10

- Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 5.2 gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

$$1.00 \text{ L } C_8H_{18} \times \frac{1000 \text{ mL } C_8H_{18}}{1 \text{ L } C_8H_{18}} \times \frac{0.692 \text{ g } C_8H_{18}}{1 \text{ mL } C_8H_{18}} \times \frac{1 \text{ mol } C_8H_{18}}{114 \text{ g } C_8H_{18}} \times \frac{-5460 \text{ kJ}}{1 \text{ mol } C_8H_{18}} = -3.31 \times 10^4 \text{ kJ}$$
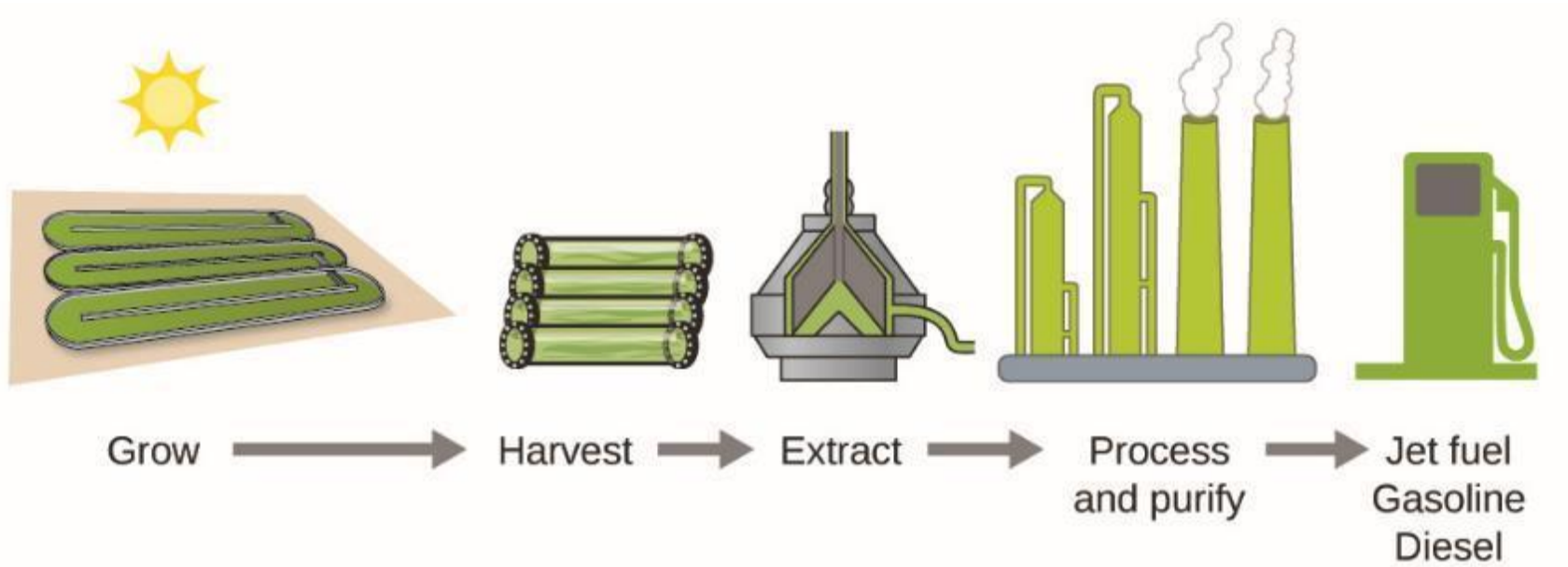
Figure 5.22
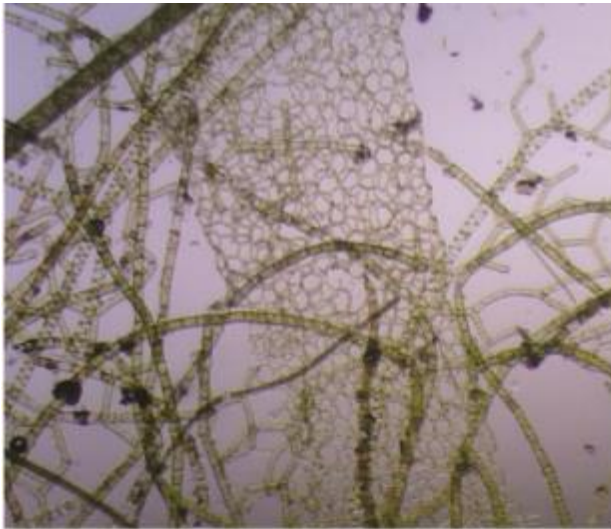
(a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

Figure 5.23

Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Standard Enthalpy of Formation

- **Standard enthalpy of formation ($\Delta H°_f$)** is an enthalpy change for a reaction in which *exactly 1 mole* of a pure substance is formed from its constituent free elements in their most stable states under standard state conditions.

- For example, $\Delta H°_f$ of $CO_2(g)$ is −393.5 kJ/mol.

$$C(s) \; + \; O_2(g) \; \longrightarrow \; CO_2(g) \quad \Delta H°_f \; = \; \Delta H° = -393.5 kJ$$

- By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions.

Example 5.12

- Write the heat of formation reaction equations for:
  (a) $C_2H_5OH(l)$
  (b) $Ca_3(PO_4)_2(s)$

- Remembering that $\Delta H°_f$ reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:
  (a) $2C(s,graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$
  (b) $3Ca(s) + \frac{1}{2}P_4(s) + 4O_2(g) \longrightarrow Ca_3(PO_4)_2(s)$

- Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Hess's Law

- There are two ways to determine the amount of heat involved in a chemical change:
    - Measure it experimentally.
    - Calculate it from other experimentally determined enthalpy changes.

- Some reactions are difficult, if not impossible, to investigate and make accurate measurements experimentally.

- For these reactions, the amount of heat involved must be calculated, usually using **Hess's law**.

- **Hess's law:** If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

- Hess's law is valid because enthalpy is a state function.

- Enthalpy changes depend only on where a chemical process starts and ends, not on the path it takes from start to finish.
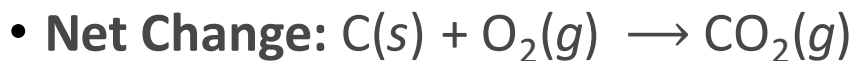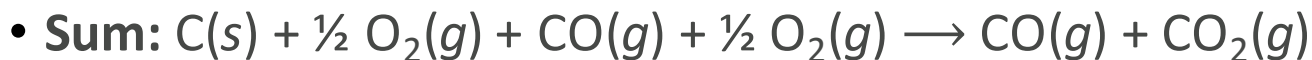
- For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process.

- The direct process is written:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H° = -394 \text{ kJ}$$

- In the two-step process:
    - First carbon monoxide is formed.
    - Then, carbon monoxide reacts further to form carbon dioxide.

- **Step 1:** $\quad C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$ $\qquad\qquad \Delta H° = -111$ kJ

- **Step 2:** $\quad CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ $\qquad\qquad \Delta H° = -283$ kJ

- **Sum:** $C(s) + \frac{1}{2} O_2(g) + CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO(g) + CO_2(g)$
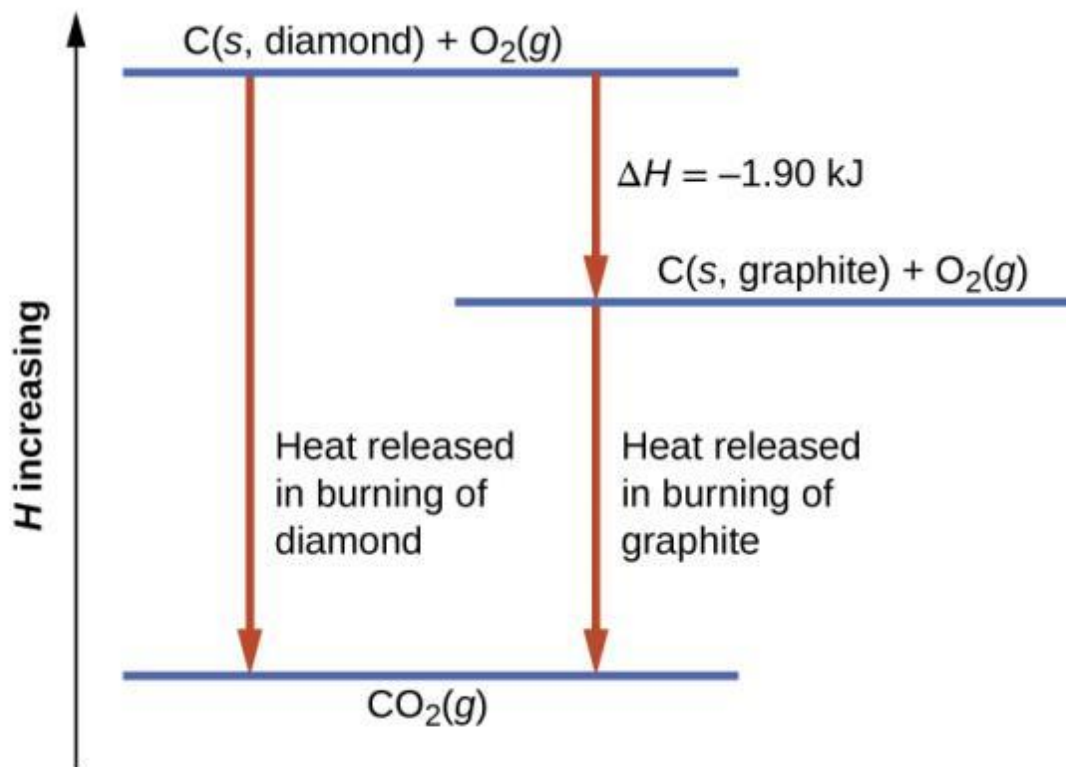
- **Net Change:** $C(s) + O_2(g) \longrightarrow CO_2(g)$

- According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps.

- The enthalpy change of the entire two-step reaction:

$$\Delta H^\circ = -111\,\text{kJ} + -283\,\text{kJ} = -394\,\text{kJ}$$

- We see that ΔH of the overall reaction is the same whether it occurs in one step or two.

Figure 5.24

The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Hess's Law and Enthalpies of Formation

- We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available.

- The stepwise reactions we consider are:
  - (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by

  - (ii) recombinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products).

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- The standard enthalpy change of the overall reaction, therefore, is equal to:
    - (ii) the sum of the standard enthalpies of formation of all the products
    - plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants.

- This is usually rearranged slightly to be written as follows:

$$\Delta H^{\circ}_{\text{reaction}} = \sum n \times \Delta H^{\circ}_{f}(\text{products}) - \sum n \times \Delta H^{\circ}_{f}(\text{reactants})$$

- With ∑ representing "the sum of" and n representing the stoichiometric coefficients.

Example 5.15

- What is the standard enthalpy change for the reaction:

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g) \quad \Delta H° = ?$$

- Use the special form of Hess's law given previously and the enthalpy of formation values found in Appendix G:

$$\Delta H^o_{reaction} = \sum n \times \Delta H^o_f(products) - \sum n \times \Delta H^o_f (reactants)$$

$$= \left[\left(2 \text{ mol HNO}_3(aq) \times \frac{-207.4 \text{ kJ}}{\text{mol}} \right) + \left(1 \text{ mol NO}(g) \times \frac{+90.2 \text{ kJ}}{\text{mol}} \right) \right]$$

$$- \left[\left(3 \text{ mol NO}_2(g) \times \frac{+33.2 \text{ kJ}}{\text{mol}} \right) + \left(1 \text{ mol H}_2O(l) \times \frac{-285.8 \text{ kJ}}{\text{mol}} \right) \right]$$

$$= -138.4 \text{ kJ}$$