Example

When consuming an ice-cold drink, one must raise the temperature of the beverage to 37.0°C (normal body temperature). Can one lose weight by drinking ice-cold beverages if the body uses up about 1 calorie per gram of water per degree Celsius (i.e. the specific heat of water = 1.00 cal/g·°C) to consume the drink?

a. Calculate the energy expended (in Cal) to consume a 12-oz beer (about 355 mL) if the beer is initially at 4.0°C. Assume the drink is mostly water and its density is 1.01 g/mL.

\[
\begin{align*}
355 \text{ mL} \times 1.01 \text{ g/mL} &= 358.55 \text{ g} \\
\Delta T &= 37°C - 4°C = 33°C \\
\text{cal} &= 358.55 \text{g} \times 33°C \times 1.00 \text{ cal/g·°C} \\
&= 11832.15 \text{ cal} = \textbf{11.83 Cal}
\end{align*}
\]
Example

b. If the label indicates 103 Cal, what is the net calorie gain or loss when a person consumes this beer? Is this a viable weight loss alternative?

\[103 \text{ Cal} - 11.83 \text{ Cal} = 91.17 \text{ Cal consumed}\]

c. Calculate the amount of heat (in kJ) required to heat 1.00 kg (~1 L) of water at 25°C to its boiling point.

\[1 \text{ kg} = 1000 \text{ g} \]
\[\Delta T = 100°C - 25°C = 75°C \]
\[\text{cal} = 1000g \times 75°C \times 1.00 \text{ cal/g·°C} \]
\[= 75000 \text{ cal} \]
\[1 \text{ cal} = 4.184 \text{ J} \]
\[75000 \text{ cal} = 313800 \text{ J} = 313.8 \text{ kJ}\]
Units of Energy

Another energy unit is the **British thermal unit** (abbreviated Btu). A Btu is the energy required to raise the temperature of 1 pound of water by 1°F when water is most dense (at 3.9°C).

The heating power of many gas cooktops is often given in Btu’s. Calculate the time (in minutes) required to heat 1.00 kg of water at 25°C to boiling using a 12,000 Btu per hour burner. (Assume complete energy transfer from the burner to the water.) Use 1 kW\cdot h = 3412 Btu and 1 kJ = 1 kW\cdot s.

Energy needed = 313.8 kJ (from last slide)

\[
313.8 \text{ kJ} = 313.8 \text{ kW} \cdot \text{s} \\
313.8 \text{ kW} \cdot \text{s}/3600 \text{ s/hr} = 0.087 \text{ kWh} \\
0.087 \text{ kWh} \cdot 3412 \text{ Btu/kWh} = 297.4 \text{ Btu needed} \\
297.4 \text{ Btu} / 12,000 \text{ Btu/hr} = 0.025 \text{ hr} = 89 \text{ s}
\]
Calorimetry

Calorimetry is used to measure heat capacity and specific heats.

**calorimeter:**
- an instrument that measures heat changes for physical and chemical processes
- insulated, so the only heat flow is between reaction system and calorimeter
Calorimetry

Coffee-Cup Calorimeter

- also called constant-pressure calorimeter since under atmospheric pressure
- polystyrene cup partially filled with water polystyrene is a good insulator → very little heat lost through cup walls
- heat evolved by a reaction is absorbed by the water, and the heat capacity of the calorimeter is the heat capacity of the water
Calorimetry

We use the following equations to solve calorimetry problems:

\[ q = n \, c_p \, \Delta T \quad \text{or} \quad q = c_s \, m \, \Delta T \]

where \( \Delta T \) = change in temperature, \( n \) = # of moles, and \( m \) = mass.

1. A 27.825 g sample of nickel is heated to 99.85°C and placed in a coffee cup calorimeter containing 150.0 g of water at 23.65°C. After the metal cools, the final temperature of metal and water is 25.15°C.

   a. What released heat? **The nickel**
   b. What absorbed heat? **The water in the calorimeter**
b. Calculate the heat absorbed by the water. (Water’s specific heat is 4.184 J/g·°C.)

\[ q = c_s m \Delta T; \quad c_s = 4.184 \text{ J/g·°C}; \quad m = 150.0 \text{ g}; \]
\[ \Delta T = 25.15 - 23.65 \text{ °C} = 1.5 \text{ °C} \]
\[ q = (4.184 \text{ J/g·°C}) \times (150.0 \text{ g}) \times (1.5 \text{ °C}) = 941.4 \text{ J} \]

c. Calculate the specific heat of the metal assuming no heat is lost to the surroundings or the calorimeter—i.e., all the heat absorbed by the water had to be released by the metal.

\[ c_s = q/m \Delta T; \quad q = 941.4 \text{ J}; \quad c_s = ? \text{ J/g·°C}; \quad m = 27.825 \text{ g}; \]
\[ \Delta T = 99.85 - 25.15 \text{ °C} = 74.7 \text{ °C} \]
\[ c_s = 941.4 \text{ J}/(27.825 \text{ g}) \times (74.7 \text{ °C}) = 0.453 \text{ J/g·°C} \]
2. When a solution consisting of 2.00 g of potassium hydroxide in 75.0 g of solution is added to 75.0 mL of 0.500 M nitric acid at 24.9°C in a calorimeter, the temperature of the resulting solution increases to 28.0°C. Assume the heat absorbed by the calorimeter is negligible.

\[ \text{HNO}_3(aq) + \text{KOH}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{KNO}_3(aq) \]

a. What released heat? \text{The neutralization reaction}

b. What absorbed heat? \text{The water in the calorimeter}
c. Calculate the amount of heat (in J) absorbed by the solution given the density of nitric acid is 1.03 g/mL. Assume the solution is sufficiently dilute that its specific heat is equal to water’s, 4.184 J/g·°C.

2.00 g KOH in 75.0 g solution = 77.0 g total
75.0 mL of 0.500 M HNO3 with density = 1.03 g/ml = 77.25 g
Total mass = 154.25 g

\[ q = c_s m \Delta T; \quad c_s = 4.184 \text{ J/g·°C}; \quad m = 154.25 \text{ g}; \]
\[ \Delta T = 28.0 - 24.9 \, ^\circ\text{C} = 3.1 \, ^\circ\text{C} \]
\[ q = (4.184 \text{ J/g·°C}) \times (154.25 \text{ g}) \times (3.1 \, ^\circ\text{C}) = 2000.7 \text{ J} \]
d. Assuming the total amount of heat absorbed by the solution was released by the reaction, calculate the enthalpy change (\( \Delta H \)) for the reaction in kJ/mol of \( \text{H}_2\text{O} \) formed.

\[
\begin{align*}
2.00 \text{ g KOH} / 56.1 \text{ g/mol} &= 0.036 \text{ mol KOH} \\
75.0 \text{ mL of 0.500 M HNO}_3 &= 0.0375 \text{ mol HNO}_3 \\
\text{KOH} + \text{HNO}_3 &\rightarrow \text{H}_2\text{O} + \text{KNO}_3 \\
&\quad 0.036 \text{ mol H}_2\text{O produced}
\end{align*}
\]

\[q = 2000.7 \text{ J; mol} = 0.036\]
\[\Delta H = \frac{q}{\text{mol}} = 2 \text{ kJ/0.036 mol} = 55.56 \text{ kJ/mol}\]
**Bomb Calorimetry**

**bomb calorimeter:** a sealed vessel (called a *bomb*) that can withstand high pressures is contained in a completely insulated chamber containing water.

- Often called a constant-volume calorimeter.
- It is essentially an isolated system, since the calorimeter contains all of the heat generated by the reaction.
- Thus, the heat of a reaction can be determined using the temperature change measured for the system and the mass of reactants used.
Bomb Calorimetry

Because the calorimeter consists of the water and the insulated chamber, the heat capacity of the calorimeter, called the calorimeter constant ($C_{\text{cal}}$) is used to calculate any heat of reaction ($\Delta H_{\text{rxn}}$).

- Note: Because the volume is constant, there is no $P\Delta V$ work done for a bomb calorimeter, so $q_{\text{rxn}} = \Delta E$.
- The pressure effects are usually negligible, so $\Delta E \approx \Delta H$, so $q_{\text{rxn}} \approx \Delta H$. \[q_{\text{rxn}} = -q_{\text{calorimeter}}\]

Thus, the heat of a reaction can be determined from the heat absorbed by the calorimeter!
How do we calculate $C_{cal}$?

The calorimeter constant can be calculated by performing a known reaction (using a standard).

What is the calorimeter constant of a bomb calorimeter if burning 1.000 g of benzoic acid in it causes the temperature of the calorimeter to rise by 7.248 °C? The heat of combustion of benzoic acid is $\Delta H_{\text{comb}} = -26.38 \text{ kJ/g}$.

$$C_{cal} = \frac{q_{cal}}{\Delta T}$$

$q_{cal} = 26.38 \text{ kJ/g} \times 1.000 \text{ g} = 26.38 \text{ kJ}$

$\Delta T = 7.248 \text{ °C}$

$C_{cal} = \frac{26.38 \text{ kJ}}{7.248 \text{ °C}} = 3.640 \text{ kJ/°C}$
How do we use $C_{\text{cal}}$?

Now that we know the $C_{\text{cal}}$ for that calorimeter, we can use it to find the heat of combustion of any combustible material.

If 5.00 g of a mixture of hydrocarbons is burned in our bomb calorimeter and it causes the temperature to rise 6.76 °C, how much energy (in kJ) is released during combustion?

$$q_{\text{cal}} = C_{\text{cal}} \Delta T$$

$C_{\text{cal}} = 3.640 \text{ kJ/°C}$; $\Delta T = 6.76 \text{ °C}$; $m=5.00 \text{ g}$,

$$q_{\text{cal}} = (3.640 \text{ kJ/°C}) \times (6.76 \text{ °C}) = 24.6 \text{ kJ}$$
Fuel Values and Food Values

**food value:** The amount of heat released when food is burned completely, also reported as a positive value in kJ/g or Cal/g (i.e., nutritional Calories where 1 Cal = 1 kcal).

- Most of the energy needed by our bodies comes from carbohydrates and fats, and the carbohydrates decompose in the intestines into glucose, $\text{C}_6\text{H}_{12}\text{O}_6$.
- The combustion of glucose produces energy that is quickly supplied to the body:

$$\text{C}_6\text{H}_{12}\text{O}_6(g) + 6 \text{ O}_2(g) \rightarrow 6 \text{ CO}_2(g) + 6 \text{ H}_2\text{O}(g) \quad \Delta H = -2803 \text{ kJ}$$
The body also produces energy from proteins and fats.

Fats can be stored because they are insoluble in water and produce more energy than proteins and carbohydrates.

The energy content reported on food labels is generally determined using a bomb calorimeter.
4. Hostess Twinkies are one of the icons of American junk food, making them also among the most maligned, especially given their unnaturally long shelf life. But are Twinkies really so bad for you?

a. Calculate the food value of a Twinkie (in Cal/g) if a 0.45 g Twinkie raises the temperature of a bomb calorimeter ($C_{cal}=6.20 \text{ kJ}/^\circ\text{C}$) by 1.06°C. (1 Cal = 4.184 kJ)

$$q_{cal} = C_{cal} \times \Delta T$$

$C_{cal} = 6.20 \text{ kJ}/^\circ\text{C}; \Delta T = 1.06 ^\circ\text{C}; m=0.45 \text{ g},$

$$q_{cal} = (6.20 \text{ kJ}/^\circ\text{C}) \times (1.06 ^\circ\text{C})/0.45\text{g} = 14.6 \text{ kJ/g}$$

$$14.6 \text{ kJ/g}/(4.184 \text{ kJ/Cal}) = 3.5 \text{ Cal/g}$$
Examples

b. If a typical Twinkie has a mass of 43 g, calculate the number of nutritional calories (Cal) in one Twinkie.

\[ 3.5 \text{ Cal/g} \times 43 \text{ g} = 150 \text{ Cal} \]
c. If a 12 fl. oz. can of Coke contains 140 Cal and a 16 oz. Starbucks Grande latte with 2% milk contains 190 Cal, is the Twinkie really so much worse than these drinks based on calorie content?

1 oz. = 30 grams (approximately)
12 oz. = 360 grams
16 oz. = 480 grams
Coke: 140 Cal/360 g = 0.389 Cal/g
Latte: 190 Cal/448 g = 0.396 Cal/g
Twinkie: 3.5 Cal/g (Yikes!)
Thermochemical Equations

thermochemical equation: shows both mass and heat / enthalpy relationships

• Consider: Water boils at 100°C and 1 atm. We can represent the boiling of 1 mole of water as a thermochemical equation:

\[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H = +44 \text{ kJ} \]

Note: \( \Delta H \) is positive since water must absorb heat to form steam.

• Consider: The formation of water from its elements releases heat:

\[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) \quad \Delta H = -571.6 \text{ kJ} \]

Note: \( \Delta H \) is negative since heat is lost to the surroundings.
Thermochemical Equations

Calculate the mass of hydrogen that must burn in oxygen to produce 50.0 kJ of heat.

\[2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) \quad \Delta H = -571.6 \text{ kJ}\]

2 mol H\textsubscript{2} produce 571.6 kJ of heat

\[
\frac{2 \text{ mol H}_2}{571.6 \text{ kJ}} = \frac{x \text{ mol}}{50 \text{ kJ}}
\]

x = 0.175 mol H\textsubscript{2} = 0.353 g H\textsubscript{2}
Consider the following thermochemical equation:

\[ 4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g) \quad \Delta H = -904 \text{ kJ} \]

a. Calculate the heat (in kJ) released when 50.0 g of ammonia react with excess oxygen.

\[
\frac{50.0 \text{ g NH}_3}{17.035 \text{ g/mol}} = 2.935 \text{ mol NH}_3
\]

\[
\frac{4 \text{ mol NH}_3}{904 \text{ kJ}} = \frac{2.935 \text{ mol}}{x \text{ kJ}}
\]

\[ x = 663.3 \text{ kJ} \]
Thermochemical Equations

b. Calculate the mass of steam produced when 675 kJ of heat are released.

\[ 4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g) \quad \Delta H = -904 \text{ kJ} \]

\[ \frac{6 \text{ mol H}_2\text{O}}{904 \text{ kJ}} = \frac{x \text{ mol}}{675 \text{ kJ}} \]

\[ x = 4.48 \text{ mol H}_2\text{O} = 80.7 \text{ g H}_2\text{O} \]
**Fuel Values**

**fuel value:** The amount of energy *released* from the combustion of hydrocarbon fuels is generally reported as a *positive value* in *kilojoules per gram* (in kJ/g).

Calculate the fuel value (as a positive value in kJ/g) given the thermochemical equations for the combustion of methane below:

\[ \text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \quad \Delta H = -803.3 \text{ kJ} \]

1 mol CH\(_4\) = 16.043 g  
Fuel Value = 803.3 kJ/16.043 g = **50.07 kJ/g**
Fuel Values

Calculate the fuel value (as a positive value in kJ/g) given the thermochemical equations for the combustion of propane below:

\[ \text{C}_3\text{H}_8(g) + 5 \text{O}_2(g) \rightarrow 3 \text{CO}_2(g) + 4 \text{H}_2\text{O}(g) \quad \Delta \text{H} = -2043.9 \text{ kJ} \]

1 mol C\textsubscript{3}H\textsubscript{8} = 44.097 g
Fuel Value = 2043.9 kJ/44.097 g = \textbf{46.35 kJ/g}
If the fuel value for butane (C$_4$H$_{10}$) is 45.75 kJ/g, calculate the heat of combustion (ΔH) in kJ per mole of butane.

1 mol C$_4$H$_{10}$ = 58.124 g
Fuel Value = 45.75 kJ/g = ΔH/58.124 g
ΔH = 2659 kJ

C$_4$H$_{10}$ + $\frac{13}{2}$O$_2$ → 4CO$_2$ + 5H$_2$O ΔH
**Hess’s Law**

**Hess’s Law of heat summation:** The enthalpy change for a reaction, $\Delta H$, is the same whether the reaction occurs in one step or in a series of steps:

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \ldots$$

This allows us to calculate $\Delta H$ from a variety of known values even if we can’t determine it experimentally.
A few reminders...

1. Sign of $\Delta H$ indicates if the reaction is exothermic ($\Delta H<0$) or endothermic ($\Delta H>0$). If the reaction is reversed, then the sign is reversed.

2. The coefficients in the chemical equation represent the numbers of moles of reactants and products for the $\Delta H$ given.

3. The physical states must be indicated for each reactant and product. Why? For $H_2O$, the liquid and the gaseous states vary by 44 kJ

4. $\Delta H$ is generally reported for reactants and products at 25°C.
Hess’s Law

Rule 1: For a reverse reaction, $\Delta H$ is equal in magnitude but opposite in sign.

If $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ $\quad \Delta H = +44 \text{ kJ}$

then $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$ $\quad \Delta H = -44 \text{ kJ}$
Rule 2: The coefficients in the chemical equation represent the numbers of moles of reactants and products for the $\Delta$H given.

$\rightarrow$ Consider heat like a reactant or product in a mole-to-mole ratio, where $\Delta$H is the heat released or absorbed for the moles of reactants and products indicated in the equation.
Hess’s Law

Rule 3: If all the coefficients in a chemical equation are multiplied by a factor \( n \)

\( \rightarrow \) ΔH is multiplied by factor \( n \):

If \( \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H = +6.01 \text{ kJ} \)

\( \rightarrow \ 2 \left[ \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \right] = 2 \text{H}_2\text{O}(s) \rightarrow 2 \text{H}_2\text{O}(l) \quad \Delta H = 2(+6.01 \text{ kJ}) = 12.0 \text{ kJ} \)

\( \rightarrow \ \frac{1}{2} \left[ \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(s) \right] = \frac{1}{2} \text{H}_2\text{O}(s) \rightarrow \frac{1}{2} \text{H}_2\text{O}(l) \quad \Delta H = \frac{1}{2} (+6.01 \text{ kJ}) = 3.01 \text{ kJ} \)
Example

Calculate the enthalpy change, $\Delta H$, for the following reaction

$$C_{\text{graphite}}(s) + 2 \text{H}_2(g) \rightarrow \text{CH}_4(g)$$

given that methane can be produced from the following series of steps:

(a) $C_{\text{graphite}}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$ \hspace{1cm} $\Delta H = -393.5$ kJ

(b) $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(l)$ \hspace{1cm} $\Delta H = -571.6$ kJ

(c) $\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$ \hspace{1cm} $\Delta H = -890.4$ kJ
Example

Rearranging the data allows us to calculate $\Delta H$ for the reaction:

(a) $\text{C}_{\text{graphite}}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$ \hspace{1cm} $\Delta H = -393.5 \text{ kJ}$

(b) $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(l)$ \hspace{1cm} $\Delta H = -571.6 \text{ kJ}$

(c) $\text{CO}_2(g) + 2 \text{H}_2\text{O}(l) \rightarrow \text{CH}_4(g) + 2 \text{O}_2(g)$ \hspace{1cm} $\Delta H = 890.4 \text{ kJ}$

$\text{C}_{\text{graphite}}(s) + 2 \text{H}_2(g) \rightarrow \text{CH}_4(g)$ \hspace{1cm} $\Delta H = -74.7 \text{ kJ}$
Example

Rearrange the following data:

(a) $\text{C}_{\text{graphite}}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H = -393.5 \text{ kJ}$

(b) $2 \text{CO}(g) + \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) \quad \Delta H = 566.0 \text{ kJ}$

to calculate the enthalpy change for the reaction:

$$2 \text{C}_{\text{graphite}}(s) + \text{O}_2(g) \rightarrow 2 \text{CO}(g)$$

$$\Delta H_{\text{total}} = -1353 \text{ kJ}$$
Hess’s Law

Additional Guidelines for Hess’ Law Problems:

• Multiply by the necessary factors to cancel all intermediate compounds.
• If the coefficients in an equation can be simplified, simplify them to get the correct coefficients for your final equation.
Example

From the following data:
(a) $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g) \quad \Delta H = -92.6 \text{ kJ}$
(b) $N_2(g) + 2 O_2(g) \rightarrow 2 NO_2(g) \quad \Delta H = 67.70 \text{ kJ}$
(c) $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l) \quad \Delta H = -571.6 \text{ kJ}$

Calculate the enthalpy change for the reaction:
$$4 NH_3(g) + 7 O_2(g) \rightarrow 4 NO_2(g) + 6 H_2O(l)$$

$$4 NH_3(g) \rightarrow 2 N_2(g) + 6 H_2(g) \quad \text{(rev., x2)} \quad \Delta H = 185.2 \text{ kJ}$$
$$2 N_2(g) + 4 O_2(g) \rightarrow 4 NO_2(g) \quad \text{(x2)} \quad \Delta H = 135.4 \text{ kJ}$$
$$6 H_2(g) + 3 O_2(g) \rightarrow 6 H_2O(l) \quad \text{(x3)} \quad \Delta H = -1714.8 \text{ kJ}$$

$\Delta H_{total} = -1394.2 \text{ kJ}$