

3.10.2: Foods- Energy in a Marshmallow

Marshmallow was originally used medicinally to soothe sore throats. It was made from the root of the marsh mallow plant, *Althaea officinalis*, sometimes mixed with sugars or other ingredients and whipped to make something like the modern marshmallow.^[1] Modern Campfire® marshmallows contain Corn Syrup, Sugar, Modified Food Starch (Corn), Dextrose, Water, Gelatin, Natural and Artificial Flavor, Tetrasodium Pyrophosphate and Blue 1^[2], and the gelatin protein made from bones and hides makes them off limits to strict vegetarians. We'll consider the marshmallow to be 7.5 g of pure sugar (sucrose) for the calculations below.

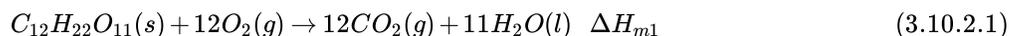


Roasting marshmallow

Let's investigate the fate of a marshmallow when you eat it, and explain in part where the food energy comes from.

Aerobic Metabolism

We'll need the energy supplied by the overall reaction for the *aerobic* metabolism of sucrose, which occurs when plenty of oxygen is available:



But that reaction lumps together a lot of interesting processes. The *hydrolysis* (cleavage by water) of sucrose into the simple sugars glucose and fructose occurs in saliva, but not without the enzyme sucrase that catalyzes the reaction:



Anaerobic Metabolism

Lactobacilli in our mouth partially convert the simple sugars to lactic acid (which causes tooth decay), in the overall reaction for glycolysis plus fermentation:



This reaction provides energy to sustain the bacteria, but it also occurs in our bodies when sugar is metabolized *anaerobically* (with limited oxygen), and the lactic acid is responsible for muscle ache the day after we exert our muscles. Lactobacilli are used in controlled recipes to create lactic acid that creates the tart or sour taste of yogurt and sauerkraut.

If bacteria don't metabolize the glucose, we do, using it to produce ATP in a process called *glycolysis* which involves about ten different reactions that end with the production of pyruvic acid ($C_3H_4O_3$). If our muscles are well oxygenated, the pyruvic acid is converted to CO_2 and H_2O and we have overall reaction (1), yielding energy that we'll calculate below. During extended exercise, *glycolysis* comes to a halt when it runs out of oxygen to make an essential reactant, NAD^+ . Then *anaerobic fermentation* takes over, producing the NAD^+ and converting the pyruvic acid to lactic acid ($C_3H_6O_3$), which builds up in muscles as a result of reaction (3). This produces a lot less energy than aerobic metabolism, as we'll see below.

The process makes just 2 ATP instead of many more that would be produced if the pyruvic acid were metabolized aerobically by overall reaction (1).

How do food chemists calculate the energy produced in all these reactions?

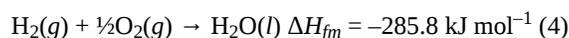
By now you can imagine that there are innumerable reactions involved in just food metabolism, and it would be virtually impossible to list all the thermochemical equations, along with the corresponding enthalpy changes.

Fortunately Hess' law makes it possible to list just *the standard enthalpy of formation* ΔH_f , for each compound, and use these ΔH_f values to calculate the ΔH_m for any reaction of interest.

Standard Enthalpy of Formation

The standard enthalpy of formation is the enthalpy change when 1 mol of a pure substance is formed from its elements. Each element must be in the physical and chemical form which is most stable at normal atmospheric pressure and a specified temperature (usually 25°C).

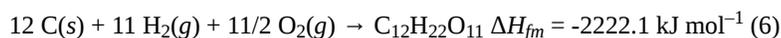
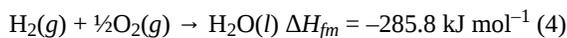
For example, since $\text{H}_2\text{O}(l)$ appears in Equation (1), we'll need its ΔH_f to calculate the energy available from a marshmallow. If we know that $\Delta H_f [\text{H}_2\text{O}(l)] = -285.8 \text{ kJ mol}^{-1}$, we can immediately write the thermochemical equation



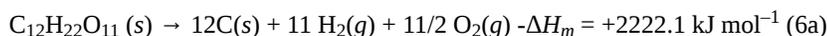
The elements H and O appear as diatomic molecules and in gaseous form because these are their most stable chemical and physical states. Note also that 285.8 kJ are given off *per mole* of $\text{H}_2\text{O}(l)$ formed. Equation (1) must specify formation of 1 mol $\text{H}_2\text{O}(l)$, and so the coefficient of O_2 must be $\frac{1}{2}$.

Using Enthalpies of Formation to Calculate the Energy from Aerobic Metabolism of Sucrose

In addition to (4), we'll need two other ΔH_f values to calculate the energy in a marshmallow. They are the ΔH_f values for the other compounds in Equation (1), CO_2 and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. All the ΔH_{fm} values can be found in standard tables like the one at the end of this section, and we can write the equations (5) and (6) knowing the definition of ΔH_f :



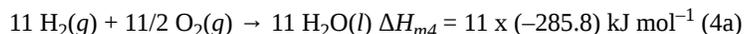
By Hess' Law, we may be able to combine equations 4, 5, and 6 to get Equation (1). First, we notice that (1) has sucrose on the left, but it's on the right in (6); so reversing (6) we get



To cancel the 12 C that does not appear in (1), we'll add 12 x Equation (5) (along with 6x its enthalpy change):



And to add the 11 $\text{H}_2\text{O}(l)$ that appears in (1), we'll add 11 x Equation (4):



If we combine Equations 6a, 5a, and 4a according to Hess' Law, we notice that 12 H_2 , 12 C, and 11/2 $\text{O}_2(g)$ appear on both the left and right, and cancel to give Equation (1)!



We can then combine the enthalpies to get the needed ΔH_m :

$$\Delta H_m = 12 \Delta H_{m5} + 12 \Delta H_{m4} - \Delta H_{m6} = 12 \times (-393.509) + 11 \times (-285.8) - (-2222.1) \text{ kJ mol}^{-1} = -5643.8 \text{ kJ mol}^{-1}$$

Notice that this value appears in the Table at the end of this section. With Hess' Law, we can always calculate an enthalpy of combustion from enthalpies of formation, or vice versa! Reaction (6) corresponding to ΔH_{fm} of sucrose does not occur, but its enthalpy can be calculated from enthalpies of reactions that do occur.

Notice that our calculation simplifies to:

$$\Delta H_m = \sum \Delta H_f (\text{products}) - \sum \Delta H_f (\text{reactants})$$

The symbol Σ means “the sum of.” So we just need to add the ΔH_f values for the products, and subtract the sum of ΔH_f values for the reactants in Equation (1). Since ΔH_f values are given *per mole* of compound, you must be sure to multiply each ΔH_f by an appropriate coefficient in from Equation (1) (for which ΔH_m is being calculated).

Calories in a Marshmallow

Now we can calculate the food energy in the marshmallow: The molar mass of sucrose is 342.3 g/mol, so the energy per gram is $-5643.8 \text{ kJ/mol} / 342.3 \text{ g/mol} = 16.49 \text{ kJ/g}$. In the 7.5 g marshmallow, remembering that 1 dietary Calorie is 4.184 kJ, we have $7.5 \text{ g} \times 16.49 \text{ kJ/g} \times (1 \text{ Cal} / 4.184 \text{ kJ}) = 29.6 \text{ Cal}$. (But who can stop at just one roasted marshmallow?)

Recap of the Calculation of a Reaction Enthalpy

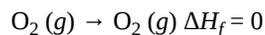
Note carefully how the problem above was solved. In step 6a the *reactant* compound $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (s) was hypothetically decomposed to its elements. This equation was the reverse of formation of the compound, and so ΔH_1 was opposite in sign from ΔH_f . In step 5a we had the hypothetical formation of the *product* $\text{CO}_2(g)$ from its elements. Since 12 mol were obtained, the enthalpy change was doubled but its sign remained the same. In step 4a we had the hypothetical formation of the *product* $\text{H}_2\text{O} (l)$ from its elements. Since 11 mol were obtained, the enthalpy change was multiplied by 11, but its sign remained the same.

Any chemical reaction can be approached similarly. To calculate ΔH_m we *add* all the ΔH_f values for the products, multiplying each by the appropriate coefficient, as in step 2 above. Since the signs of ΔH_f for the reactants had to be reversed in step 1, we *subtract* them, again multiplying by appropriate coefficients.

Again, this can be summarized by the important equation

$$\Delta H_m = \sum \Delta H_f (\text{products}) - \sum \Delta H_f (\text{reactants})$$

One further point arises from the definition of ΔH_f . *The standard enthalpy of formation for an element in its most stable state must be zero.* That's why ΔH_f for O_2 doesn't appear in the calculation above; its value is zero, corresponding to the formation of O_2 from its elements. There's no change in the reaction below, so $\Delta H_f = 0$:

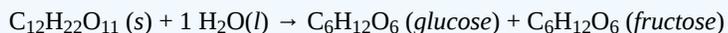


Standard enthalpies of formation for some common compounds are given in the table below, and more are given in Table of Some Standard Enthalpies of Formation at 25°C. These values may be used to calculate ΔH_m for any chemical reaction so long as all the compounds involved appear in the tables. To see how and why this may be done, consider the following example.

Energy of Sucrose Hydrolysis in Saliva

✓ Example 3.10.2.1: Standard Enthalpies of Formation

Use standard enthalpies of formation to calculate ΔH_m for the reaction



Solution

$$\Delta H_m = \sum \Delta H_f (\text{products}) - \sum \Delta H_f (\text{reactants})$$

From the table below, ΔH_f for glucose, fructose, sucrose and water are -1271, -1266.6 (they may actually be the same, but measured by different methods), -2222.1, and -285.8 kJ mol^{-1} respectively. Note that we were careful to use $\Delta H_f [\text{H}_2\text{O}(l)]$ not $\Delta H_f [\text{H}_2\text{O}(g)]$ or (l) . Substituting these values in the equation above gives

$$\Delta H_m = [1 \text{ mol glucose} \times (-1271 \text{ kJ mol}^{-1}) + 1 \text{ mol fructose} \times (-1266.6 \text{ kJ mol}^{-1})] - [1 \text{ mol sucrose} \times (-2222.1 \text{ kJ mol}^{-1}) + 1 \text{ mol water} \times (-285.8 \text{ kJ mol}^{-1})] = -29.7 \text{ kJ mol}^{-1}.$$

The process is actually exothermic, releasing a small amount of heat energy. The measured energy for hydrolysis of maltose to 2 glucose units is only -4.02 $\text{kJ}^{[3]}$.

Energy in Glucose Metabolism and Anaerobic Formation of ATP

✓ Example 3.10.2.2: Anaerobic Metabolism

Use the table of standard enthalpies of formation at 25°C to calculate ΔH_m for the reaction below (glycolysis + fermentation), which is associated with the production of 2 mol ATP (as well as NADH) in anaerobic metabolism in your body. The ΔH_f for lactic acid and glucose are -687 and -1271 kJ mol⁻¹ respectively.



Solution

$$\Delta H_m = \sum \Delta H_f (\text{products}) - \sum \Delta H_f (\text{reactants})$$

$$= [2 \Delta H_f (\text{C}_3\text{H}_6\text{O}_3) - [\Delta H_f (\text{C}_6\text{H}_{12}\text{O}_6)]]$$

$$= [2 \text{ mol lactic acid} \times (-687) \text{ kJ mol}^{-1}] - [1 \text{ mol glucose} \times (-1271) \text{ kJ mol}^{-1}]$$

$$= -1374 + 1271.1 \text{ kJ} = -103 \text{ kJ}.$$

This energy is used in part to make 2ATP molecules rather than being released entirely as heat. Note that -5643.8 kJ mol⁻¹ resulted from the aerobic metabolism of sucrose (above) but only 2 (-103)kJ = -206 kJ would result from its anaerobic metabolism (since 1 mol of sucrose yields 2 mol of glucose).

Solutions to Example 3.10.2

Compound	ΔH_f kJ mol ⁻¹	ΔH_f kcal mol ⁻¹	ΔH_c kJ mol ⁻¹
H ₂ O(g)	-241.818	-57.79	-
H ₂ O(l)	-285.8	-68.3	-
H ₂ O ₂ (l)	-187.78	-44.86	-
CO(g)	-110.525	-26.41	-
CO ₂ (g)	-393.509	-94.05	-
NH ₃ (g)	-46.11	-11.02	-
C ₂ H ₂ (g)	+226.73	+54.18	-
C ₃ H ₆ O ₃ lactic acid	-687 ^[4]	-164.08 ^[5]	-
C ₃ H ₄ O ₃ pyruvic acid	-584.5 ^[6]	-	-
C ₆ H ₁₂ O ₆ glucose	-1271 ^[7]	+	-2803 ^[8]
C ₆ H ₁₂ O ₆ galactose	-1286 ^[9] -1286.3 ^[10]	-	-2803.7 ^[11]
C ₆ H ₁₂ O ₆ fructose	-1265.6 ^[12]	-	-2812 ^[13]
C ₁₂ H ₂₂ O ₁₁ sucrose	-2375 ^[14] -2222.1 ^{[15][16]}	-	-5645 ^[17] -5646 ^[18] -5644 ^[19]
C ₁₂ H ₂₂ O ₁₁ maltose	-	-	-5644 ^[20]
C ₆ H ₁₂ O ₆ lactose	-2236.7 ^[21]	-	-5648 ^[22] -5629.5 ^[23]

Compound	ΔH_f kJ mol ⁻¹	ΔH_f kcal mol ⁻¹	ΔH_c kJ mol ⁻¹
C ₂ H ₆ O ₁ ethanol	–	–	–1367 ^[24]
C ₆ H ₁₄ O ₆ sorbitol	–5644 ^{1[25]}	–	–
C ₁₈ H ₃₄ O ₂ oleic acid	–772 ^{1[26]}	–	–
C ₁₈ H ₃₀ O ₂ linolenic acid	–665 ^{1[27]}	–	–
C ₅₇ H ₁₀₄ O ₆ triolein	–2390 ^{1[28]} –2193.7 ^[29]	–	–35224 ^[30] –35099.6 ^[31]

1. Estimate, based on a theoretical calculation

The most general references are NIST, this bond energy based calculator and for QSPR calculated values, Int. J. Mol. Sci. 2007, 8, 407-432.

From ChemPRIME: 3.9: Standard Enthalpies of Formation

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