Learning Objectives

• To understand the relationship between thermochemistry and nutrition.

The thermochemical quantities that you probably encounter most often are the caloric values of food. Food supplies the raw materials that your body needs to replace cells and the energy that keeps those cells functioning. About 80% of this energy is released as heat to maintain your body temperature at a sustainable level to keep you alive. The nutritional Calorie (with a capital C) that you see on food labels is equal to 1 kcal (kilocalorie). The caloric content of food is determined from its enthalpy of combustion ($\Delta H_{\text{comb}}$) per gram, as measured in a bomb calorimeter, using the general reaction

$$\text{food} + \text{excess } \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g}) \quad \text{(5.8.1)}$$

There are two important differences, however, between the caloric values reported for foods and the $\Delta H_{\text{comb}}$ of the same foods burned in a calorimeter. First, the $\Delta H_{\text{comb}}$ described in joules (or kilojoules) are negative for all substances that can be burned. In contrast, the caloric content of a food is always expressed as a positive number because it is stored energy. Therefore,

$$\text{caloric content} = -\Delta H_{\text{comb}} \quad \text{(5.8.2)}$$

Second, when foods are burned in a calorimeter, any nitrogen they contain (largely from proteins, which are rich in nitrogen) is transformed to $\text{N}_2$. In the body, however, nitrogen from foods is converted to urea $[(\text{H}_2\text{N})_2\text{C}=\text{O}]$, rather than $\text{N}_2$ before it is excreted. The $\Delta H_{\text{comb}}$ of urea measured by bomb calorimetry is $-632.0 \text{ kJ/mol}$. Consequently, the enthalpy change measured by calorimetry for any nitrogen-containing food is greater than the amount of energy the body would obtain from it. The difference in the values is equal to the $\Delta H_{\text{comb}}$ of urea multiplied by the number of moles of urea formed when the food is broken down. This point is illustrated schematically in the following equations:

$$\text{food} + \text{excess } \text{O}_2(\text{g}) \xrightarrow[\Delta H_1 < 0]{\text{\cancel{(H}_2\text{N})_2\text{C}=\text{O(\text{s})}}} 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g}) \quad \text{(5.8.3)}$$

which adds up to

$$\text{food} + \text{excess } \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g}) \quad \text{(5.8.4)}$$

All three $\Delta H$ values are negative, and, by Hess’s law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. The magnitude of $\Delta H_1$ must be less than $\Delta H_3$, the calorimetrically measured $\Delta H_{\text{comb}}$ for a food. By producing urea rather than $\text{N}_2$, therefore, humans are excreting some of the energy that was stored in their food.
Because of their different chemical compositions, foods vary widely in caloric content. As we saw previously, for instance, a fatty acid such as palmitic acid produces about 39 kJ/g during combustion, while a sugar such as glucose produces 15.6 kJ/g. Fatty acids and sugars are the building blocks of fats and carbohydrates, respectively, two of the major sources of energy in the diet. Nutritionists typically assign average values of 38 kJ/g (about 9 Cal/g) and 17 kJ/g (about 4 Cal/g) for fats and carbohydrates, respectively, although the actual values for specific foods vary because of differences in composition. Proteins, the third major source of calories in the diet, vary as well. Proteins are composed of amino acids, which have the following general structure:

![General structure of an amino acid.](image)

An amino acid contains an amine group (−NH₂) and a carboxylic acid group (−CO₂H).

In addition to their amine and carboxylic acid components, amino acids may contain a wide range of other functional groups: R can be hydrogen (−H); an alkyl group (e.g., −CH₃); an aryl group (e.g., −CH₂C₆H₅); or a substituted alkyl group that contains an amine, an alcohol, or a carboxylic acid (Figure \(\PageIndex{1}\)). Of the 20 naturally occurring amino acids, 10 are required in the human diet; these 10 are called essential amino acids because our bodies are unable to synthesize them from other compounds. Because R can be any of several different groups, each amino acid has a different value of \(\Delta H_{\text{comb}}\). Proteins are usually estimated to have an average \(\Delta H_{\text{comb}}\) of 17 kJ/g (about 4 Cal/g).
Figure \(\PageIndex{1}\): The Structures of 10 Amino Acids. Essential amino acids in this group are indicated with an asterisk.

**Example \(\PageIndex{1}\)**

Calculate the amount of available energy obtained from the biological oxidation of 1.000 g of alanine (an amino acid). Remember that the nitrogen-containing product is urea, not \(\text{N}_2\), so biological oxidation of alanine will yield less energy than will combustion. The value of \(\Delta H_{\text{comb}}\) for alanine is \(-1577\) kJ/mol.

![Alanine molecule](image)

**Given:** amino acid and \(\Delta H_{\text{comb}}\) per mole

**Asked for:** caloric content per gram

**Strategy:**
A. Write balanced chemical equations for the oxidation of alanine to CO$_2$, H$_2$O, and urea; the combustion of urea; and the combustion of alanine. Multiply both sides of the equations by appropriate factors and then rearrange them to cancel urea from both sides when the equations are added.

B. Use Hess’s law to obtain an expression for $\Delta H$ for the oxidation of alanine to urea in terms of the $\Delta H_{comb}$ of alanine and urea. Substitute the appropriate values of $\Delta H_{comb}$ into the equation and solve for $\Delta H$ for the oxidation of alanine to CO$_2$, H$_2$O, and urea.

C. Calculate the amount of energy released per gram by dividing the value of $\Delta H$ by the molar mass of alanine.

Solution:

The actual energy available biologically from alanine is less than its $\Delta H_{comb}$ because of the production of urea rather than N$_2$. We know the $\Delta H_{comb}$ values for alanine and urea, so we can use Hess’s law to calculate $\Delta H$ for the oxidation of alanine to CO$_2$, H$_2$O, and urea.

A We begin by writing balanced chemical equations for (1) the oxidation of alanine to CO$_2$, H$_2$O, and urea; (2) the combustion of urea; and (3) the combustion of alanine. Because alanine contains only a single nitrogen atom, whereas urea and N$_2$ each contain two nitrogen atoms, it is easier to balance Equations 1 and 3 if we write them for the oxidation of 2 mol of alanine:

$$\begin{align*}
\text{(1) } & \quad 2C_3H_7NO_2(s) + 6O_2(g) \rightarrow 5CO_2(g) + 5H_2O(l) + (H_2N)_2C=O(s) \\
\text{(2) } & \quad (H_2N)_2C=O(s) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + N_2(g) \\
\text{(3) } & \quad 2C_3H_7NO_2(s) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l) + N_2(g)
\end{align*}$$

Adding Equations 1 and 2 and canceling urea from both sides give the overall chemical equation directly:

$$\begin{align*}
\text{(1) } & \quad 2C_3H_7NO_2(s) + 6O_2(g) \rightarrow 5CO_2(g) + 5H_2O(l) + \cancel{(H_2N)_2C=O(s)} \\
\cancel{\text{(2) }} & \quad \cancel{(H_2N)_2C=O(s)} + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + \cancel{N_2(g)} \\
\text{(3) } & \quad \text{(1) } 2C_3H_7NO_2(s) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l) + \cancel{N_2(g)}
\end{align*}$$

B By Hess’s law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. We know that $\Delta H_3 = 2\Delta H_{comb}$ (alanine), $\Delta H_2 = \Delta H_{comb}$ (urea), and $\Delta H_1 = 2\Delta H$ (alanine → urea). Rearranging and substituting the appropriate values gives

$$\Delta \{H\{1\}\} = \Delta \{H\{3\}\} - \Delta \{H\{2\}\}$$

Thus $\Delta H$ (alanine → urea) = $-2522$ kJ/(2 mol of alanine) = $-1261$ kJ/mol of alanine. Oxidation of alanine to urea rather
than to nitrogen therefore results in about a 20% decrease in the amount of energy released (−1261 kJ/mol versus −1577 kJ/mol).

C The energy released per gram by the biological oxidation of alanine is

\[
\left(\frac{-1261 \; \text{kJ}}{1 \; \text{mol}} \right) \left(\frac{1 \; \text{mol}}{89.094 \; \text{g}} \right) = -14.15 \; \text{kJ/g}
\]

This is equal to −3.382 Cal/g.

Exercise 

Calculate the energy released per gram from the oxidation of valine (an amino acid) to CO₂, H₂O, and urea. Report your answer to three significant figures. The value of Δ\text{H}_{\text{comb}} for valine is −2922 kJ/mol.

Answer

−22.2 kJ/g (−5.31 Cal/g)

The reported caloric content of foods does not include Δ\text{H}_{\text{comb}} for those components that are not digested, such as fiber. Moreover, meats and fruits are 50%−70% water, which cannot be oxidized by O₂ to obtain energy. So water contains no calories. Some foods contain large amounts of fiber, which is primarily composed of sugars. Although fiber can be burned in a calorimeter just like glucose to give carbon dioxide, water, and heat, humans lack the enzymes needed to break fiber down into smaller molecules that can be oxidized. Hence fiber also does not contribute to the caloric content of food.

Table: Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef

<table>
<thead>
<tr>
<th>Composition</th>
<th>Calories</th>
</tr>
</thead>
<tbody>
<tr>
<td>97.5 g of water</td>
<td>× 0 Cal/g = 0</td>
</tr>
<tr>
<td>58.7 g of protein</td>
<td>× 4 Cal/g = 235</td>
</tr>
<tr>
<td>69.3 g of fat</td>
<td>× 9 Cal/g = 624</td>
</tr>
</tbody>
</table>
We can determine the caloric content of foods in two ways. The most precise method is to dry a carefully weighed sample and carry out a combustion reaction in a bomb calorimeter. The more typical approach, however, is to analyze the food for protein, carbohydrate, fat, water, and “minerals” (everything that doesn’t burn) and then calculate the caloric content using the average values for each component that produces energy (9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals). An example of this approach is shown in Table \( \PageIndex{1} \) for a slice of roast beef. The compositions and caloric contents of some common foods are given in Table \( \PageIndex{2} \).  

Table \( \PageIndex{2} \): Approximate Compositions and Fuel Values of Some Common Foods

<table>
<thead>
<tr>
<th>Food (quantity)</th>
<th>Approximate Composition (%)</th>
<th>Food Value (Cal/g)</th>
<th>Calories</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Carbohydrate</td>
<td>Protein</td>
</tr>
<tr>
<td>beer (12 oz)</td>
<td>92</td>
<td>3.6</td>
<td>0.3</td>
</tr>
<tr>
<td>coffee (6 oz)</td>
<td>100</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>milk (1 cup)</td>
<td>88</td>
<td>4.5</td>
<td>3.3</td>
</tr>
<tr>
<td>egg (1 large)</td>
<td>75</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>butter (1 tbsp)</td>
<td>16</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>apple (8 oz)</td>
<td>84</td>
<td>15</td>
<td>~0</td>
</tr>
<tr>
<td>bread, white (2 slices)</td>
<td>37</td>
<td>48</td>
<td>8</td>
</tr>
<tr>
<td>brownie (40 g)</td>
<td>10</td>
<td>55</td>
<td>5</td>
</tr>
<tr>
<td>hamburger (4 oz)</td>
<td>54</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>fried chicken (1 drumstick)</td>
<td>53</td>
<td>8.3</td>
<td>22</td>
</tr>
<tr>
<td>carrots (1 cup)</td>
<td>87</td>
<td>10</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Because the Calorie represents such a large amount of energy, a few of them go a long way. An average 73 kg (160 lb) person needs about 67 Cal/h (1600 Cal/day) to fuel the basic biochemical processes that keep that person alive. This energy is required to maintain body temperature, keep the heart beating, power the muscles used for breathing, carry out chemical reactions in cells, and send the nerve impulses that control those automatic functions. Physical activity increases the amount of energy required but not by as much as many of us hope (Table \( \PageIndex{2} \)). A moderately active individual requires about 2500–3000 Cal/day; athletes or others engaged in strenuous activity can burn 4000 Cal/day. Any excess caloric intake is stored by the body for future use, usually in the form of fat, which is the
most compact way to store energy. When more energy is needed than the diet supplies, stored fuels are mobilized and oxidized. We usually exhaust the supply of stored carbohydrates before turning to fats, which accounts in part for the popularity of low-carbohydrate diets.

Table \(\PageIndex{3}\): Approximate Energy Expenditure by a 160 lb Person Engaged in Various Activities

<table>
<thead>
<tr>
<th>Activity</th>
<th>Cal/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>sleeping</td>
<td>80</td>
</tr>
<tr>
<td>driving a car</td>
<td>120</td>
</tr>
<tr>
<td>standing</td>
<td>140</td>
</tr>
<tr>
<td>eating</td>
<td>150</td>
</tr>
<tr>
<td>walking 2.5 mph</td>
<td>210</td>
</tr>
<tr>
<td>mowing lawn</td>
<td>250</td>
</tr>
<tr>
<td>swimming 0.25 mph</td>
<td>300</td>
</tr>
<tr>
<td>roller skating</td>
<td>350</td>
</tr>
<tr>
<td>tennis</td>
<td>420</td>
</tr>
<tr>
<td>bicycling 13 mph</td>
<td>660</td>
</tr>
<tr>
<td>running 10 mph</td>
<td>900</td>
</tr>
</tbody>
</table>

Example \(\PageIndex{2}\))

What is the minimum number of Calories expended by a 72.6 kg person who climbs a 30-story building? (Assume each flight of stairs is 14 ft high.) How many grams of glucose are required to supply this amount of energy? (The energy released during the combustion of glucose was calculated in Example 5.5.4).

**Given:** mass, height, and energy released by combustion of glucose

**Asked for:** calories expended and mass of glucose needed

**Strategy:**

A. Convert mass and height to SI units and then substitute these values into Equation 5.6 to calculate the change in potential energy (in kilojoules). Divide the calculated energy by 4.184 Cal/kJ to convert the potential energy change to Calories.

B. Use the value obtained in Example 5.5.4 for the combustion of glucose to calculate the mass of glucose needed to supply this amount of energy.
Solution:

The energy needed to climb the stairs equals the difference between the person’s potential energy \( PE \) at the top of the building and at ground level.

A Recall that \( PE = mgh \). Because \( m \) and \( h \) are given in non-SI units, we must convert them to kilograms and meters, respectively

\[
\text{PE} = \left( 72.6 \; \text{kg} \right) \left( 9.81 \; \text{m/s}^2 \right) \left( 128 \; \text{m} \right) = 8.55 \times 10^4 \; \left( \text{kg} \cdot \text{m}^2/\text{s}^2 \right) = 91.2 \; \text{kJ}
\]

To convert to Calories, we divide by 4.184 kJ/kcal:

\[
\text{PE} = \left( 91.2 \; \cancel{\text{kJ}} \right) \left( \frac{1 \; \text{kcal}}{4.184 \; \cancel{\text{kJ}}} \right) = 21.8 \; \text{kcal} = 21.8 \; \text{Cal}
\]

B Because the combustion of glucose produces 15.6 kJ/g (Example 5), the mass of glucose needed to supply 85.5 kJ of energy is

\[
\text{PE} = \left( 91.2 \; \cancel{\text{kJ}} \right) \left( \frac{1 \; \text{g \; glucose}}{15.6 \; \cancel{\text{kJ}}} \right) = 5.85 \; \text{g \; glucose}
\]

This mass corresponds to only about a teaspoonful of sugar! Because the body is only about 30% efficient in using the energy in glucose, the actual amount of glucose required would be higher: \((100\%/30\%) \times 5.85 \; \text{g} = 19.5 \; \text{g}\). Nonetheless, this calculation illustrates the difficulty many people have in trying to lose weight by exercise alone.

Exercise \( \PageIndex{2} \))

Calculate how many times a 160 lb person would have to climb the tallest building in the United States, the 110-story Willis Tower in Chicago, to burn off 1.0 lb of stored fat. Assume that each story of the building is 14 ft high and use a calorie content of 9.0 kcal/g of fat.

Answer

About 55 times

The calculations in Example 5.8.2 ignore various factors, such as how fast the person is climbing. Although the rate is irrelevant in calculating the change in potential energy, it is very relevant to the amount of energy actually required to ascend the stairs. The calculations also ignore the fact that the body’s conversion of chemical energy to mechanical work is significantly less than 100% efficient. According to the average energy expended for various activities listed in Table 5.8.3, a person must run more than 4.5 h at 10 mph or bicycle for 6 h at 13 mph to burn off 1 lb of fat \((1.0 \; \text{lb} \times 454 \; \text{g/lb} \times 9.0 \; \text{Cal/g} = 4100 \; \text{Cal})\). But if a person rides a bicycle at 13 mph for only 1 h per day 6 days a week, that person will burn off 50 lb of fat in the course of a year (assuming, of course, the cyclist doesn’t increase his or her intake of calories to compensate for the exercise).

Summary

Thermochemical concepts can be applied to determine the actual energy available in food. The nutritional **Calorie** is equivalent to 1 kcal (4.184 kJ). The caloric content of a food is its \( \Delta H_{\text{comb}} \) per gram. The combustion of nitrogen-
containing substances produces N\textsubscript{2}(g), but the biological oxidation of such substances produces urea. Hence the actual energy available from nitrogen-containing substances, such as proteins, is less than the Δ\textsubscript{H\text{comb}} of urea multiplied by the number of moles of urea produced. The typical caloric contents for food are 9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals.

Contributors and Attributions

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