Solutions for Chapter 7 End-of-Chapter Problems

Problem 7.1.
(a) Assuming all the food energy, 180 Cal, from eating a slice of pizza goes to keep your heart beating at 1 J of energy for each beat, the number of beats that can be sustained is:

\[
\text{180 Cal} = (180 \text{ Cal}) \left( \frac{1 \text{ kcal}}{1 \text{ Cal}} \right) \left( \frac{4184 \text{ kJ}}{1 \text{ kcal}} \right) \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right) \left( \frac{1 \text{ beat}}{1 \text{ J}} \right) = 7.5 \times 10^8 \text{ beats}
\]

At a pulse rate (heartbeat rate) of about 80 per minute, this would keep you going for about:

\[
7.5 \times 10^8 \text{ beats} = (7.5 \times 10^8 \text{ beats}) \left( \frac{1 \text{ min}}{80 \text{ beats}} \right) = 9.4 \times 10^6 \text{ min} \approx 5 \text{ yr}
\]

(b) If the efficiency of use of this food energy is about 27%, the value calculated for capturing the energy from glucose oxidation in Section 7.9, the answers in part (a) would be only 27% as large: \(2.0 \times 10^8 \text{ beats}; 2.5 \times 10^6 \text{ min} \approx 18 \text{ yr}\)

Problem 7.2.
(a) Once they have been ignited both the pasta and potato chip, in Investigate This 7.1, continue to burn on their own. They release energy in the form of light and enough thermal energy to keep their temperatures high enough to continue burning. You might find that a potato chip burns somewhat better than pasta, because the fat is a better fuel than starch. This is reflected in their nutritional Calorie values as well. A gram of starch provides about 4 Calories (17 kJ) and a gram of fat about 9 Calories (38 kJ).

(b) The oxidation of glucose is used as an example throughout this chapter. You know that the oxidation is quite exothermic, which is shown by the burning pasta, potato chip, and marshmallow (mainly sugars including glucose). It doesn’t matter that the glucose units are strung together as a polymer in starch or separated in a marshmallow -- each still oxidizes to produce a large output of enthalpy.

Problem 7.3.
If a baked, rather than a fried, potato chip were used in Investigate This 7.1, the baked chip will still burn, but probably not to burn as vigorously as the fried chip because there is less residual fat available as fuel on the baked chip. The raw potato slice may not burn at all because it has a high water content. The Olestra® chip will also burn quite well, for the Olestra is a long-chain polymeric fatty acid. It does not produce heat value in the body because it cannot be metabolized.

Problem 7.4.
Potential energy and kinetic energy are the two types of energy. Mechanical energy and thermal energy are both examples of kinetic energy. [Chemical energy stored in chemical bonds is a form of potential energy not included in this listing.] This is a visual representation of the relationship.
Problem 7.5.

[NOTE: For an excellent discussion of the forces acting on a helium-filled balloon see, J. E. Harriman, “On the Buoyancy of a Helium-Filled Balloon,” J. Chem. Educ. 2005, 82, 246-7. The discussion requires use of the barometric formula for the variation of atmospheric pressure with height above some reference level, but should be accessible to students who know the formula or who will accept it.]

(a) This diagram illustrates a tethered helium-filled balloon represented similarly to the model for the movement of combustion gases in Figure 7.2. The smaller dots inside the balloon (circle) represent He atoms and the larger dots outside the balloon represent the molecules in the air, mainly N₂ and O₂.

(b) The helium atoms in the balloon are in constant, random motion. They do not exhibit any directed motion. The same is true for the gases in the air outside the balloon (assuming constant temperature). What is represented crudely in the sketch is the variation in pressure (hence, number of particles) in the gravitational field of the Earth. Pressure decreases with height, so more air molecules are shown below the balloon than above and similarly, more He atoms are shown nearer the bottom of the balloon. The net result is a force (from collisions of the molecules and atoms with the outside and inside walls of the balloon) pushing the balloon up. The balloon is motionless, because this upward force pulls the string up, which results in an exactly balanced downward force in the string that is held motionless by its connection to some heavy object.

If the string is cut or untied, there is no longer a downward force counteracting the net upward buoyant force of the gases, and the balloon will rise. The helium atoms in the balloon are still in
constant, random motion, keeping the balloon fully inflated. If we were inside the balloon and could observe the He atoms in motion, we would see no difference between the tethered and untethered motion. However, if we make our observations from a fixed location outside the balloon, the He atoms would have a nonrandom upward component to their motion because they are rising. You might think this directionality would decrease the number of collisions inside the balloon at the bottom and increase them at the top. But this is not the case, because the balloon itself is moving and the top is moving away from the atoms inside as the bottom is moving toward them. The directionality of the atomic movements is just balanced by the directionality of the balloon moving with the same net velocity.

**Problem 7.6.**

(a) Since the temperature of the water in a waterfall increases when it falls and hits the pool at the bottom, its internal energy must have increased.

(b) Work has been done on the water to increase its internal energy (and, hence, its temperature). The work is done on the water when its potential energy at the top of the fall is converted to kinetic (directed) motion as it is falling and then this directed motion is changed to random motion when it hits the pool at the bottom and rapidly decelerates due to the force of the collision.

**Problem 7.7.**

Water molecules in ice are held in place by hydrogen bonds and move only slightly within the crystal lattice. When heat, thermal energy, is added to the solid, the molecules vibrate in place more rapidly and take up a little more space (on the average), but the change is quite small and the solid does only a tiny bit of work pushing back on its surroundings. Molecules in liquid water molecules are more free to move about, but are also hydrogen bonded and held rather close to one another. As with the solid, addition of thermal energy causes more rapid motion and the molecules take up a little more space (water expands a bit when heated), but, again, the change is rather small (although larger than in ice), so the liquid does only a small amount of work pushing back on its surroundings. In the vapor phase, where water molecules are on average, quite distant from their neighbors, hydrogen bonding is negligible. Almost all the heat energy added to the vapor phase water is transformed into more rapid translational motion, kinetic energy, and the average volume per molecule increases substantially. The increase in volume of the gas can do a substantial amount of work as it pushes back on its surroundings.

**Problem 7.8.**

Economic and environmental factors are important to every consumer, so it is important for automotive engineers to design engines that convert the highest possible percentage of energy to work. Whatever the price of fuel, consumers want to obtain the maximum number of miles possible per unit of fuel. This can only be done if the chemical energy from the fuel is converted efficiently as possible to work, and not wasted as heat. Efficient conversion of fuel energy to work also means release of lower concentrations of possible pollutants (carbon dioxide, carbon monoxide, nitrogen oxides, and hydrocarbons from fossil fuels) into the atmosphere.

**Problem 7.9.**

(a) A silver spoon at room temperature, when placed in a cup of hot water, becomes too warm to touch, because thermal energy is transferred by conduction. The water molecules are moving more rapidly, on the average, than the silver atoms in the spoon. Thermal energy is transferred
from the warmer, more energetic water molecules to the cooler, less energetic silver atoms in contact with the hot liquid. The energized silver atoms then transfer some of their energy to their neighbors and eventually the whole spoon becomes uncomfortably warm.

(b) When an apple pie is baked in an electric oven, thermal energy transfer is taking place through both conduction and convection. The electric heating unit will transfer thermal energy to molecules of gases in the air directly in contact with the unit; this is conduction. The warmer air rises, allowing the denser, cooler air to circulate near the heating coil; this sets up a convection current. (In ovens advertised as “convection ovens”, there is at least one fan to help distribute the air evenly.) The molecules of hot gas that are in contact with the pie will conduct thermal energy into the pie, eventually resulting in baking the pie. The rack on which the pie pan sits will also get thermal energy by conduction from the air molecules and transfer some of this thermal energy to the pie by conduction.

(c) When the water in an outdoor swimming pool cools from 25 °C to 20 °C as the summer season changes into autumn, the water temperature is going down because thermal energy is being lost by contact between warmer water molecules and the cooler air molecules. Conduction is involved directly at the water/air interface, but convection currents in both water and air are likely the major factors in transferring the thermal energy to the surface and away from the surface.

(d) When you sunbathe with your back exposed to the sun, until your back feels very warm, thermal energy is being transferred from the sun to your back by means of long wavelength infrared electromagnetic radiation. As the molecules in the skin on your back absorb radiation, the molecules move faster. This means that their temperature increases, which is what you sense. [Infrared radiation is accompanied by the more energetic ultraviolet rays, so remember to use sunscreen to avoid skin damage.]

Problem 7.10.
Since the cooler air near the ice rink floor has a higher density, it will stay near the floor for a relatively long time. The ice rink floor will remain cool until it is warmed up by heat radiating from the sunlit roof and walls and conduction from the roof and the walls to the floor materials. Although convection currents will not be set up with the higher density gas below the lower density gas, diffusion of gas molecules will occur and warmer molecules will transfer thermal energy to cooler molecules over time. None of these processes is going to be fast so bringing the floor and roof to the same temperature will take a long time.

Problem 7.11.
To warm an individual whose core temperature is too low, a convection method might be to place the person on a hammock or cot in a small room with a heated floor (much like an oven, but only warm, not hot). Warm air displaced from the floor by cooler air from the ceiling of the room would contact the person and transfer thermal energy from the air molecules to her/his body. A radiation method may consist of placing the person under a bank of “heat lamps,” electric lamps that emit a large fraction of infrared electromagnetic radiation. Most of the thermal transfer to the patient will be radiative. A disadvantage of this set up is that the radiation travels in straight lines and will transfer energy only to the side of the body facing the lamps. Using banks of lamps on both sides or putting reflective material on the side opposite the lamps will help with this problem. Wrapping the victim in an electric blanket will be the most efficient process of warming. In this method, heat is transferred by conduction, direct contact with the
warm surface, and it will be relatively easy to control the amount of thermal energy transferred can be so the individual will be heated at an appropriate rate and uniformly.

**Problem 7.12.**
In your bank statement, the difference between the ending and initial balance corresponds to a state function:

\[ \Delta Balance = Balance_{\text{final}} - Balance_{\text{initial}} \]

All of the transactions correspond to path-dependent functions. They describe all the different expenditures and deposits that are responsible for the overall change in balance. The order in which they occur does not matter, that is, there are many possible paths to the final balance.

**Problem 7.13.**
This football play has moved the team from its own 35-yard line, past midfield, to the opponent’s 40-yard line. The team has moved the ball 25 yards closer to the end zone where they can score. The net gain in yardage is an example of a state function, a function that depends only on the initial and final states. The path taken does not matter. Only the gain in yardage counts as far as the game is concerned. (Of course the record books will note a completed pass by the quarterback and receiver, because fans of the game—as well as coaches—are interested in the paths taken as well as the outcome.)

**Problem 7.14.**
A significant fraction of the heat energy in a fossil-fuel burning power plants producing electricity is transferred to the water used to cool the turbines, and there are many sources of friction in the turbines and generator that lower their efficiency. Even when the electricity has been generated, there will be losses over long-distance power lines usually required to reach the power grid. Most students will intuitively recognize that 100% conversion of thermal energy to work seems unlikely and the introduction to this chapter tells them it is not possible. Heat losses must present serious limitations, given that the best engineers have only found a 42% efficiency rate possible. A more complete answer to this question will be possible after studying Chapter 8, where the second law of thermodynamics and entropy are studied in more detail.

**Problem 7.15.**
(a) The change from a battery being fully charged battery to being totally discharged battery is a state function no matter how the process of discharge is carried out. The paths may be quite different, but the end result is exactly the same, a dead battery. State functions do not depend on the path taken to achieve the present state.

(b) When a battery is used to power a flashlight, much of the energy lost by the battery will be used to heat the filament in the light bulb and some of this energy is released as radiant energy, light (both visible and infrared). Batteries do get warm as they are being used, so there is some thermal energy transfer by contact with the surroundings. When a battery is used to power a toy car, there will be a small amount of thermal energy transfer by friction between the toy car and the roadbed on which the car runs. Much of the energy lost will be changed to mechanical work done in moving the toy car and some of it will be lost in the friction within the motor and other moving parts of the car.
Problem 7.16.
The state functions will be identical for a plane, a helicopter, a parachutist, and a hawk descending from 1892 feet to 892 feet, as each object will make an altitude change of 1000 feet to land safely on the ground. The path functions will be quite different. The airplane and helicopter are obliged to follow certain traffic patterns, with designated altitudes and descent rates into the airport. The helicopter can make a more direct descent, but still has to stay out of the way of other traffic. The parachute jumper will likely be following a spiral pattern but dropping pretty much vertically to land safely. The bird will take whatever path it wants to, with little regard to the airplane, helicopter, or parachute jumper. Interestingly enough, the bird also lands into the wind, just as the other airborne objects plan to do!

Problem 7.17.
(a) The enthalpy change for a system open to the atmosphere is dependent on the identity of the reactants and products. The change in enthalpy for any process or reaction depends on the initial and final states of the system, that is, on the identity of the reactants and products. This is a correct statement.
(b) The enthalpy change for a system open to the atmosphere is zero. An enthalpy change may be zero for a reaction, but this is not, in general the case, so this is not a correct statement.
(c) The enthalpy change for a system open to the atmosphere is negative. An enthalpy change may be negative for a reaction, but this is not necessarily true in general, so this is not a correct statement.
(d) The enthalpy change for a system open to the atmosphere is \( q_P \). A measure of the enthalpy change for a process is the heat exchanged with the surroundings at constant pressure. This is a correct statement.
(e) The enthalpy change for a system open to the atmosphere is positive. An enthalpy change may be positive for a reaction, but this is not necessarily true in general, so this is not a correct statement.

Problem 7.18.
(a) An open system refers to a part of the universe being studied that can exchange matter and energy with its surroundings. Some open system examples include an open aquarium, a cup of coffee, and hot springs. Your body is an open system since you exchange both energy (in the form of heat) and matter (food, \( O_2 \), \( CO_2 \), \( H_2O \)) with the surroundings.
(b) In a closed system, only energy is exchanged with its surroundings. An example of such a system is a cup with hot coffee that is tightly closed so no vapors may escape, but the cup is not insulated so heat energy may be exchanged with surroundings.
(c) An isolated system does not exchange matter or energy with its surroundings. An example of a nearly isolated system might be a properly stoppered Thermos® bottle of coffee. A stopper prevents water vapor from escaping (or other matter from entering), while the vacuum construction keeps heat from being lost to (or gained from) the surroundings.
(d) An exothermic process is a process that releases heat to its surroundings. Reactions of sodium metal with water, burning of a match, or condensation of steam are examples of exothermic processes.
(e) An endothermic process is a process that absorbs heat from its surroundings. Melting ice or evaporation of rubbing alcohol are examples of endothermic processes.
Problem 7.19.
If we pour coffee (presumably hot) from a properly stoppered Thermos® bottle into a mug, the coffee, which was nearly an isolated system in the stoppered and insulated Thermos® bottle, becomes an open system that can exchange matter and energy with its surroundings. A closed system can exchange energy, but not matter, with its surroundings. If, in our coffee example, we transferred the coffee to a mug with a tight fitting lid, energy could be exchanged through the walls of the mug, but no matter, including water vapor and the odor producing molecules from the coffee, could escape (and no matter, such as sugar or cream, could be added).

Problem 7.20.
From the standpoint of thermodynamics, Earth is an open system, because matter and energy are continually exchanged with the surroundings. The most obvious example is electromagnetic radiation from the sun, which maintains the temperature of the planet. Sunlight is also responsible for the production of essentially all the food on the planet via photosynthesis in green plants. The oxygen that maintains aerobic life is a by-product of photosynthesis. Matter in the form of meteorites and atoms and ions from the sun and other sources fall to the earth from outer space. The Earth, of course, radiates some energy back to space and atoms and molecules in the upper atmosphere are continuously lost to space.

Problem 7.21.
The diagram shows an experiment in which a hot silver bar is added to a beaker of water at room temperature.

(a) If the object of the experiment is to find the specific heat of the silver, we have a couple of ways to define the system and the surroundings. In one ideal case, the silver bar and the water form the collection of atoms and molecules under consideration, the system, and we assume that the system is isolated, so no energy or matter can enter from the surroundings, including the beaker, the thermometer, the air above the water (and everything else in the universe). This definition neglects the obvious necessity for energy transfer between the water and the thermometer required to make the thermometer respond to the changing water temperature, but we assume this is a tiny effect. For this case, no thermal energy is gained or lost by the system, so we set the sum of any energy changes within the system equal to zero, that is,

$$\Delta E_{\text{silver}} + \Delta E_{\text{water}} = 0$$

To use this equation to find the specific heat of the silver, you need to know the mass of the silver bar, the mass of the water, the specific heat of water, and the temperature changes for the silver and water when they have come to the same final temperature. A second ideal division of the world into system and surroundings is quite similar, except that you treat the silver bar as the system and the water as the surroundings and assume nothing else in the universe changes. In this case, the energy change in the silver bar and the energy change...
in the water are the same, except the silver loses energy and the water gains energy, that is, they have opposite signs:

$$\Delta E_{\text{silver}} = -\Delta E_{\text{water}}$$

To find the specific heat of the silver, you need the same information as in the previous case. Note that the equations you have to work with are identical, simply rearranged. It is probably conceptually simpler to choose the silver and water together as an isolated system (which is what we have done in Section 7.6 of the text).

(b) If you already know the specific heat of the silver, you can use this experimental set up to determine how “ideal” the experiment actually is. That is, you can test if there is significant thermal energy transfer to and/or through the walls of the glass beaker or to the thermometer. In this case it is useful to define the system as the silver bar and the water and everything else, the beaker, thermometer, air around the beaker, and the table the apparatus is on, as the surroundings. Energy must still be conserved, so the sum of the energy changes in each part of the system and the surroundings must be zero:

$$\Delta E_{\text{silver}} + \Delta E_{\text{water}} + \Delta E_{\text{surroundings}} = 0$$

To use this equation, we need the same information as in part (a), with the addition of the specific heat of the silver. With all this information, we can calculate the first two terms in the equation and then solve for $$\Delta E_{\text{surroundings}}$$. If the set up is reasonably close to ideal, $$\Delta E_{\text{surroundings}}$$ will be close to zero. It’s possible that $$\Delta E_{\text{surroundings}}$$ could be a significant fraction, perhaps five to ten percent, of the size of the other energy changes, thus making this not a particular good set up for the determination discussed in part (a). It is virtually certain that $$\Delta E_{\text{surroundings}} > 0$$, since the surroundings are at a lower temperature than the system (except for the water at the very beginning), thermal energy will leave the system and go into the surroundings, a positive change in its thermal energy.

(c) The experimental diagram illustrates an open system, because matter and energy can be exchanged with the surroundings. For example, water molecules can evaporate from or condense onto the surface of the water. Heat may be exchanged between the system and the surroundings. Therefore, this cannot be a closed system because matter can be exchanged. It is not an isolated system as there is no attempt to control thermal exchanges between the system and the surroundings.

**Problem 7.22.**
To accurately measure the thermal energy change for reaction, we need to account for heat that goes to heating (in the case of exothermic reaction) or cooling (in the case of endothermic reaction) the calorimeter itself (that is the container, thermometer, and so on, exclusive of the water, which we explicitly account for in our calculations). The heat lost or gained to the calorimeter must be experimentally determined for each calorimeter to assure the accuracy of calorimetric measurements.

**Problem 7.23.**
[NOTE: There is a typographical error in the problem statement in the text (1st and 2nd printings). The sign of the enthalpy change should be positive (an endothermic reaction) not negative. Energy is required to decompose ammonia to its elements.]

The equation for decomposition of gaseous ammonia, $$\text{NH}_3(g)$$, is:
\[
\text{NH}_3(g) \rightarrow \frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \quad \Delta H = 45.9 \text{ kJ}
\]
This reaction equation and enthalpy change indicate that the formation of gaseous ammonia (a) evolves 45.9 kJ for each mole of ammonia formed. This completion for the sentence is **correct**. The reaction equation and enthalpy change are for the decomposition of ammonia. The sign of the enthalpy change will be reversed when the reaction goes in the opposite direction to form ammonia from its elements. For formation of a mole of ammonia, \(\Delta H = -45.9 \text{ kJ}\), that is, energy is evolved—the reaction is exothermic.

(b) evolves 23 kJ for each mole of nitrogen used. This completion for the sentence is **incorrect**. Energy will be evolved [see part (a)], but for each mole of nitrogen that reacts, twice as much energy is evolved, that is \(\Delta H = -91.8 \text{ kJ}\), because the enthalpy change shown with the equation is for only one-half mole of nitrogen.

(c) absorbs 45.9 kJ for each mole of ammonia formed. This completion for the sentence is **incorrect**, because the formation evolves energy [see part (a)].

(d) absorbs 23 kJ for each mole of nitrogen used. This completion for the sentence is **incorrect**, because the formation evolves energy [see part (a)].

(e) is an exothermic process. This completion for the sentence is **correct** [see part (a)].

**Problem 7.24.**
The setup for this experiment is like that shown in Problem 7.21, except that the container here is an insulated calorimeter, so no energy is transferred in or out of the calorimeter after the hot metal is added. The net change in energy in the calorimeter is zero and we can write:

\[
\Delta E_{\text{metal}} + \Delta E_{\text{water}} = 0 = m_{\text{metal}}c_{\text{metal}}\Delta T_{\text{metal}} + m_{\text{water}}c_{\text{water}}\Delta T_{\text{water}}
\]
All of the quantities in this equation are known or can be calculated from the data given in the problem. We have \(\Delta T_{\text{metal}} = 25.0 \, ^\circ\text{C} - 100.0 \, ^\circ\text{C} = -75 \, ^\circ\text{C}\) and \(\Delta T_{\text{water}} = 25.0 \, ^\circ\text{C} - 23.0 \, ^\circ\text{C} = 2.0 \, ^\circ\text{C}\). Rearrange the equation to solve for \(c_{\text{metal}}\):

\[
c_{\text{metal}} = \frac{m_{\text{water}}c_{\text{water}}\Delta T_{\text{water}}}{m_{\text{metal}}\Delta T_{\text{metal}}} = \frac{(20.0 \, \text{g})(4.184 \, \text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1})(2.0 \, ^\circ\text{C})}{(10.0 \, \text{g})(-75.0 \, ^\circ\text{C})} = 0.22 \, \text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}
\]
In the table, the specific heat of silver metal is 0.22 J·g⁻¹·°C⁻¹ (and none of the other possibilities is close to this value), so it is likely that the metal in this experiment is silver.

**Problem 7.25.**
The student in this problem twice added a mass of hot metal to a calorimeter containing water. The temperature of the hot water bath was essentially the same in both trials and we assume that there was the same amount of water in the calorimeter for each trial. The temperature change of the water in the first trial was 1.2 \(^\circ\text{C}\) and, in the second trial was 2.2 \(^\circ\text{C}\). His instructor had noted a problem with his first trial that the student corrected in the second trial. If the second trial gives a correct (or at least more correct result), then we can conclude that the temperature change in the first trial was in error and must have been too small. The only way the temperature change could be smaller than it should have been is if the metal was not as hot as in should have been, that is, not as hot as the water bath used to heat it. The problem statement says that “he transferred it [the hot metal] slowly to a calorimeter.” Here’s the student’s error. He has to transfer the hot metal as fast as possible from the hot bath to the calorimeter, so it does not lose thermal energy to the surroundings (the air and the tongs used to pick it up). Our
Chemical Energetics: Enthalpy  Chapter 7

Assume that the total volume of the solution formed when 100. mL of 0.5M HCl and 100. mL of 0.5M of NaOH are mixed is 200. mL. The mass of the solution, assuming that its density is 1.0 g·mL⁻¹, is 2.0 × 10² g [= (200. mL)(1.0 g·mL⁻¹)]. The temperature change caused by the acid-base reaction is \( \Delta T_{\text{solution}} = 22.2 \, ^\circ C - 19.0 \, ^\circ C = 3.2 \, ^\circ C \). The temperature of the solution increased, which means that thermal energy is released from the reaction system, so the reaction is exothermic: \( \Delta H < 0 \). The enthalpy change for the reaction and the thermal energy (or enthalpy) change for the solution in the calorimeter have to sum to zero, since no energy is transferred in or out of the calorimeter. (We assume that the acid and base solutions began at the same temperature, so that the only change in the mixed solution temperature is caused by the reaction.) We can write the energy conservation as:

\[
\Delta H + m_{\text{solution}} c_{\text{solution}} \Delta T_{\text{solution}} = 0 = \Delta H + (2.0 \times 10^2 \, g)(4.18 \, \text{J·g}^{-1}·\text{°C}^{-1})(3.2 \, \text{°C})
\]

\[
\Delta H = -2.7 \times 10^3 \, \text{J} = -2.7 \, \text{kJ}
\]

To find the enthalpy change per mole of reactants, we have to calculate the number of moles of reactants that reacted and convert our result to kJ·mol⁻¹. The reaction that occurs is:

\[
\text{HCl(}aq\text{)} + \text{NaOH(}aq\text{)} \rightarrow \text{H}_2\text{O(}aq\text{)} + \text{NaCl(}aq\text{)}
\]

A mole of NaOH(\(aq\)) reacts for each mole of HCl(\(aq\)) that reacts and we mixed the same number of moles of each, so the number of moles that react is:

mol reactant = (0.100 L)(0.5 mol·L) = 0.05 mol

\( \Delta H(\text{per mole}) = \frac{-2.7 \, \text{kJ}}{0.05 \, \text{mol}} = 54 \, \text{kJ}·\text{mol}^{-1} = 5 \times 10^1 \, \text{kJ}·\text{mol}^{-1} \)

The data are only good enough to justify one significant figure in the final result.

Problem 7.27.
(a) An endothermic dissolution process takes energy from its surroundings, the water in which the dissolution occurs. Since energy leaves the water, it gets cooler, so when the cold pack in which the dissolution occurred is placed on your skin, energy is transferred from your warm skin to the cool/cold solution. When energy leaves your skin, you feel cold, as we discussed in Chapter 1, Section 1.10 when analyzing evaporation of sweat from your skin.

(b) If the cold pack contains ample water to dissolve 50.0 g of ammonium nitrate, then the number of moles that dissolve is:

mol \( \text{NH}_4\text{NO}_3 = (50.0 \, \text{g \text{NH}_4\text{NO}_3})(\frac{1 \, \text{mol \text{NH}_4\text{NO}_3}}{80.0 \, \text{g \text{NH}_4\text{NO}_3}}) = 0.625 \, \text{mol} \)

The enthalpy change for this dissolution is:

\( \Delta H = (\Delta H(\text{per mole}))(\text{mol NH}_4\text{NO}_3) = (25.7 \, \text{kJ}·\text{mol}^{-1})(0.625 \, \text{mol}) = 16.1 \, \text{kJ} = 1.61 \times 10^4 \, \text{J} \)
For the ideal case, we assume that no thermal energy leaves or enters the cold pack as the dissolution occurs, so the sum of the enthalpy/energy changes that occur is zero in the 175 g (=[(125 g) + (50.0 g)] of solution:

\[
\Delta H + m_{\text{solution}}c_{\text{solution}}\Delta T_{\text{solution}} = 0 = \Delta H + (175 \text{ g})(4.184 \text{ J} \cdot \text{g}^{-1} \cdot \text{°C}^{-1})(T_{\text{final}} - 25 \text{ °C})
\]

\[
T_{\text{final}} = \frac{-\left(1.61 \times 10^4 \text{ J}\right) - (175 \text{ g})(4.184 \text{ J} \cdot \text{g}^{-1} \cdot \text{°C})(-25 \text{ °C})}{(175 \text{ g})(4.184 \text{ J} \cdot \text{g}^{-1} \cdot \text{°C})} = 3 \text{ °C}
\]

(c) To get the result in part (b), we assumed that there is no heat loss or gain between the heat pack and the surroundings, that is, that there are no thermal energy transfers. This assumption cannot be correct, since the cold pack is not insulated (and would be useless to us, if it were).

(d) If the final temperature of the cold pack is about 7 °C, we know that the enthalpy change calculated in part (b) is either incorrect or not all the change resulted in change in the solution temperature. The most likely explanation is that there was probably energy transfer from the warmer surroundings to the solution as dissolution was occurring, so the maximum cooling calculated in part (b) for the ideal case is not observed.

Problem 7.28.

(a) The balanced equation for the complete combustion of ethanol using full Lewis structures for each reactant and product molecule is:

(b) Check the models you have made of each reactant and product molecule in this reaction to be sure they have the appropriate number and kind of single and double bonds.

(c) The total enthalpy input that will be required to break all the bonds in the reactants is the sum of all the bond enthalpies (each multiplied by the appropriate stoichiometric factor to account for the number of this kind of bond in the reactant molecules):

\[
\sum BH_{\text{reactants}} = (5 BH_{\text{C-H}} + BH_{\text{C-C}} + BH_{\text{C-O}} + BH_{\text{O-H}}) + (3 BH_{\text{O=O}})
\]

\[
= [(5 \times 414 \text{ kJ}) + (347 \text{ kJ}) + (351 \text{ kJ}) + (460 \text{ kJ})] + [(3 \times 499 \text{ kJ})] = 4725 \text{ kJ}
\]

(The stoichiometric coefficients represent numbers of moles of bonds broken for each mole of reaction. To make the expression easier to read, we have cancelled the stoichiometric moles with the per mole units of the bond enthalpies.) The sign of \(\sum BH_{\text{reactants}}\) is positive, which shows that bond breaking is an endothermic process.

(d) The total enthalpy that will be released in forming all bonds in the products is the sum of all the bond enthalpies (each multiplied by the appropriate stoichiometric factor to account for the number of this kind of bond in the reactant molecules and each with a negative sign to denote the release of energy as a bond is formed):

\[
\sum (-BH_{\text{products}}) = 2 \cdot 2 \cdot (-BH_{\text{C=O}}) + 3 \cdot 2 \cdot (-BH_{\text{O-H}})
\]

\[
= 4 \times (-799 \text{ kJ} \cdot \text{mol}^{-1}) + (6 \times (-460 \text{ kJ} \cdot \text{mol}^{-1}) = -5956 \text{ kJ}
\]

The sign of \(\sum (-BH_{\text{products}})\) is negative, which shows that bond formation is an exothermic process.

(e) The net enthalpy change, \(\Delta H\), in this combustion reaction is:
\[ \Delta H = \sum BH_{\text{reactants}} + \sum (-BH_{\text{products}}) = +4725 \text{ kJ} + (-5956 \text{ kJ}) = -1231 \text{ kJ} \]

The combustion of alcohol is an exothermic process overall, just as is expected, if the substance is being used as a fuel. The experimental reaction enthalpy will involve a reactant (ethanol) and product (water) in their liquid states, but the calculations based on bond enthalpies assume all species are gases. Since this is an exothermic reaction, the ethanol is at a higher energy than the products. Converting gaseous ethanol to liquid will lower its energy, so the effect would be to reduce the experimental relative to calculated energy. Converting gaseous water to liquid will lower its energy and the effect would be to widen the energy gap between the reactants and products and thus increase the experimental relative to calculated energy. Which effect would predominate? Three moles of water are liquefied, but only one mole of ethanol is liquefied. The molar enthalpy of vaporization (or condensation) of ethanol and water are about the same (Table 1.2 in Chapter 1), so the water effect would be larger and the calculated energy would likely be an underestimate. (The value calculated from standard enthalpies of formation – Section 7.8 – is about -1368 kJ·mol\(^{-1}\), which, as predicted, is somewhat larger than the value, -1231 kJ·mol\(^{-1}\), from bond enthalpies.)

(f) Values for food energy are determined with combustion reactions carried out in calorimetric experiments, so the value calculated here is an estimate for ethanol’s fuel value in our bodies. We need to be mindful of the caveat from part (e) that the calculation of the enthalpy of combustion using average bond enthalpies for gaseous compounds at 25 °C is only an estimate. Average bond energies are certainly likely to be somewhat different than the actual values in the molecules under consideration and there error is introduced when the compounds are not gases.

**Problem 7.29.**

The more stable isomer, ethanol or dimethyl ether, will require greater energy to dissociate it into atoms. We can use bond enthalpies to calculate the enthalpy change for atomization of each isomer and compare the results.

<table>
<thead>
<tr>
<th>Bond</th>
<th># Bonds</th>
<th>(\Sigma BH), kJ</th>
<th>(\Sigma BH), kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>5</td>
<td>2070</td>
<td>6</td>
</tr>
<tr>
<td>C-C</td>
<td>1</td>
<td>347</td>
<td></td>
</tr>
<tr>
<td>O-H</td>
<td>1</td>
<td>460</td>
<td></td>
</tr>
<tr>
<td>C-O</td>
<td>1</td>
<td>351</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>3228</td>
<td>Total</td>
</tr>
</tbody>
</table>

Ethanol requires more enthalpy to atomize to the same collection of atoms, so it is the more stable of these two isomers by about 42 kJ (per mole of isomer).

**Problem 7.30.**

We can use average bond enthalpies to estimate the enthalpy change for the reaction in which two amino acids join to form a peptide bond, releasing a water molecule:
One way to approach this problem is to sum the enthalpy change for breaking all the bonds in the reactants and the enthalpy change for making all the bonds in the products. This is more work than we need to do, because only a few bonds are broken and made going from reactants to products. If all the others are included, they just cancel out in the breaking and making. In this case, a C–O and N–H bond need to be broken in the reactants and a C–N and O–H bond made in the reactants:

\[
\Delta H = \sum BH_{\text{reactants}} + \sum (-BH_{\text{products}}) = (BH_{C-O} + BH_{N-H}) + [(-BH_{C-N}) + (-BH_{O-H})] = (\text{kJ}) + (\text{kJ}) + [(-\text{kJ}) + (-\text{kJ})] = 740 \text{ kJ} + 736 \text{ kJ} = +4 \text{ kJ}
\]

(Stoichiometric coefficients, all 1 mol in this case, represent numbers of moles of bonds broken for each mole of reaction. To make the expression easier to read, we have cancelled the stoichiometric moles with the per mole units of the bond enthalpies.)

**Problem 7.31.**

All the bonds in the open-chain and cyclic forms of glucose are the same, except those involved in making the cyclic form from the open-chain form. This change involves breaking a C=O on carbon-1 and making two C-O bonds in its place. An O-H bond also has to be broken, but another is made, so they cancel out. Thus, the difference is 745 kJ required to break the C=O compared to –702 kJ released when 2 C–O bonds are made. Thus, the change from the open chain to cyclic form is endothermic by about 43 kJ (per mole of glucose) and the open-chain form is the more stable. In nature, almost all glucose molecules exist in cyclic forms. There must be another stabilizing influence (or bond enthalpy calculations for glucose, which is a solid, are not accurate enough to give us the actual enthalpy difference).

**Problem 7.32.**

(a) Note that, for the reactions of both diazomethane and diazirine reacting to give ethene and nitrogen gas, we can ignore the C–H bonds, since there are four in reactants and four in the products. We have to focus on the carbon-nitrogen, and nitrogen-nitrogen bonds. For the reaction of two moles of diazomethane, we have:

\[
\Delta H_{\text{rxn}} = \{2BH(C=\text{N}) + 2BH(N=\text{N})\} + \{[-BH(C=C)] + 2[-BH(N=\text{N})]\}
\]

\[
\Delta H_{\text{rxn}} = 2\cdot(615 \text{ kJ}) + 2\cdot(418 \text{ kJ}) + [(-620 \text{ kJ}) + 2\cdot(-941.4 \text{ kJ})] = -437 \text{ kJ}
\]

For the reaction of two moles of diazirine, we have:

\[
\Delta H_{\text{rxn}} = \{4BH(C=\text{N}) + 2BH(N=\text{N})\} + \{[-BH(C=C)] + 2[-BH(N=\text{N})]\}
\]

\[
\Delta H_{\text{rxn}} = 4\cdot(276 \text{ kJ}) + 2\cdot(418 \text{ kJ}) + [(-620 \text{ kJ}) + 2\cdot(-941.4 \text{ kJ})] = -563 \text{ kJ}
\]

These reactions are highly exothermic with the predominant contribution in both cases coming from the great stability of the triple-bonded nitrogen product. Note that that only difference between these two calculations is the breaking of different kinds of carbon-nitrogen bonds. For diazomethane, two C=N bonds are broken and, for diazirine, four C–N bonds are broken. Recall that the enthalpy change required to break one C=N bond is greater than twice the enthalpy change to break two C–N bonds. The difference is 63 kJ. For two moles of diazomethane and diazirine, the difference in reaction enthalpies is 126 kJ [= 2\cdot(63 \text{ kJ})], reflecting the difference in carbon-nitrogen bonds broken.
(b) An enthalpy-level diagram (like Figure 7.11) that combines the two reactions is:

Diazomethane is the more stable molecule, relative to diazirine. Complicating factors that might make the conclusions based on average bond enthalpies suspect include the strain of making the three-membered ring (which distorts the usual bonding angles for carbon and nitrogen and will change the bond enthalpies) in diazirine and/or the formal separation of charge in the diazomethane molecule that could make it less stable than a comparable molecule without formal charge.

(c) You might argue that the strain energy in diazirine is responsible for its higher energy (63 kJ·mol⁻¹ higher, based on these bond enthalpy calculations), but the argument is not wholly satisfactory. To complicate matters, we find experimentally that diazirine can be kept as a gas in the dark at room temperature indefinitely, whereas samples of gaseous diazomethane react as shown here and on the walls of their containers within a few hours. Based on exothermicity, the reactions shown here seem very favorable, although we know that exothermicity is not a good criterion for deciding the direction of a reaction. Diazomethane does react, but some factor slows the diazirine reaction so much that it is undetectable.

**Problem 7.33.**
As you see, the molecules in this table are isomers, and their complete combustion will give identical products in each case: 6 molecules of CO₂ and 6 molecules of H₂O for each molecule of sugar oxidized. The identical values of their enthalpies of combustion (to within 0.3%) indicates that the bonding must be essentially identical in these isomers. That is, there must be the same number of

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Formula</th>
<th>( \Delta H_{\text{combustion}} ) kJ·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>fructose</td>
<td>C₆H₁₂O₆</td>
<td>−2812</td>
</tr>
<tr>
<td>galactose</td>
<td>C₆H₁₂O₆</td>
<td>−2803</td>
</tr>
<tr>
<td>glucose</td>
<td>C₆H₁₂O₆</td>
<td>−2803</td>
</tr>
</tbody>
</table>
C–C, C–H, C–O, C=O, and O–H bonds in all three molecules. This is true if you compare their open-chain forms with one another or their cyclic forms with one another (in nature, the cyclic forms vastly predominate).

**Problem 7.34.**
(a) Disaccharides are sugars formed by the combination of two simpler sugars, for example:

In this reaction a C–O bond is broken in one sugar and an O–H bond in the other. Then to make the products, a C–O bond is made between the two sugars and an O–H bond is made to produce the water (from the OH that had left a sugar). Exactly the same number and kind of bonds are broken and made. Bond enthalpy calculations (which we do not have to do, if there is no change in the kind and number of bonds) give an estimated $\Delta H_{\text{reaction}} \approx 0$ kJ for this reaction.

(b) One way to estimate the enthalpy of combustion of maltose is to break the reaction into two reactions: hydrolysis of maltose to give two glucose and then combustion of the glucose:

The sum of these two reactions is:

This is the combustion reaction for maltose; we predict $\Delta H_{\text{rxn}} = -5606$ kJ to be compared with the experimental value of $-5644$ kJ. The difference is small (only about 0.6%), but the combustion enthalpies are experimental values that are good to at least four significant figures. This means that the estimated value of 0 kJ for the formation of maltose (or the reverse, its hydrolysis) is incorrect. The actual value for the hydrolysis above must be about $-36$ kJ, in order to make the sum of the two reaction enthalpies above equal to the measured enthalpy of combustion of maltose. We know that bond enthalpies are averages that can be off by a few percent for any particular bond in a molecule, so we shouldn’t be surprised that this small discrepancy occurs. It is a warning, however, not to trust bond enthalpies when the quantity of interest is the difference between two large values — small errors in the large values can lead to large percentage discrepancies in their difference.

**Problem 7.35.**
(a) We can use average bond enthalpies to estimate the standard enthalpy change (in kJ per mole of hydrazine) for the reaction between hydrazine and hydrogen peroxide:

Let’s cancel the H–O bonds before going through all the arithmetic. Four are broken on the left and eight are made on the right, so we will include four in the products, but ignore them in the reactants. The $\Delta H_{\text{rxn}}$ for this reaction is given by:

$$\Delta H_{\text{rxn}} = -BH(\text{N≡N}) - 4BH(\text{H–O}) + 4BH(\text{H–N}) + BH(\text{N–N}) + 2BH(\text{O–O})$$
\[ \Delta H_{\text{rxn}} = -(941 \text{ kJ}) - (1840 \text{ kJ}) + (193 \text{ kJ}) + (284 \text{ kJ}) = -732 \text{ kJ} \]

(b) We can use average bond enthalpies to estimate the standard enthalpy change for the reaction between two moles of ammonia and hydrogen peroxide (in kJ per two moles of ammonia):

\[ 2\text{NH}_3(g) + 3\text{HOOH}(g) \rightarrow \text{N}_2(g) + 6\text{H}_2\text{O}(g) \]

In this case, canceling the H–O bonds leaves a net of six in the products:

\[ \Delta H_{\text{rxn}} = -6BH(\text{N} \equiv \text{N}) + 6BH(\text{H} – \text{O}) + 3BH(\text{O} – \text{O}) \]

\[ \Delta H_{\text{rxn}} = -(941 \text{ kJ}) – (2760 \text{ kJ}) + (2358 \text{ kJ}) + (426 \text{ kJ}) = -917 \text{ kJ} \]

Two moles of ammonia reacting release about 25% more enthalpy than a mole of hydrazine.

(c) A mole of hydrazine is 32.0 g of hydrazine, so the enthalpy change from hydrazine is \(-22.9 \text{ kJ} \cdot \text{g}^{-1} \left[ = \frac{(-732 \text{ kJ})}{32.0 \text{ g}} \right] \). The comparable value for ammonia is \(-26.97 \text{ kJ} \cdot \text{g}^{-1} = \frac{(-917 \text{ kJ})}{34.0 \text{ g}} \). Since more enthalpy is released by the ammonia reaction, why isn’t ammonia used, instead of hydrazine as the fuel? There are quite practical reasons for using hydrazine. Probably the most important, from an engineering point of view, is that hydrazine is a liquid at room temperature, Table 7.4, and can be easily stored and pumped around in the rocket. Ammonia, on the other hand, is a gas at room temperature and has to be refrigerated and/or kept under high pressure to store it as a liquid. This just increases the complexity of the rocket. Consider also the oxidant, hydrogen peroxide. About one-and-one-half times as much peroxide is required for the oxidation of ammonia as for an equal mass of hydrazine. Therefore, the amount of fuel and oxidant together is less for hydrazine. The same size rocket can carry a somewhat greater payload with the hydrazine fuel because less mass of fuel and oxidant are needed. Work out for yourself the enthalpy change for reaction of one gram of the stoichiometric mixture of fuel and oxidant for each fuel.

Problem 7.36.

(a) The two bonds that have to be broken in the reactants and the three that have to be made in the product, in order to react ethene and water to produce ethanol, are indicated here:

Using the data in the Web Companion, Chapter 7, Section 7.7, page 3, breaking a mole of the H–O and C=C bonds requires:

\[ \Delta H_{\text{break}} = (460 \text{ kJ}) + (620 \text{ kJ}) = 1080 \text{ kJ} \]

Making the C–H, C–O, and C–C bonds releases energy, so the enthalpy change is negative:

\[ \Delta H_{\text{make}} = -[(414 \text{ kJ}) + (351 \text{ kJ}) + (347 \text{ kJ})] = -1112 \text{ kJ} \]

The net change in enthalpy is the sum of these two values

\[ \Delta H_{\text{net}} = 1080 + (-1112) = -32 \text{ kJ} \]
(b) In the *Web Companion*, you find that breaking all the bonds in the reactants requires 3196 kJ (per mole of reaction) and making all bonds in the product releases –3228 (per mole of reaction). The net change for the reaction is –32 kJ. The results for the two methods are identical.

(c) Finding that the results of the two methods are identical is expected. When all the bonds in the reactants are broken (atomizing the molecules), we are breaking several kinds of bonds, several C–H bonds, for example, that will simply be remade in the product. Our assumption in using average bond enthalpies is that the bond enthalpy for a given kind of bond is the same in all molecules. Thus when the bonds are remade in the product, exactly the same amount of enthalpy is released as was required to break the bonds in the first place -- the breaking and making simply cancel out. The only bond breaking and making that contribute to a net difference for the reaction are those that are different in the reactants and product, which is what we focused on in part (a). You can see this argument graphically in the *Web Companion*, Chapter 7, Section 7.7, page 3, if you first break the two bonds selected in the *Companion*, Chapter 7, Section 7.7, page 2, and then break all the others to atomize the reactants. Now when you make the product bonds, first make all those that are the same in the product as in the reactants and then, finally, make the three new bonds. Compare the lengths of the bars on the graph for the breaking and making the same set of bonds.

**Problem 7.37.**

Carbon–hydrogen bond-dissociation enthalpies are shown here for two different hydrogen atoms in the reactions of propene and 2-butene:

\[
\begin{align*}
\text{dissociation enthalpy} & \quad \text{kJ mol}^{-1} \\
(1) \quad & \text{H} - \text{C} = \text{C} - \text{H} + \text{H} \quad 361 \\
(2) \quad & \text{H} - \text{C} = \text{C} - \text{H} + \text{H} \quad 430 \\
(3) \quad & \text{H} - \text{C} = \text{C} - \text{H} + \text{H} \quad 358 \\
(4) \quad & \text{H} - \text{C} = \text{C} - \text{H} + \text{H} \quad 430
\end{align*}
\]

(a) This enthalpy level diagram represents the enthalpies of the reactant and the products from reactions (1) and (2). It takes less enthalpy to produce the products from reaction (1). Thus, the free radicals formed in reaction (1) are more stable by 69 kJ·mol\(^{-1}\) than those formed in reaction (2). A similar diagram can be drawn for the reactant and products from reactions (3) and (4) to show that the products from reaction (3) are 72 kJ·mol\(^{-1}\) more stable than those from reaction (4).
(b) The “equivalent” Lewis structures for the three- and four-carbon free radicals formed in reactions (1) and (3) are:

The structures for the three-carbon radical are identical in energy, so we know from our discussion in Chapter 5, Section 5.7, that the electrons involved are delocalized and of lower energy than they would be if the two pi electrons and single free-radical electron did not interact. The two four-carbon structures are not quite identical, but the sigma bonding to the carbon atoms with the free radical electron is very similar in the two structures (the bonding is to two hydrogen atoms in the first and to a hydrogen atom and carbon atom in the second structure), so we can treat the structures as almost energy-equivalent and again see that there is electron delocalization to lower the energy of this free radical, compared to the one with the free-radical electron on the doubly-bonded carbon.

Problem 7.38.
The rhombic allotrope of sulfur, the familiar light yellow powder, is the more stable allotrope at room temperature. At higher temperatures, near the melting point, the triclinic allotrope must be more stable, since it is the form that crystallizes from the molten sulfur. Upon standing at room temperature, the rhombic allotrope forms slowly on the surface of the triclinic needles, which indicates a slow transformation to the more stable form. If we wait long enough, all the needles change back to the light yellow powder.

Problem 7.39.
We can use standard enthalpies of formation to find the enthalpy for the reaction producing urea from ammonia and carbon dioxide:

\[
2\text{NH}_3(g) + \text{CO}_2(g) \rightarrow \text{H}_2\text{NC(O)NH}_2(s) + \text{H}_2\text{O}(l)
\]

The standard enthalpies of formation for ammonia, carbon dioxide, urea, and water are \(-46.1\), \(-393.5\), \(-333.0\), and \(-285.8\) kJ·mol\(^{-1}\), respectively. The standard enthalpy change for the reaction is (where the stoichiometric coefficients – units of mol – are not shown, if they are unity):

\[
\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{f}}(\text{H}_2\text{O}(l)) + \Delta H^\circ_{\text{f}}(\text{H}_2\text{NC(O)NH}_2(s)) - 2\Delta H^\circ_{\text{f}}(\text{NH}_3(g)) - \Delta H^\circ_{\text{f}}(\text{CO}_2(g))
\]

\[
\Delta H^\circ_{\text{rxn}} = (-285.8 \text{ kJ}) + (-333.0 \text{ kJ}) - (-92.2 \text{ kJ}) - (-393.5 \text{ kJ}) = -133.1 \text{ kJ}
\]
Problem 7.40.

[NOTE: The problem is misstated when it asks for the enthalpy of vaporization (change from liquid to gas) of urea. We can get the enthalpy of sublimation (change from solid to gas) but have no way to estimate the enthalpy change from liquid to gas, because we have no way to estimate the enthalpy change from solid to liquid.]

To estimate the enthalpy of sublimation of urea, we recall that bond enthalpy values are applicable to gas phase molecules. We could use bond enthalpies to calculate the enthalpy change for the reaction in Problem 7.39 with the urea and water as gases and compare the result with the enthalpy change calculated in the solution for Problem 7.39 with the urea as a solid and water as a liquid. The difference is an estimate of the enthalpy of sublimation of urea plus the enthalpy of vaporization of water. For the gas phase reaction we have:

\[ \Delta H_{\text{rxn}} = \Sigma BH_{\text{reactants}} + \Sigma(-BH_{\text{products}}) \]

\[ \Delta H_{\text{rxn}} = \{6BH(H-N) + 2BH(C=O in CO_2)\} \]
\[ + \{2[-BH(H-O)] + 4[-BH(H-N)] + 2[-BH(C-N)] + [-BH(C=O)]\} \]

\[ \Delta H_{\text{rxn}} = \{(2358 \text{ kJ}) + (1598 \text{ kJ})\} + \{(-920 \text{ kJ}) + (-1572 \text{ kJ}) + (-552 \text{ kJ}) + (-745 \text{ kJ})\} \]

\[ \Delta H_{\text{rxn}} = \{3956 \text{ kJ}\} + \{-3789 \text{ kJ}\} = 167 \text{ kJ} \]

These changes are represented on this enthalpy diagram sketch (not to scale):

![Enthalpy Diagram](image)

Enthalpy is required to make gaseous urea and water from ammonia and carbon dioxide. The enthalpy change going from solid urea and liquid water to the gases is 300 kJ [= (133 kg) + (167 kJ)]. The enthalpy of vaporization of water is 44 kJ·mol⁻¹, so the condensation of water releases enthalpy, –44 kJ. This leaves 256 kJ as the enthalpy required to change solid urea to gaseous urea. Our estimate for the enthalpy of sublimation of urea is about 256 kJ·mol⁻¹.

Problem 7.41.

(a) The fermentation of glucose to ethanol and carbon dioxide is represented by this reaction:

\[ C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g) \]
From Appendix B, the standard enthalpies of formation of glucose, ethanol, and carbon
dioxides are $-1274.4$ kJ·mol$^{-1}$, $-277.69$ kJ·mol$^{-1}$, and $-393.51$ kJ·mol$^{-1}$, respectively. The
standard enthalpy change for the fermentation reaction is:

$$
\Delta H_{\text{reaction}} = \Sigma n_p \Delta H^0_f(\text{products}) - \Sigma n_r \Delta H^0_f(\text{reactants})
$$

$$
\Delta H^o_{\text{reaction}} = 2(-277.69 \text{ kJ}) + 2(-393.51 \text{ kJ}) - (-1274.4 \text{ kJ}) = -68.0 \text{ kJ}
$$

(Stoichiometric coefficients represent numbers of moles of bonds broken for each mole of
reaction. To make the expression easier to read, we have cancelled the stoichiometric moles
with the per mole units of the bond enthalpies.)

(b) Since $\Delta H^o_{\text{reaction}}$ is negative (enthalpy is released), the fermentation reaction is exothermic.

(c) If a reaction is exothermic, the reactant (glucose) has higher enthalpy than the products
(ethanol and carbon dioxide).

(d) The standard enthalpy change we calculated for the reaction is the change for the reaction as
represented by the equation in part (a), where all quantities are molar quantities. That is, 68.0 kJ
are released when one mole of glucose gives two moles of ethanol (and two moles of carbon
dioxide). If fewer than two moles of ethanol are produced, this means that less than one mole of
glucose has reacted. We calculate the standard enthalpy change for the reaction producing 5.0 g
of ethanol ($\text{EtOH} = \text{C}_2\text{H}_5\text{OH}$), $\Delta H^o$, like this:

$$
5.0 \text{ g EtOH} = (5.0 \text{ g EtOH}) \frac{1 \text{ mol EtOH}}{46.0 \text{ g}} \left( \frac{-68.0 \text{ kJ}}{2 \text{ mol EtOH}} \right) = -3.7 \text{ kJ}
$$

(e) The quantity of heat released when 95.0 g of $\text{C}_2\text{H}_5\text{OH}(l)$ is formed at constant pressure is $q_P$,
which is equal to $\Delta H^p$ for the reaction at one atmosphere pressure:

$$
95.0 \text{ g EtOH} = (95.0 \text{ g EtOH}) \frac{1 \text{ mol EtOH}}{46.0 \text{ g}} \left( \frac{-68.0 \text{ kJ}}{2 \text{ mol EtOH}} \right) = -70.2 \text{ kJ}
$$

Problem 7.42.

(a) The gas phase reaction of methanoic (formic) acid with ammonia produces formamide
(which contains a peptide bond) and water:

$$
\text{H}_2\text{C}^\text{O} + \text{N}^-\text{H}_\text{H} \rightarrow \text{H}^-\text{C}^\text{O} + \text{H}^-\text{N}^-\text{H} + \text{H}^-\text{O}^-\text{H}
$$

In this reaction, a C–O and N–H bond are broken and a C–N and O–H bond are made. We can
use average bond enthalpies to estimate the enthalpy change for the reaction:

$$
\Delta H = \sum BH_{\text{reactants}} + \sum (-BH_{\text{products}}) = (BH_{\text{C–O}} + BH_{\text{N–H}}) + [(-BH_{\text{C–N}}) + (-BH_{\text{O–H}})]
$$

$$
= (740 \text{ kJ} + 736 \text{ kJ}) + (740 \text{ kJ} + 736 \text{ kJ}) = 740 \text{ kJ} + 736 \text{ kJ} = 4 \text{ kJ}
$$

(Stoichiometric coefficients, all 1 mol in this case, represent numbers of moles of bonds broken
for each mole of reaction. To make the expression easier to read, we have cancelled the
stoichiometric moles with the per mole units of the bond enthalpies.) This value and one we
calculated for peptide bond formation in Problem 7.30 for a different reaction are identical,
+4 kJ. This is not surprising, because the equation used to get the enthalpies of reaction is
identical in the two cases. The equation is the same, because the reaction is the same in terms of bonds broken and made in forming the peptide bond from a carboxylic acid and an amine.

(b) We can also use standard enthalpies of formation to calculate the change in enthalpy for this reaction, assuming reactants and products are gases in their standard states. The enthalpies of formation of gaseous methanoic acid and formamide are $-379$ and $-186 \text{ kJ mol}^{-1}$, respectively.

\[
\Delta H_{\text{reaction}} = \Sigma n_p \Delta H_f^o (\text{products}) - \Sigma n_r \Delta H_f^o (\text{reactants})
\]

\[
\Delta H_{\text{reaction}} = \Delta H_f^o [\text{HC(O)NH}_2] + \Delta H_f^o [\text{H}_2\text{O}] - \Delta H_f^o [\text{HC(O)OH}] - \Delta H_f^o [\text{NH}_3]
\]

\[
\Delta H_{\text{reaction}} = (-186 \text{ kJ}) + (-242 \text{ kJ}) - (-379 \text{ kJ}) - (-46 \text{ kJ}) = -k
\]

(Stoichiometric coefficients, all 1 mol in this case, represent numbers of moles of reactants and products for each mole of reaction. To make the expression easier to read, we have cancelled the stoichiometric moles with the per mole units of the enthalpies of formation.)

(c) We used average bond enthalpies for the calculation in part (a) and standard enthalpies of formation in part (b) and both give values close to zero kilojoules for the formation of one mole of peptide bonds. This excellent agreement is probably somewhat fortuitous, since average bond enthalpies are not likely to be exactly correct for the bonds in any particular molecule. Although the bond enthalpy calculation predicts a slightly endothermic reaction and the enthalpy of formation gives a slightly exothermic reaction, this is not a major discrepancy when the values are so close to zero and we know that bond enthalpy calculations are almost certain to be off a bit from the experimental value obtained from enthalpy of formation data.

Problem 7.43.

(a) The equation for the combustion of ammonia and its standard enthalpy change are:

\[
4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g) \quad \Delta H^o_{\text{reaction}} = -905 \text{ kJ}
\]

We can use the standard enthalpies of formation for NO(g) and H₂O(g) and the standard enthalpy change for the reaction to calculate the standard enthalpy of formation for NH₃(g).

\[
\Delta H^o_{\text{reaction}} = \Sigma n_p \Delta H_f^o (\text{products}) - \Sigma n_r \Delta H_f^o (\text{reactants})
\]

\[
-905 \text{ kJ} = [4(90.25 \text{ kJ}) + 6(-241.82 \text{ kJ})] - [4(\Delta H_f^o (\text{NH}_3)) + 5(0 \text{ kJ})]
\]

\[
\Delta H_f^o (\text{NH}_3) = -46 \text{ kJ mol}^{-1}
\]

(Stoichiometric coefficients represent numbers of moles of reactants and products for each mole of reaction. To make the expression easier to read, we have cancelled the stoichiometric moles with the per mole units of the enthalpies of formation.)

(b) The value for $\Delta H_f^o (\text{NH}_3)$ from Appendix B in the textbook is $-46.11 \text{ kJ mol}^{-1}$. This is excellent agreement with the result from part (a) and points up the fact that the table values are often determined by means of values for combustion reactions, which are relatively straightforward to run.

Problem 7.44.

Three reactions that can take place in the process of coal gasification are:

Reaction 1: C(s) + H₂O(g) $\rightarrow$ H₂(g) + CO(g)

Reaction 2: C(s) + 1/2O₂(g) $\rightarrow$ CO(g)
Chemical Energetics: Enthalpy

Chapter 7

Reaction 3: \( \text{C}(s) + 2\text{H}_2\text{O}(g) \rightarrow \text{CH}_4(g) + \text{O}_2(g) \)

The enthalpy of reaction for each of these three reactions is:

Reaction 1:
\[
\Delta H_{\text{rxn}}^o = \Delta H_{\text{f}}^o(\text{H}_2) + \Delta H_{\text{f}}^o(\text{CO}) - \Delta H_{\text{f}}^o(\text{C}) - \Delta H_{\text{f}}^o(\text{H}_2\text{O})
\]
\[
\Delta H_{\text{rxn}}^o = (0 \text{ kJ}) + (-110.53 \text{ kJ}) - (0 \text{ kJ}) - (-241.82 \text{ kJ})
\]
\[
\Delta H_{\text{rxn}}^o = +131.29 \text{ kJ}
\]

Reaction 2:
\[
\Delta H_{\text{rxn}}^o = \Delta H_{\text{f}}^o(\text{CO}) - \Delta H_{\text{f}}^o(\text{C}) - 1/2 \Delta H_{\text{f}}^o(\text{O}_2)
\]
\[
\Delta H_{\text{rxn}}^o = (-110.53 \text{ kJ}) - (0 \text{ kJ}) - (0 \text{ kJ}) = -110.53 \text{ kJ}
\]

Reaction 3:
\[
\Delta H_{\text{rxn}}^o = \Delta H_{\text{f}}^o(\text{CH}_4) + \Delta H_{\text{f}}^o(\text{O}_2) - \Delta H_{\text{f}}^o(\text{C}) - 2\Delta H_{\text{f}}^o(\text{H}_2\text{O})
\]
\[
\Delta H_{\text{rxn}}^o = (-74.81 \text{ kJ}) + (0 \text{ kJ}) - (0 \text{ kJ}) - 2(-241.82 \text{ kJ})
\]
\[
\Delta H_{\text{rxn}}^o = +408.83 \text{ kJ}
\]

The most (only) exothermic reaction is Reaction 2 and the most endothermic is Reaction 3. Thus, Reaction 2 is the most energetically favorable and Reaction 3 is the least. This does not imply that chemists should work to control the reaction conditions to maximize Reaction 2. The main goal of coal gasification is to produce fuels and starting materials for synthesis. CO and H\(_2\) are the most desirable products, because they can be used as starting materials for several syntheses as well as being a good fuel mixture (called water gas).

Problem 7.45.
In a coupled reaction, the reaction providing the energy does not proceed unless the reaction requiring the energy occurs. For example, the exothermic oxidation of glucose is coupled with the endothermic formation of adenosine triphosphate, ATP\(^{4-}\), from adenosine diphosphate, ADP\(^{3-}\). The reverse reaction, the hydrolysis of ATP\(^{4-}\) to ADP\(^{3-}\) is exothermic and is coupled to other energy-requiring biological functions such as locomotion, information processing, and synthesizing new biological molecules.

Problem 7.46.
The principal role of ATP is to act as an energy carrier from reactions that produce energy, such as the oxidation of glucose, to reactions that require energy, such as the synthesis of proteins, movement of muscles, and transport of molecules and ions in and out of cells. ATP is not a storage molecule for energy because there is only a small amount of it in a cell that rapidly cycles between energy producing and energy requiring processes. One analogy that is often used is that ATP is like the money in your wallet or purse. The storage place for your money is the savings account in your bank (this money is like fuel molecules in your body), but you can’t purchase anything with that money, because it resides in the bank. If you take some of the money out of the bank and have it in your wallet or purse, you can spend it for things you need or want (just as you synthesize new molecules or move about using the energy from ATP hydrolysis). When the money you carry is used up, you can return to the bank for more. (All of
this assumes that you have a savings account with a reasonable amount of money, just as you must have fuel—from your food—in order to continue to produce ATP to sustain yourself.)

**Problem 7.47.**
(a) Waste heat from power plants is generally carried in the form of steam that has passed through the turbines that run the generators to produce electricity. To capture energy from this steam to evaporate seawater (to desalt it), requires that the power plant be sited on the seacoast. To be useful in producing a lot of water, this has to be a large power plant, which could be a limitation, if such a large power facility is not needed. Although the steam could be used directly to heat seawater in a distillation apparatus, such a single stage process is not very efficient and is difficult to make into a continuous process. At present, most of the coupled power/desalting facilities use a continuous multistage flash evaporation technology in which the brine is evaporated at reduced pressure in a series of stages. The waste heat from power plants is often used for heating buildings in cold and temperate climates and is not available for desalting. The largest power/desalting facilities are in the warm countries of the Middle East where the steam would be wasted, if not used for desalting. Systems that couple power generation with desalting are 10-20% more energy efficient than those that carry out the processes separately (that is, use some of the power generated to run a desalting process). A schematic diagram of a multistage flash evaporation system is shown here.

![Diagram of a multistage flash evaporation system](http://www.twdb.state.tx.us/Desalination/The%20Future%20of%20Desalination%20in%20Texas/documents/C4.pdf)

(b) Examples of other energetically coupled processes will vary depending on the background of the students. They may present examples from engineering, other biological applications, or from ecology courses. [Note that this question could be assigned as a web-based research question.]

**Problem 7.48.**
The function of Mg$^{2+}$ in many ATP$^4$-coupled reactions is to complex with the negatively charged ATP ions. (Complexation of cations by Lewis bases was the subject of Chapter 6,
Section 6.6.) The complex has a three dimensional structure that fits appropriately in the folds of the enzymes that catalyze these reactions, whereas, the free ATP\(^+\) does not.

**Problem 7.49.**

(a) The equation for the uncoupled oxidation of pyruvic acid is:

\[
2\text{C}_3\text{H}_4\text{O}_3(l) + 5\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \quad \Delta H^\circ_{\text{pyruv oxid}} = -2332 \text{ kJ}
\]

\(\Delta H^\circ_{\text{pyruv oxid}}\) has been calculated from the standard heats of formation:

\[
\Delta H^\circ_{\text{pyruv oxid}} = [6(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ})] - [2(-585.8 \text{ kJ})] = -2332 \text{ kJ}
\]

(Stoichiometric coefficients represent numbers of moles of reactants and products for each mole of reaction. To make the expression easier to read, we have cancelled the stoichiometric moles with the per mole units of the enthalpies of formation.)

(b) Recall that \(\Delta H^\circ_{\text{reaction}} = 21 \text{ kJ\cdotmol}^{-1}\) for the formation of one ATP\(^+\) from ADP\(^-\) and HOPO\(_3^2\)\(^-\) . Therefore, the energy required to form 30 ATP\(^+\) will be 30 times as great.

\[
30\text{ADP}^3^-(aq) + 30\text{HOPO}^2^-_3(aq) + 30\text{H}^+_3\text{O}^+(aq) \rightarrow 60\text{H}_2\text{O}(l) + 30\text{ATP}^4^-(aq)
\]

\(\Delta H^\circ_{\text{reaction}} = (30 \text{ mol})(21 \text{ kJ\cdotmol}^{-1}) = 630 \text{ kJ}\)

For the reaction of pyruvic acid oxidation coupled to ATP\(^+\) formation, we have:

\(\Delta H^\circ_{\text{coupled reaction}} = (-2332 \text{ kJ}) + 630 \text{ kJ} = -1703 \text{ kJ}\).

The efficiency (percent) energy recovered in the form of ATP\(^+\) is:

\[
\% \text{ efficiency} = \left( \frac{630 \text{ kJ}}{2332 \text{ kJ}} \right) 100\% = 27\%
\]

If the metabolic reactions actually occurred with all species in their standard states, only 630 kJ of the 2332 kJ released in the oxidation would be captured in the production of ATP\(^+\). The remaining 1703 kJ would be lost as heat.

**Problem 7.50.**

You should, by all means, invest in an inventor who claims to have built a device that is able to do about 0.8 kJ of work for every 1 kJ of thermal energy put into it (after you have seen proof that his device can actually do what he says). This device is about 80\% efficient in converting random thermal motion to the directed motion of work. This is a good deal better than the best engines now available. There is no violation of the first law here, since he is not getting out more than he puts in. The “lost” energy presumably remains in the device in some form or is expelled as thermal energy to some other part of the surroundings. The inventors you have to look out for are those who claim to get more work out of a thermal engine than the thermal energy they put in; that is a violation of the first law.

**Problem 7.51.**

The work on a gas, \(w\), associated with change in volume of a gas at constant pressure is – \(P_{\text{ext}}\Delta V\). For a change from 10. L to 1.0 L at a constant pressure of 5.0 atmospheres the work is:

\[
w = -P_{\text{ext}}\Delta V = -(5 \text{ atm}) \cdot (1.0 \text{ L} - 10.0 \text{ L}) = 45 \text{ L} \cdot \text{atm}
\]

\[
45 \text{ L} \cdot \text{atm} = (45 \text{ L} \cdot \text{atm}) \left( \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = 4.6 \times 10^3 \text{ J} = 4.6 \text{ kJ}
\]
Work is being done on the gas, as the volume is decreasing from 10.0 L to 1.0 L. A positive sign for \( w \) is associated with work done on the system.

**Problem 7.52.**
The value of \( q_p \), the thermal (heat) energy required to cause the volume of a hot-air balloon to change from \( 5.0 \times 10^6 \) L to \( 5.5 \times 10^6 \) L at a constant pressure of 1.0 atm, is given in the problem statement: \( 1.5 \times 10^8 \) J. This is the thermal energy added to the system at constant pressure. The pressure-volume work done in this process is:

\[
w = -P_{\text{ext}} \Delta V = -(1.0 \text{ atm})[(5.5 \times 10^6 \text{ L}) - (5.0 \times 10^6 \text{ L})] \left( \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = -5 \times 10^7 \text{ J}
\]

The negative sign for the work makes sense, because the gas is expanding and doing work on the surroundings (pushing back the atmospheric gases), so work is leaving the system. The change in internal energy, \( \Delta E \), for this process is:

\[
\Delta E = q_P + w = q_P + (-P_{\text{ext}} \Delta V)
\]
\[
\Delta E = (1.5 \times 10^8 \text{ J}) - (5 \times 10^7 \text{ J}) = 1.0 \times 10^8 \text{ J}
\]

**Problem 7.53.**
The chemical energy of reaction of the metal with oxygen in a photographic flash bulb is transformed to light energy and heat energy in the course of the reaction. As long as the bulb does not explode, this is a constant volume reaction. This means no pressure-volume work is done on or by the gas, so \( w = 0 \). Thus, \( \Delta E = q_V + w = q_V \), where the subscript reminds us that the reaction is carried out at constant volume.

**Problem 7.54.**
Assume that the gaseous chemical reaction in which the system loses heat and contracts takes place at constant pressure (because we have been given no way to analyze a reaction in which the pressure changes). Since \( \Delta H = q_p \) and \( q_p \) is negative (heat leaves the system), we know that \( \Delta H \) is negative for this process. We also know that \( \Delta H = \Delta E + P \Delta V \). The system contracts so \( V_{\text{final}} < V_{\text{initial}} \) and \( \Delta V = V_{\text{final}} - V_{\text{initial}} \) is negative. This means that \( P \Delta V \) will be negative, because \( P \) is always a positive value. \( \Delta E \) may be either positive or negative depending on the magnitude of \( \Delta H \) and \( P \Delta V \). In summary: \( P \Delta V \) is “-”; \( \Delta H \) is “-”; and, \( \Delta E \) may be “+” or “-”, depending on the relative magnitudes of \( \Delta H \) and \( P \Delta V \).

**Problem 7.55.**
(a) The pressure-volume work performed on the gas in the syringe in Experiment A is less than that performed in Experiment B. Given that the cross-sectional area is the same for both syringes and the pressure is the same in both experiments, the pressure-volume work is directly proportional to the value of \( \Delta x \), which is smaller for Experiment A. The mathematical relationship is:

\[
w = -P_{\text{ext}} \times A \times \Delta x
\]

The sign of the work is positive, because \( \Delta x \) is negative, which is correct for work done on the system.

(b) Although \( \Delta x \) is the same for both Experiment A and the third experiment with a wider bore syringe, \( \Delta V \) is not the same because the cross-sectional area of the syringe is greater in the third
experiment. Because pressure-volume work is a product of the pressure, which is the same in both experiments, and the change in volume, the work done in the third experiment is greater than that done in Experiment A.

Problem 7.56.
Assume that this reaction occurs at constant temperature and pressure:

\[ 3\text{H}_2(g) + \text{N}_2(g) \rightarrow 2\text{NH}_3(g) \]

To analyze the changes taking place, we note that 3 volumes of H\(_2\)(g) react with 1 volume of \(\text{N}_2\)(g) to produce 2 volumes of \(\text{NH}_3\)(g). Thus, \(\Delta V = -2\) volumes \([= (2\text{ volumes}) - (4\text{ volumes})]\) and work, \(w = -P_{\text{ext}}\Delta V\), is greater than zero, indicating that work must be done on (enter) the system during this change.

Problem 7.57.
(a) A driver’s side airbag might typically contain about 95 g of sodium azide that reacts to produce the nitrogen used to inflate the airbag:

\[ 2[\text{Na}^+][\text{N}_3^-](s) \rightarrow 2\text{Na}(g) + 3\text{N}_2(g) \]

This stoichiometric equation shows that 3 moles of nitrogen gas are produced for every two moles of the azide that react. The azide has a molar mass of 65 g. Therefore:

\[ 95\text{ g azide} = (95\text{ g azide}) \left( \frac{1 \text{ mol azide}}{65 \text{ g}} \right) \left( \frac{3 \text{ mol N}_2}{2 \text{ mol azide}} \right) = 2.2 \text{ mol N}_2 \text{ produced} \]

If a mole of nitrogen gas occupies about 25 L at 25 °C, the volume occupied by 2.2 mol N\(_2\) is 55 L \([= (2.2 \text{ mol})(25 \text{ L·mol}^{-1})]\) so the airbag is about 55 L in volume, which is approximately 2 cubic feet (or you can imagine about 25 empty, two-liter soft drink bottles suddenly appearing in front of you when the airbag deploys).

(b) The external pressure against which the airbag pushes to inflate is atmospheric pressure, \(P_{\text{atm}} = 1.01 \times 10^5\) Pa (N·m\(^{-2}\)). The volume change, \(\Delta V\), of the gas is 55 \(\times\) 10\(^{-3}\) m\(^3\) (since we go from no gas to a final volume of 55 L and a liter is 10\(^{-3}\) m\(^3\) = a cubic decimeter). Thus, \(w\), the work done on the gas is:

\[ w = -P_{\text{atm}}\Delta V = -(1.01 \times 10^5 \text{ N·m}^{-2}) \cdot (55 \times 10^{-3} \text{ m}^3) = -5.6 \text{ kJ} \]

The work done on the gas is negative, because the gas actually does work on its surroundings (that is, work leaves the system) pushing back the atmospheric gases.

(c) We know that \(\Delta H = \Delta E + P_{\text{ext}}\Delta V\) and that the pressure-volume product is a positive 5.6 kJ. Therefore, the measured thermal energy release at constant volume, \(q_V = \Delta E\), will be smaller by 5.6 kJ than that measured at constant pressure, \(q_P = \Delta H\).

Problem 7.58.
We are asked to calculate the amount of work that was done and the standard change in internal energy, \(\Delta E^\circ\), when 0.5 mol of H\(_2\)(g) was reacted with 0.3 mol of O\(_2\)(g), at a constant pressure of 1.0 atm, with a change in volume of –6.1 liters. The stoichiometry and standard enthalpy change for the reaction are:

\[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) \quad \Delta H^\circ = -484 \text{ kJ} \]
Since $\Delta E^\circ = \Delta H^\circ - P_{ext}\Delta V$, we will first need to calculate both $\Delta H^\circ$ and $P_{ext}\Delta V$ (for the amount of reaction that actually occurs) to obtain the value for $\Delta E^\circ$. The initial amounts of $\text{H}_2(g)$ and $\text{O}_2(g)$ are not in the 2:1 molar ratio of the balanced equation. $\text{H}_2(g)$ is the limiting reagent and is consumed completely while 0.05 mol of $\text{O}_2(g)$ remains unreacted. The enthalpy value given with the reaction equation is for the reaction of two moles of $\text{H}_2(g)$ with one mole of $\text{O}_2(g)$. $\Delta H^\circ$ for the reaction of 0.5 mol of $\text{H}_2(g)$ is:

$$\Delta H^\circ \ [\text{for} \ 0.5 \ \text{mol} \ \text{H}_2(g)] = \left[0.5 \ \text{mol} \ \text{H}_2(g)\right] \left(-484 \ \text{kJ} \ \frac{2 \ \text{mol} \ \text{H}_2(g)}{}\right) = -121 \ \text{kJ}$$

The work, $w$, done on the gas is

$$w = -P_{ext}\Delta V = -(1.0 \ \text{atm})(-6.1 \ \text{L})\left(\frac{101 \ \text{J}}{1 \ \text{L} \cdot \text{atm}}\right) = 6.2 \times 10^2 \ \text{J} = 0.62 \ \text{kJ}$$

The work is positive, so work is done on the system, which is consistent with the observation that the volume of the system decreased (because the number of moles of gas decreased from 0.8 mol to 0.55 mol). Finally, we have the change in internal energy:

$$\Delta E^\circ = \Delta H^\circ - P_{ext}\Delta V = -121 \ \text{kJ} + 0.62 \ \text{kJ} = -120 \ \text{kJ}$$

Problem 7.59.

(a) Consider a 10 mL sample of pure water at 25 °C and 1 atm pressure (state A). The sample is cooled to 1 °C and then the pressure is reduced to 0.5 atm (state B). It takes 5 hours to carry out the change from state A to state B. The sample is then heated and the pressure is raised to 1 atm. In one minute the water is back at 25 °C (the sample is back at state A). The internal energy change in going from state A to B is equal to, but opposite in sign to the internal energy change going from state B to A. This statement is true. Internal energy is a state function. The difference in the internal energies of two states is independent of the path taken between the states.

(b) The work done in changing from state A to B and the work done in changing from state B to A in part (a) are numerically the same but opposite in sign. This statement is false. Work depends on the path, that is, the method of going from one state to another. In this case the volume changes are the same (but opposite in sign) going from A to B and from B to A. If each change is carried out at constant external pressure the path from A to B is at 0.5 atm and the path from B to A is at 1 atm, The pressures are not the same, so the numerical values of the work cannot be the same.

(c) The enthalpy change for a change of state of a system is independent of the exact state of the reactants or products. This statement is false. The enthalpy change for a change of state depends on the exact state of the reactants or products.

(d) At constant pressure the amount of heat absorbed or evolved by a system is called the enthalpy change, $\Delta H$. This statement is true. The heat absorbed or evolved by a system in a constant pressure change is equal to the enthalpy change for the process: $\Delta H = q_P$.

(e) If volume does not change, the amount of heat released during a change of state of a system is equal to the decrease in internal energy of that system. This statement is true. The heat released by a system in a constant volume change is equal to the internal energy change for the process: $\Delta E = q_V$. 
(f) If a reaction is spontaneous, it is always exothermic. This statement is false. Endothermic reactions which are spontaneous include freezing water at temperatures below 0 °C and dissolving many salts (for example NH₄NO₃).

(g) If the enthalpy change for this reaction, N₂(g) + O₂(g) →2NO(g), is 180.5 kJ, then the enthalpy change for this reaction, 1/2N₂(g) + 1/2O₂(g) →NO(g), is 90.2 kJ. This statement is true. The enthalpy change for a reaction is directly proportional to the number of moles of reaction that occur.

Problem 7.60.
(a) The NH₄Cl solution is cool to touch, because NH₄Cl(s) dissolution is endothermic, ΔH = 14.8 kJ·mol⁻¹. Heat is transferred from the surroundings (including the solution, the beaker, and your hand) to the reaction. The CaCl₂ solution is warm to touch, because CaCl₂(s) dissolution is exothermic, ΔH = –82.9 kJ·mol⁻¹. Heat is transferred from the reaction to the surroundings (including the solution, the beaker, and your hand).

(b) In order to maintain the temperature of the beaker of solution as dissolution occurs, we have to add 15.1 kJ of heat per mole of NH₄Cl(s) that dissolves. For the CaCl₂ solution, we have to remove 82.9 kJ of heat per mole of CaCl₂(s) that dissolves.

(c) To determine ΔH° for dissolution of salts in water, the concentration of the dissolved salt must be considered. The above values for the enthalpy changes are obtained by measuring enthalpy changes for different final concentrations and extrapolating to the limit of infinite dilution.

Problem 7.61.
[NOTE: Data for ΔH°ᵢ of NH₄Cl(s), –314.43 kJ·mol⁻¹, and of CaCl₂(s), –795.8 kJ·mol⁻¹, from Appendix B are required for the is problem, as well as the data from Problem 7.60. The ΔH°ᵢ for Cl⁻(aq) given in this problem statement is slightly different than the value in Appendix B. We will use the value in the problem statement for the calculations here.]

We can represent the dissolution reaction for NH₄Cl(s) as:

\[ \text{NH}_4\text{Cl(s)} \rightarrow \text{NH}_4^+(aq) + \text{Cl}^-\text{(aq)} \]

Using ΔH°ᵢ[\text{NH}_4\text{Cl(s)}] = –314.43 kJ·mol⁻¹, from Appendix B, the enthalpy of dissolution from Problem 7.60, and ΔH°ᵢ for Cl⁻(aq) = –167.4 kJ·mol⁻¹, from this problem statement, we can find ΔH°ᵢ[\text{NH}_4^+(aq)]:

\[
\Delta H^\circ_{\text{dissolution}} = \{\Delta H^\circ_i[\text{NH}_4^+(aq)] + \Delta H^\circ_i[\text{Cl}^-(aq)]\} - \{\Delta H^\circ_i[\text{NH}_4\text{Cl(s)}]\}
\]

\[
\Delta H^\circ_i[\text{NH}_4^+(aq)] = \Delta H^\circ_{\text{dissolution}} - \Delta H^\circ_i[\text{Cl}^-(aq)] + \Delta H^\circ_i[\text{NH}_4\text{Cl(s)}]
\]

\[
\Delta H^\circ_i[\text{NH}_4^+(aq)] = (15.1 \text{ kJ·mol}^{-1}) - (-167.4 \text{ kJ·mol}^{-1}) + (-314.43 \text{ kJ·mol}^{-1})
\]

\[
\Delta H^\circ_i[\text{NH}_4^+(aq)] = -131.9 \text{ kJ·mol}^{-1}
\]

Similarly, we represent the dissolution reaction for CaCl₂(s) as:

\[ \text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq) \]

The analysis to find ΔH°ᵢ[\text{Ca}^{2+}(aq)] is just like that for ΔH°ᵢ[\text{NH}_4^+(aq)], except that we have to account for the two moles of Cl⁻(aq) produced in this dissolution:

\[
\Delta H^\circ_{\text{dissolution}} = \{\Delta H^\circ_i[\text{Ca}^{2+}(aq)] + 2\Delta H^\circ_i[\text{Cl}^-(aq)]\} - \{\Delta H^\circ_i[\text{CaCl}_2(s)]\}
\]
\[ \Delta H^\circ_{\text{f}[\text{Ca}^2+(aq)]} = \Delta H^\circ_{\text{dissolution}} - 2\Delta H^\circ_{\text{f}[\text{Cl}^{-}(aq)]} + \Delta H^\circ_{\text{f}[\text{CaCl}_2(s)]]} \]
\[ \Delta H^\circ_{\text{f}[\text{Ca}^2+(aq)]} = (-82.9 \text{ kJ mol}^{-1}) - 2(-167.4 \text{ kJ mol}^{-1}) + (-795.8 \text{ kJ mol}^{-1}) \]
\[ \Delta H^\circ_{\text{f}[\text{Ca}^2+(aq)]} = -543.9 \text{ kJ mol}^{-1} \]

**Problem 7.62.**
Berthelot’s suggestion that all chemical processes that proceed spontaneously are exothermic was incorrect. Endothermic processes that are spontaneous include freezing water at temperatures below 0 °C and dissolving many salts (for example NH₄NO₃).

**Problem 7.63.**
Consider two samples of gas in identical size containers.
(a) If the temperature of the two samples is the same, then the pressure of gas in each container is the same. This statement is false. Although the temperature and volume of the gas samples are the same, we have no information about the quantity of gas, that is, the number of moles of gas, in each container. The one with more moles will have the higher pressure, since \( P = \frac{nRT}{V} \) and all the quantities inside the parentheses on the right are the same for both samples. We can amend the statement in two ways: (1) If the temperature and number of moles of gas is the same, then the pressure of gas in each container is the same or (2) If the temperature of the two samples is the same, then the pressure will be higher in the container with the greater number of moles of gas.
(b) If the temperature and pressure of the two samples are the same, then the number of moles of gas in each container is the same. This statement is true, since \( n = \frac{PV}{RT} \) and all the quantities on the right are the same for both samples.
(c) If the gas in each container is the same and the temperature and number of moles of gas in each container are the same, then the number of collisions with the wall per unit time is the same in both containers. This statement is true. To see why this is so, we note that the pressure of the gas in each container is the same, since \( P = \frac{nRT}{V} \) and all the quantities on the right are the same for both samples. Pressure is a result of collisions of the gas molecules with the walls. Since the gas molecules and the pressure are the same in each container, the number of collisions per unit time must be the same in each container.

**Problem 7.64.**
(a) The rubber balloon filled with helium decreased in size and buoyancy overnight because the helium atoms inside were able to escape (slowly) through tiny holes in the stretched rubber. After enough helium had escaped, the mass of the rubber balloon plus the remaining helium was greater than the mass of air displaced by the now smaller balloon and the balloon no longer floated. This is a density phenomenon. When there is a lot of helium in a balloon, its volume is large and displaces air with a larger mass than the combined mass of the helium plus the rubber. Thus the balloon is buoyed up (and will keep going up, as you know, if you have ever let go of a helium balloon outdoors).
(b) Two identical rubber balloons, one filled with helium gas and the other with air decreased in size overnight, but not to the same size. The larger balloon contains air. Molecules of air and atoms of helium leak from the balloons through the tiny holes, but the helium atoms have lower mass, so are moving faster than the air molecules, hit the holes more often, and leak out faster. Air molecules from the outside can also leak into the balloons, but the rate is slower because the pressure inside the balloons is slightly above atmospheric pressure and the net flow of gas is generally outward.
Problem 7.65.
From the ideal gas equation we know that \( V = \frac{nRT}{P} \). If the pressure remains the same, but the volume of gas in the cylinder increases (the sort of change illustrated in Figure 7.20), the change that occurs must involve an increase in number of moles of gas, \( n_f > n_i \), at constant temperature, an increase in the temperature of the gas, \( T_f > T_i \), without a change in number of moles, or some combination of changes in the number of moles and temperature, such that the product of their final values, \( n_fT_f \), is greater than the product of their initial values, \( n_iT_i \). A reaction that produces more moles of gaseous products than were present initially, such as the reaction in Investigate This 7.72 is a possibility for increasing the number of moles. Some gas phase combustion reactions begin and end with same number moles of gas, but release a great deal of energy which increases the temperature of the products. One example is:

\[
\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(g)
\]

Problem 7.66.
We can justify the statement that “a mole of nitrogen gas occupies about 25 L at 25 °C and 1 atm pressure” by calculating the volume of an ideal gas under these conditions. The value of \( R \) in appropriate units is \( 8.21 \times 10^{-2} \) L·atm·mol\(^{-1}\)·K\(^{-1} \). With \( n = 1 \) mol, \( P = 1 \) atm, and \( T = 298 \) K, we get:

\[
V = \frac{nRT}{P} = \frac{(1 \text{ mol})(8.21 \times 10^{-2} \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})}{1 \text{ atm}} = 24.5 \text{ L} = 25 \text{ L}
\]

This calculation does not depend on the identity of the gas, so all gases that we can approximate as behaving ideally occupy about 25 L at 25 °C and 1 atm pressure. Gases well above the boiling point of their liquid at 25 °C and 1 atm pressure can be treated as ideal, so oxygen also fits this rule of thumb: molar volume is 25 L at 25 °C and 1 atm.

[NOTE: Although not as accurate as the molar volume of 22.4 L at STP, this 25-at-25 rule of thumb is quite adequate for many calculations that do not involve precise stoichiometry.]

Problem 7.67.
(a) We can use the ideal gas equation to calculate the expected pressure for a gas in fixed volume container that is heated from –3 °C (270 K) to, where its pressure is 38.3 kPa to 267 °C (540 K). At constant \( V \) and \( n \), we know that \( P/T = nR/V = \) constant. Thus, we can write:

\[
\frac{P_1}{P_2} = \frac{T_1}{T_2} = \frac{38.3 \text{ kPa}}{270 \text{ K}} = \frac{P_2}{540 \text{ K}}
\]

\[
P_2 = 76.6 \text{ kPa}
\]

We could also have observed that the absolute temperature doubled, so the pressure also should have doubled, as the calculations indicate.

(b) The measured pressure in the container at 540 K is 137.2 kPa, which is almost twice as high (actual factor is 1.79 times as high) as we would have predicted from the ideal gas equation. Evidently the number of moles of gas in the container has increased, since the volume has remained constant. The simplest explanation is that some of the gas molecules we added to the container might have dissociated to give two or more molecules for each molecule initially present. An example of such a case is the dissociation of an \( \text{N}_2\text{O}_4 \) molecule to give two \( \text{NO}_2 \) molecules (see Chapter 9, Section 9.11).
Problem 7.68.  
(a) We use the ideal gas equation to find, \( n \), the number of moles of gas in the 327-mL flask at 150 °C (423 K) and 33.2 kPa pressure:

\[
\frac{PV}{RT} = \frac{(33.2 \text{ kPa})(0.327 \text{ L})}{(8.315 \text{ L·kPa·mol}^{-1}·\text{K}^{-1})(423 \text{ K})} = 3.09 \times 10^{-3} \text{ mol}
\]

(b) Now we know that a 0.237 g sample of the hydrocarbon is \( 3.09 \times 10^{-3} \) mol, so we have:

molar mass of the compound = \( \frac{0.237 \text{ g}}{3.09 \times 10^{-3} \text{ mol}} \) = 76.8 g·mol\(^{-1}\)

We know that the ratio of carbon to hydrogen atoms in the hydrocarbon is one-to-one, so its molecular formula is \( \text{C}_z\text{H}_z \) and:

molar mass of the compound = \( z(12.0 \text{ g·mol}^{-1}) + z(1.01 \text{ g·mol}^{-1}) = z(13.0 \text{ g·mol}^{-1}) \)

We equate our two values for the molar mass and solve for \( z \) to get the molecular formula:

\[
z(13.0 \text{ g·mol}^{-1}) = 76.8 \text{ g·mol}^{-1}
\]

\[
z = 5.9 = 6
\]

The molecular formula of the hydrocarbon is \( \text{C}_6\text{H}_6 \). The most common hydrocarbon with this formula is benzene, which is a liquid at room temperature and a gas at 150 °C, so its properties are consistent with the compound in this problem.

Problem 7.69.  
(a) We use the ideal gas equation to find, \( n \), the number of moles of \( \text{CO}_2 \) gas in the 127.5-mL container at a pressure of 83.35 kPa and temperature of 295.3 K:

\[
\frac{PV}{RT} = \frac{(83.35 \text{ kPa})(0.1275 \text{ L})}{(8.315 \text{ L·kPa·mol}^{-1}·\text{K}^{-1})(295.3 \text{ K})} = 4.328 \times 10^{-3} \text{ mol}
\]

(b) The reaction equation for the decomposition of \( \text{CaCO}_3(s) \) is:

\[
\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)
\]

Thus, one mole of \( \text{CaCO}_3(s) \) yields one mole of \( \text{CO}_2(g) \), so there are \( 4.328 \times 10^{-3} \) mol of \( \text{CaCO}_3(s) \) in the original sample.

(c) To get the percentage of \( \text{CaCO}_3(s) \) in the original sample, we need the mass of \( \text{CaCO}_3(s) \) in the original sample, which we get by converting the known number of moles to mass:

mass \( \text{CaCO}_3(s) \) = \( (4.328 \times 10^{-3} \text{ mol})(100.08 \text{ g·mol}^{-1}) = 0.4331 \text{ g} \)

The percentage of the original sample that is \( \text{CaCO}_3(s) \) is:

\[
\% \text{CaCO}_3(s) = \left( \frac{0.4331 \text{ g}}{1.587 \text{ g}} \right) 100 \% = 27.29 \%
\]

Problem 7.70.  
(a) \( \Delta E^\circ \) and \( \Delta H^\circ \) are different for the fermentation process because the number of moles of gas changes during the reaction from zero to two:

\[
\text{C}_6\text{H}_{12}\text{O}_6(s) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(l) + 2\text{CO}_2(g)
\]
(b) The internal energy change, $\Delta E^\circ$, for this reaction is equal to, $q_V$, the thermal energy transferred into or out of the system if the reaction is carried out at constant volume. If the reaction is carried out at constant pressure, the change in internal energy is still the same (it is a state function), but now work is done by the system in pushing back the atmosphere. Under this condition, the system loses energy as pressure-volume work, so $\Delta E^\circ = q_P - P\Delta V = \Delta H^\circ - P\Delta V$, where $\Delta H^\circ$ is substituted for $q_P$, the amount of thermal energy transferred at constant pressure. Since $P\Delta V$ is positive for the fermentation reaction (gas is formed, so $\Delta V > 0$), the equation relating $\Delta E^\circ$ and $\Delta H^\circ$ shows that $\Delta E^\circ$ will be more negative than $\Delta H^\circ$. Using the ideal gas equation, we showed that $P\Delta V = (\Delta n)RT$, equation (7.59). Thus:

$$\Delta E^\circ = \Delta H^\circ - (\Delta n)RT$$

Since $\Delta n = 2$ mol, we have $(\Delta n)RT = (2 \text{ mol})(8.315 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K}) = 4.96 \times 10^{-3} \text{ J}$, assuming reaction at 298 K. Thus, $\Delta E^\circ$ will be more negative than $\Delta H^\circ$ by 4.96 kJ.

Problem 7.71.

(a) The balanced stoichiometric equation for the reaction of magnesium with hydronium ion is:

$$\text{Mg}(s) + 2\text{H}_3\text{O}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{H}_2(g) + 2\text{H}_2\text{O}(l)$$

If the magnesium reacts completely in this experiment, the number of moles that react is:

$$0.1372 \text{ g Mg} = (0.1372 \text{ g}) \frac{1 \text{ mol Mg}}{24.31 \text{ g}} = 5.644 \times 10^{-3} \text{ mol Mg}$$

The original acidic solution contained $5 \times 10^{-2} \text{ mol H}_3\text{O}^+ [= (0.5 \text{ M})(0.1 \text{ L})]$, which is about five times as much as needed to react with all the Mg. Assume that the specific heat of the solution is $4.184 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$, that 100.0 mL is 100.0 g, and that the heat capacity of the calorimeter is zero. Since no thermal energy leaves or enters the calorimeter, the sum of the thermal energy changes in the calorimeter is zero:

$$0 = q_P(\text{reaction}) + (100.0 \text{ g})[25.69 - 19.32) \text{ K}](4.184 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1})$$

$$q_P(\text{reaction}) = -(100.0 \text{ g})[25.69 - 19.32) \text{ K}](4.184 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}) = -2.67 \text{ kJ}$$

$$\Delta H_{\text{reaction}} = \left(\frac{-2.67 \text{ kJ}}{5.644 \times 10^{-3} \text{ mol Mg}}\right) = -473 \text{ kJ} \cdot \text{mol}^{-1}$$

(b) Since a gas is formed, we need to correct for the pressure-volume work done. One mole of gas is formed for every mole of Mg reacted, so $\Delta n = 1$ and we have:

$$\Delta E = \Delta H - \Delta nRT = (-473 \text{ kJ} \cdot \text{mol}^{-1}) - (1 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})$$

$$\Delta E = (-473 \text{ kJ} \cdot \text{mol}^{-1}) - (2.47 \text{ kJ} \cdot \text{mol}^{-1}) = -475 \text{ kJ} \cdot \text{mol}^{-1}$$

(c) You could measure $\Delta E$ directly by carrying out the reaction in a sealed container (like a bomb calorimeter) with some arrangement to drop the Mg in the acid when the container had been sealed. In theory, the precision of the data above is good enough to measure the half percent difference between $\Delta E$ and $\Delta H$. However, in order actually to get data that are accurate enough to observe this difference, you would have to take account of the actual mass of the calorimetric liquid, its true specific heat, and (probably most important) the heat capacity of the calorimeter.
Problem 7.72.
[NOTE: The illustration that accompanies this problem is modeled after one from Science 1998, 282, 1844. A similar illustration plus 4 movies of the motion of the filament (made to be fluorescent) is available at: http://www.res.titech.ac.jp/seibuku/nature/f1rotate.html. There are also other sources of such an illustration.]

(a) Recall that work is equal to force times the distance through which the force acts. In one revolution the shaft of the molecular motor illustrated in this problem moves about 1 nm = \(1 \times 10^{-9}\) m while exerting a force of about \(100 \times 10^{-12}\) N, so:

\[
\text{work in a revolution} = (100 \times 10^{-12} \text{ N})(1 \times 10^{-9} \text{ m}) = 1 \times 10^{-19} \text{ N·m (or J)}
\]

(b) Our estimate in this chapter was that the hydrolysis of ATP produces about 21 kJ·mol\(^{-1}\). Hydrolysis of one molecule of ATP would produce:

\[
21 \text{ kJ·mol}^{-1} = (21 \text{ kJ·mol}^{-1}) \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right) \left( \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molec}} \right) = 3.5 \times 10^{-20} \text{ J·molec}^{-1}
\]

Since hydrolysis of three molecules of ATP is required for each revolution of the motor, the energy provided by the ATP hydrolysis is about \((3 \text{ molec})(3.5 \times 10^{-20} \text{ J·molec}^{-1}) \approx 1 \times 10^{-19} \text{ J}.

(c) The enthalpy supplied by the ATP is essentially the same as the work done by the motor. The motor is 100% efficient in converting its energy source into work. Even if our estimates are off somewhat, this molecular motor appears to be an extremely efficient device.

Problem 7.73.
The balanced equation for the combustion of glycylglycine is:

\[
\text{C}_4\text{H}_8\text{O}_3\text{N}_2 + \frac{13}{2}\text{O}_2 \rightarrow 2\text{NO}_2 + 4\text{CO}_2 + 4\text{H}_2\text{O} \quad \Delta H^\circ_{\text{combustion}} = -1966 \text{ kJ}
\]

The balanced equation for the combustion of glycine is:

\[
\text{C}_2\text{H}_5\text{O}_2\text{N} + \frac{13}{4}\text{O}_2 \rightarrow \text{NO}_2 + 2\text{CO}_2 + \frac{5}{2}\text{H}_2\text{O} \quad \Delta H^\circ_{\text{combustion}} = -981 \text{ kJ}
\]

(Don’t worry at this stage about the somewhat strange stoichiometric coefficients required to write the equations for one mole of glycylglycine and glycine.) In order to use the combustion data to find the enthalpy change for the hydrolysis of glycylglycine to glycine, we need to combine the combustion reactions in a way that will give us the hydrolysis equation as the result of the combination. If we double the glycine combustion reaction, reverse it, and add it to the glycylglycine combustion reaction, we will get the desired hydrolysis reaction:

\[
\begin{align*}
2\text{NO}_2 + 4\text{CO}_2 + 5\text{H}_2\text{O} & \rightarrow 2\text{C}_2\text{H}_4\text{O}_2\text{N} + \frac{13}{2}\text{O}_2 \quad -2\Delta H^\circ_{\text{combustion}} = -2(-981 \text{ kJ}) \\
\text{C}_4\text{H}_8\text{O}_3\text{N}_2 + \frac{13}{2}\text{O}_2 & \rightarrow 2\text{NO}_2 + 4\text{CO}_2 + 4\text{H}_2\text{O} \Delta H^\circ_{\text{combustion}} = -1966 \text{ kJ}
\end{align*}
\]

\[
\begin{align*}
\text{C}_4\text{H}_8\text{O}_3\text{N}_2 + \text{H}_2\text{O} & \rightarrow 2\text{C}_2\text{H}_5\text{O}_2\text{N} \quad \Delta H^\circ_{\text{hydrolysis}} = -4 \text{ kJ}
\end{align*}
\]

[The bond between the two glycine amino acids in glycylglycine is a peptide bond, which we have encountered previously in Problems 7.30 and 7.42. In Problem 7.42, standard enthalpy of formation data were used to find that formation of a peptide bond (plus a molecule of water) is endothermic, \(\Delta H^\circ_{\text{reaction}} = 4 \text{ kJ·mol}^{-1}\) (of peptide bonds formed). Here, we have calculated that hydrolysis of a peptide bond, the reverse of the formation, is exothermic by \(-4 \text{ kJ·mol}^{-1}\) (of peptide bonds hydrolyzed). The two values are consistent with one another.]
**Problem 7.74.**

[NOTE: The illustration in this problem is modeled after one found at 
http://www.physics.umn.edu/groups/demo/demo_gifs/4B70_10.GIF where its use as a physics
demonstration is described. The history of the fire piston can be found at
http://www.geocities.com/CollegePark/4201/piston.html. Other sites (all lists of physics demos
done at various colleges—some have photos of the actual syringe) are:
http://www.wfu.edu/Academic-departments/Physics/demolabs/demos/4/4B7010.jpg,
http://www.physics.umd.edu/deptinfo/facilities/lecdem/i5-22.htm,

(a) To get $\Delta E$ for the gas compressed in a fire syringe that is 15 cm long and has a cross-
sectional area of 0.20 cm$^2$, we need the temperature change upon compression, the number of
moles of gas in the syringe, and the heat capacity of air, 21 kJ·mol$^{-1}$·K$^{-1}$. The temperature
change is from room temperature, about 300 K, to about 1000 K (value given in the problem
statement), so $\Delta T = 700$ K. The initial volume of gas in the cylinder is:

$$V = (15 \text{ cm})(0.20 \text{ cm}^2) = 3.0 \text{ cm}^3 (\text{mL})$$

The number of moles of gas is:

$$3.0 \text{ mL} = (3.0 \text{ mL}) \left( \frac{1 \text{ mol}}{25000 \text{ mL}} \right) = 1.2 \times 10^{-4} \text{ mol}$$

The internal energy change is:

$$\Delta E = n \times C_V \times \Delta T = (1.2 \times 10^{-4} \text{ mol})(21 \text{ J·mol}^{-1}·\text{K}^{-1})(700 \text{ K}) \approx 1.8 \text{ J}$$

(b) If no thermal energy is exchanged with the surroundings during the compression, $q$ is zero
for the compression and the work done on the gas is equal to its change in internal energy:

$$w = \Delta E = 1.8 \text{ J}. \text{ This work is the result of a decrease in volume of the gas to } \frac{1}{20}\text{th of its initial}
\text{ volume (part of the description in the problem statement). The change in volume, } \Delta V, \text{ is:}$$

$$\Delta V = (\frac{1}{20})(3.0 \text{ mL}) - (3.0 \text{ mL}) = -(\frac{19}{20})(3.0 \text{ mL}) = -2.9 \text{ mL} = -2.9 \times 10^{-3} \text{ L}$$

The work on the gas is:

$$w = 1.8 \text{ J} = (1.8 J) \left( \frac{1 \text{ L·atm}}{101.3 \text{ J}} \right) = 1.8 \times 10^{-2} \text{ L·atm} = -P\Delta V = -P(-2.9 \times 10^{-3} \text{ L})$$

$$P = (1.8 \times 10^{-2} \text{ L·atm})/(2.9 \times 10^{-3} \text{ L}) = 6.2 \text{ atm}$$

This is the pressure that has to be applied to the gas in the piston to obtain the amount of work
required to compress the gas in the fire syringe.

(c) To get pressure in pound·in$^{-2}$, multiply pressure in atmospheres by 15 pound·in$^{-2}$·atm$^{-1}$. The
result for the pressure in part (b) is about 93 pound·in$^{-2}$. Since 1 in = 2.54 cm, a square inch, in$^2$,
is $(2.54 \text{ cm})^2 = 6.5 \text{ cm}^2$. The area of the piston in square inches is:

$$0.20 \text{ cm}^2 = (0.20 \text{ cm}^2) \left( \frac{1 \text{ in}^2}{6.5 \text{ cm}^2} \right) = 0.030 \text{ in}^2$$

About 3 pounds of force [$= (93 \text{ pound·in}^{-2})(3.0 \times 10^{-2} \text{ in}^2)$] is required to produce a pressure of
93 pound·in$^{-2}$ on the tiny piston. Three pounds of force is easy for most teenagers or adults to
exert, so the fire piston should be easy to use.
(d) Before the compression, the molecules are moving randomly and relatively slowly (short arrows). During the compression, the molecules have a large component of motion in the direction of the compression superimposed on their random motion. When the compression stops, the large component of motion gets randomized and the molecules are again moving randomly but at much greater speed (longer arrows) corresponding to a higher temperature.

(e) The maximum temperature of the compressed gas is not the relevant variable here. The amount of energy available in the compressed gas is what you have to consider. The calculation in part (a) shows that the internal energy change of the gas is a little less than 2 J. Handbooks show that the specific heat of paper or cotton (both made of cellulose, a glucose polymer) is in the ballpark of 1 J·g⁻¹·K⁻¹. The kindling temperature of paper is 451 °F (which is the source of the title, “Fahrenheit 451,” of a Ray Bradbury story about book burning) or about 233 °C. Thus, you have to raise the temperature of paper about 200 degrees from room temperature to get it to burn. One gram of paper would require about 200 J of energy to increase its temperature this much. Since you only have about 2 J of energy in the compressed air of the fire piston, you have enough energy to raise the temperature of about 10 mg of paper or cotton to its kindling point. That is why you use a wisp of cotton in the demonstration. To start a larger fire, you use the glowing tinder to ignite some further small pieces of material and finally build up to a real fire. The match was a great invention and quickly made fire pistons obsolete.

**Problem 7.75.**

Begin this problem by writing the balanced equation for the reaction whose standard enthalpy change you are to calculate:

\[ 2\text{PH}_3(g) + 4\text{O}_2(g) \rightarrow \text{P}_2\text{O}_5(g) + 3\text{H}_2\text{O}(g) \]

The atomization reactions need to be combined in such a way that their sum is equal to the balanced equation. You can think of the solution as atomizing the reactants and then recombining the atoms to give the products. Some of the atomization reactions given in the problem statement will need to be used more than once. For example, the atomization of PH₃(g) must be used twice, so \(2[\text{PH}_3(g) \rightarrow \text{P}(g) + 3\text{H}(g)]\) becomes \(2\text{PH}_3(g) \rightarrow 2\text{P}(g) + 6\text{H}(g)\) and \(\Delta H^°\) for the reaction is also doubled as shown below. The reactions for recombination to give the products are needed in the reverse direction, which changes the sign of \(\Delta H^°\) from (+) to (−). The reactions, their standard enthalpy changes, and their sum are (species that cancel out in the summation are lined out):
<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2\text{PH}_3(g) \rightarrow 2\text{P}(g) + 6\text{H}(g) )</td>
<td>( 2(965 \text{ kJ}) = 1930 \text{ kJ} )</td>
</tr>
<tr>
<td>( 4\text{O}_2(g) \rightarrow 8\text{O}(g) )</td>
<td>( 4(490 \text{ kJ}) = 1960 \text{ kJ} )</td>
</tr>
<tr>
<td>( 2\text{P}(g) + 5\text{O}(g) \rightarrow \text{P}_2\text{O}_5(g) )</td>
<td>( -3382 \text{ kJ} )</td>
</tr>
<tr>
<td>( 6\text{H}(g) + 3\text{O}(g) \rightarrow 3\text{H}_2\text{O}(g) )</td>
<td>( 3(-930 \text{ kJ}) = -2790 \text{ kJ} )</td>
</tr>
<tr>
<td>( 2\text{PH}_3(g) + 4\text{O}_2(g) \rightarrow \text{P}_2\text{O}_5(g) + 3\text{H}_2\text{O}(g) )</td>
<td>( -2282 \text{ kJ} )</td>
</tr>
</tbody>
</table>

This \( \Delta H^\circ \) value is for 2 moles of \( \text{PH}_3 \) reacting. Therefore, for the combustion of 1 mole of \( \text{PH}_3 \), \( \Delta H^\circ = -1141 \text{ kJ} \).