

Chemistry, The Central Science, 11th edition
Theodore L. Brown; H. Eugene LeMay, Jr.;
and Bruce E. Bursten

Chapter 5

Thermochemistry

Dr. Ayman Nafady



Energy

- Energy is the ability to do work or transfer heat.
 - Energy used to cause an object that has mass to move is called **work**.
 - Energy used to cause the temperature of an object to rise is called **heat**.



Potential Energy

Potential energy is energy an object possesses by virtue of its position or chemical composition.



Kinetic Energy

Kinetic energy is energy an object possesses by virtue of its motion.

$$KE = \frac{1}{2} mv^2$$



Units of Energy

- The SI unit of energy is the joule (J).

$$1 \text{ J} = 1 \frac{\text{kg m}^2}{\text{s}^2}$$

- An older, non-SI unit is still in widespread use: the calorie (cal).

$$1 \text{ cal} = 4.184 \text{ J}$$



Definitions: System and Surroundings



- The **system** includes the molecules we want to study (here, the hydrogen and oxygen molecules).
- The **surroundings** are everything else (here, the cylinder and piston).

Definitions: Work

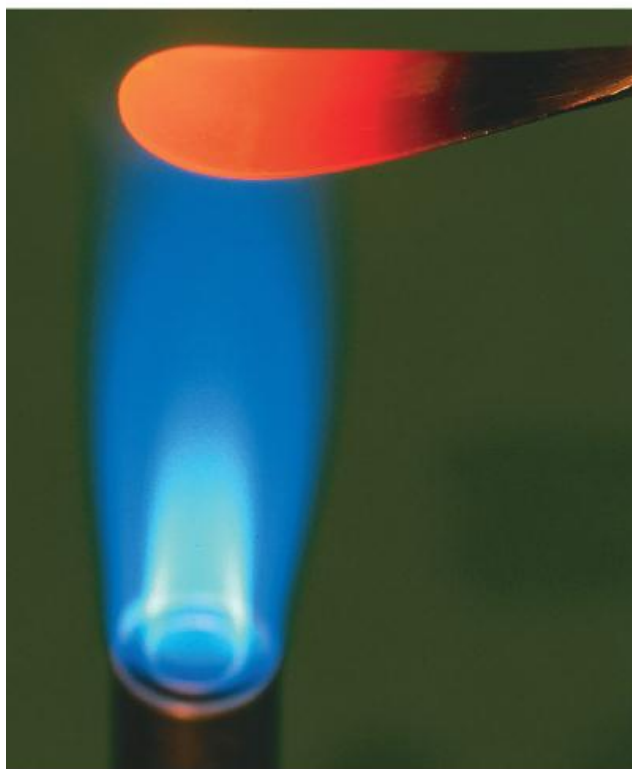
- Energy used to move an object over some distance is **work**.

- $w = F \times d$

where w is work, F is the force, and d is the distance over which the force is exerted.



Heat



- Energy can also be transferred as heat.
- Heat flows from warmer objects to cooler objects.

Conversion of Energy



- Energy can be converted from one type to another.
- For example, the cyclist above has potential energy as she sits on top of the hill.

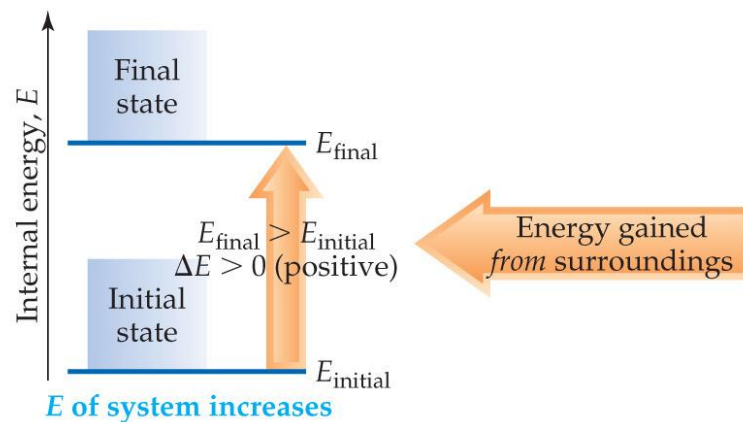
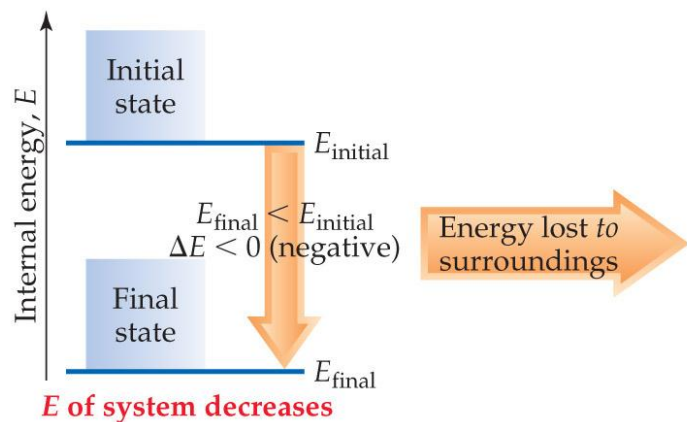
Conversion of Energy



- As she coasts down the hill, her potential energy is converted to kinetic energy.
- At the bottom, all the potential energy she had at the top of the hill is now kinetic energy.

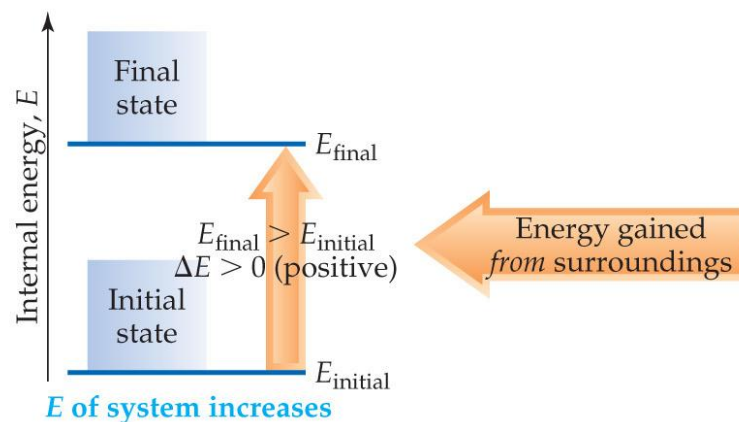
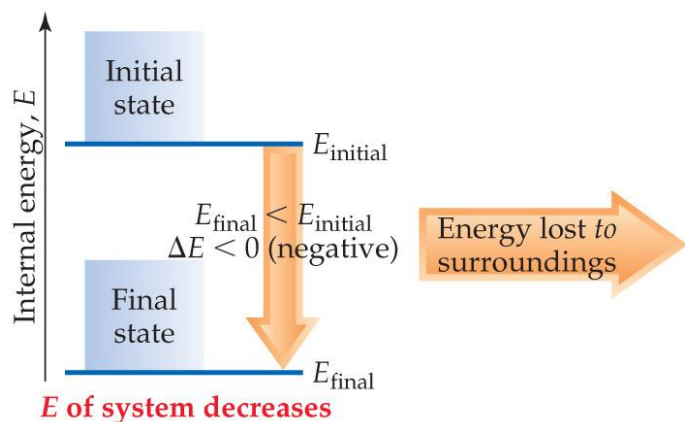
First Law of Thermodynamics

- Energy is neither created nor destroyed.
- In other words, the total energy of the universe is a constant; if the system loses energy, it must be gained by the surroundings, and vice versa.



Internal Energy

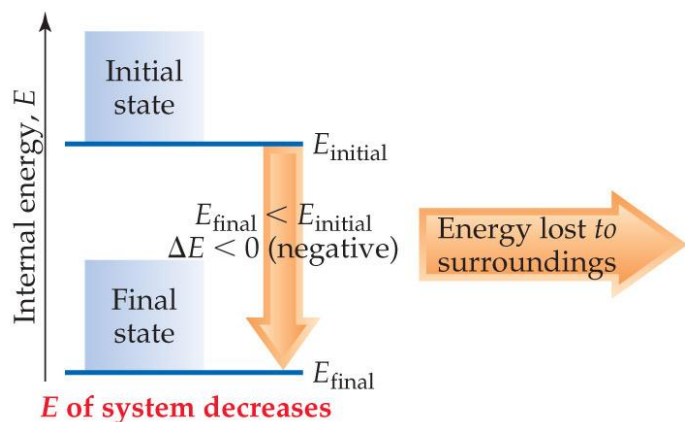
The internal energy of a system is the sum of all kinetic and potential energies of all components of the system; we call it E .



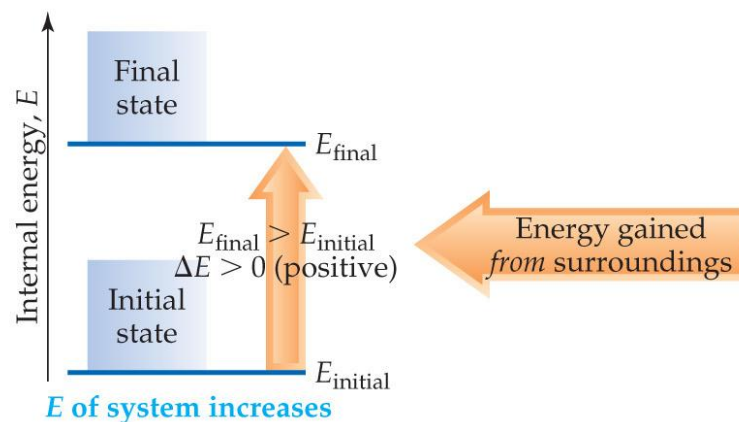
Internal Energy

By definition, the change in internal energy, ΔE , is the final energy of the system minus the initial energy of the system:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$



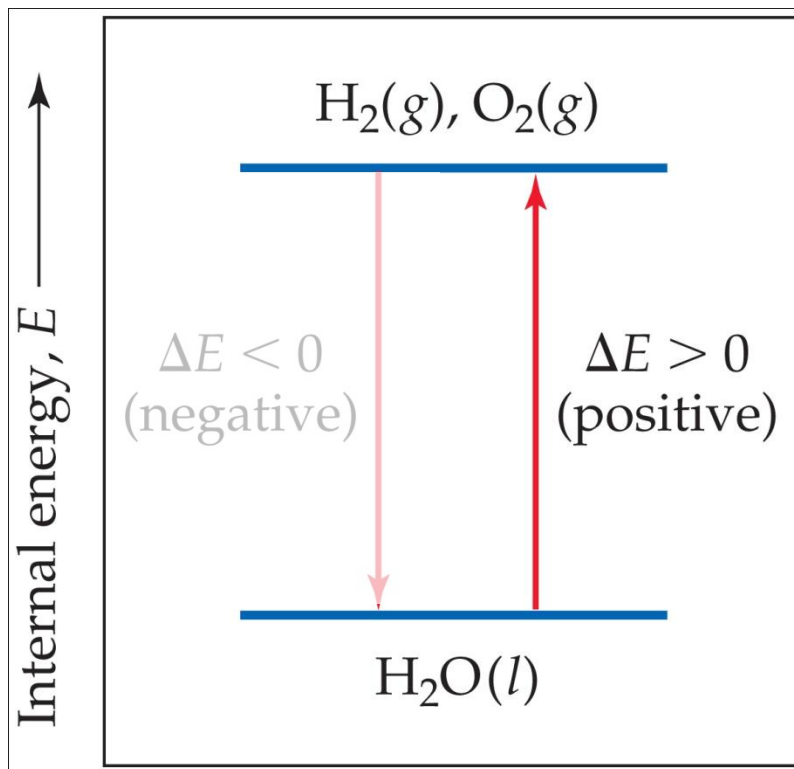
System loses energy



System gains energy

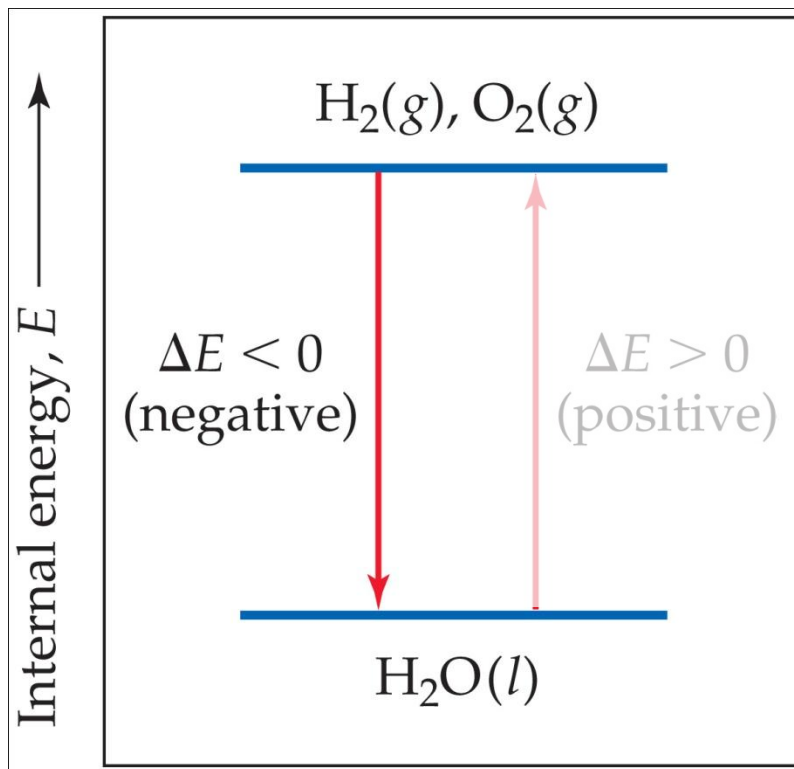


Changes in Internal Energy



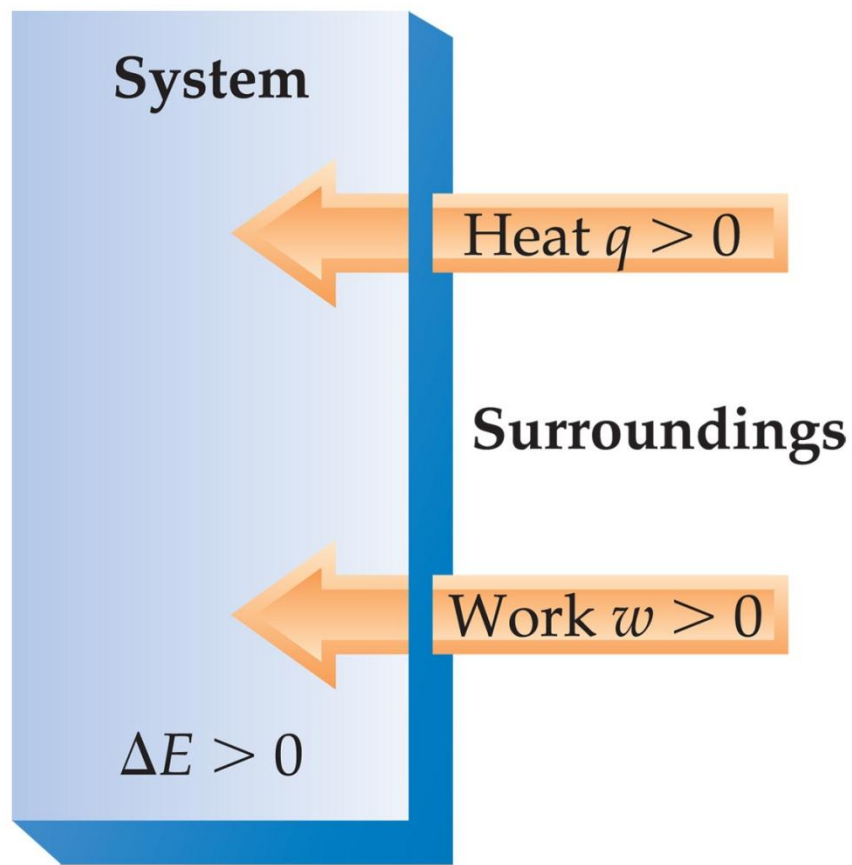
- If $\Delta E > 0$, $E_{\text{final}} > E_{\text{initial}}$
 - Therefore, the system *absorbed* energy from the surroundings.
 - This energy change is called **endergonic**.

Changes in Internal Energy



- If $\Delta E < 0$, $E_{\text{final}} < E_{\text{initial}}$
 - Therefore, the system *released* energy to the surroundings.
 - This energy change is called **exergonic**.

Changes in Internal Energy



- When energy is exchanged between the system and the surroundings, it is exchanged as either heat (q) or work (w).
- That is, $\Delta E = q + w$.

ΔE , q , w , and Their Signs

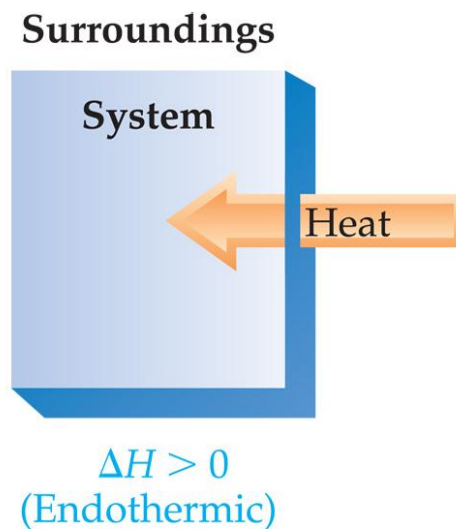
TABLE 5.1 ■ Sign Conventions for q , w , and ΔE

| | | |
|----------------|---|---|
| For q | + means system <i>gains</i> heat | – means system <i>loses</i> heat |
| For w | + means work done <i>on</i> system | – means work done <i>by</i> system |
| For ΔE | + means <i>net gain</i> of energy by system | – means <i>net loss</i> of energy by system |



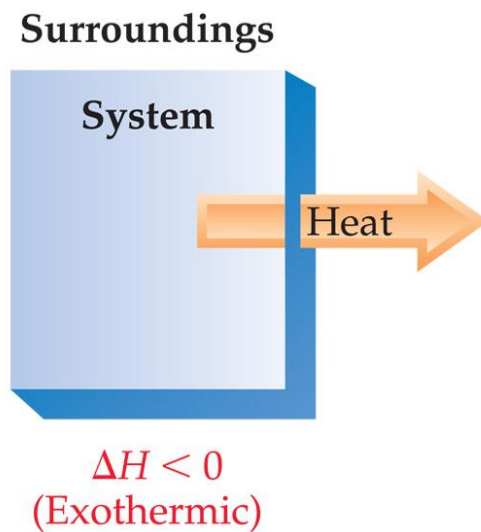
Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.



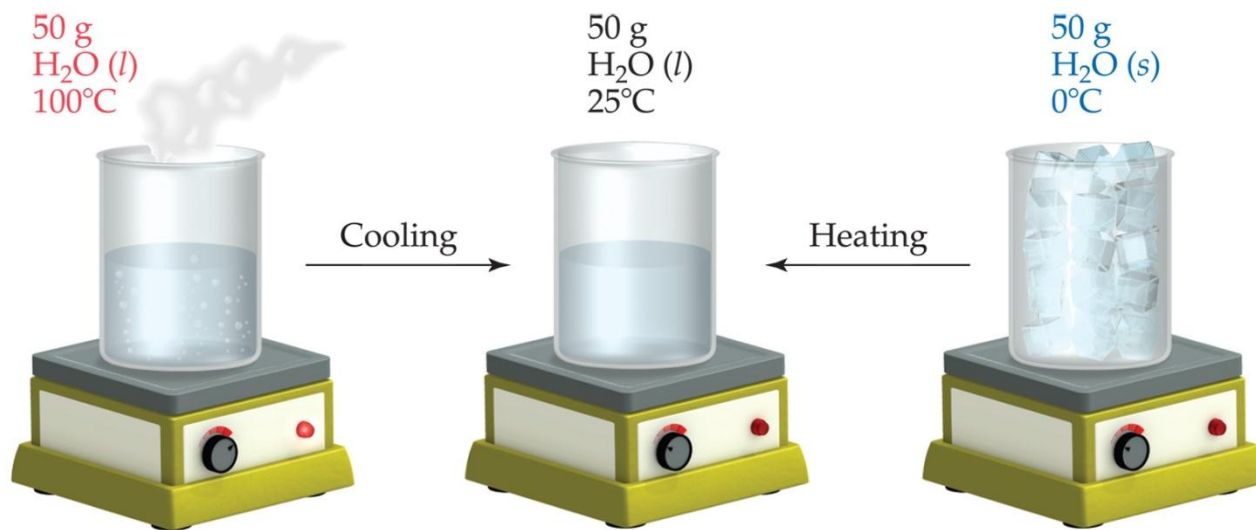
Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.
- When heat is released by the system into the surroundings, the process is **exothermic**.



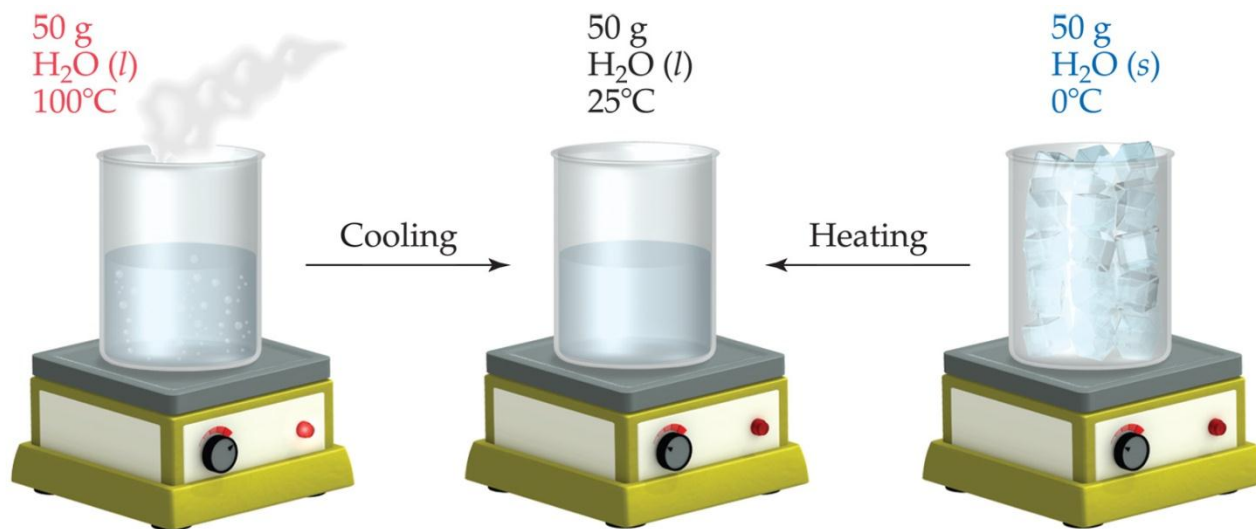
State Functions

Usually we have no way of knowing the internal energy of a system; finding that value is simply too complex a problem.



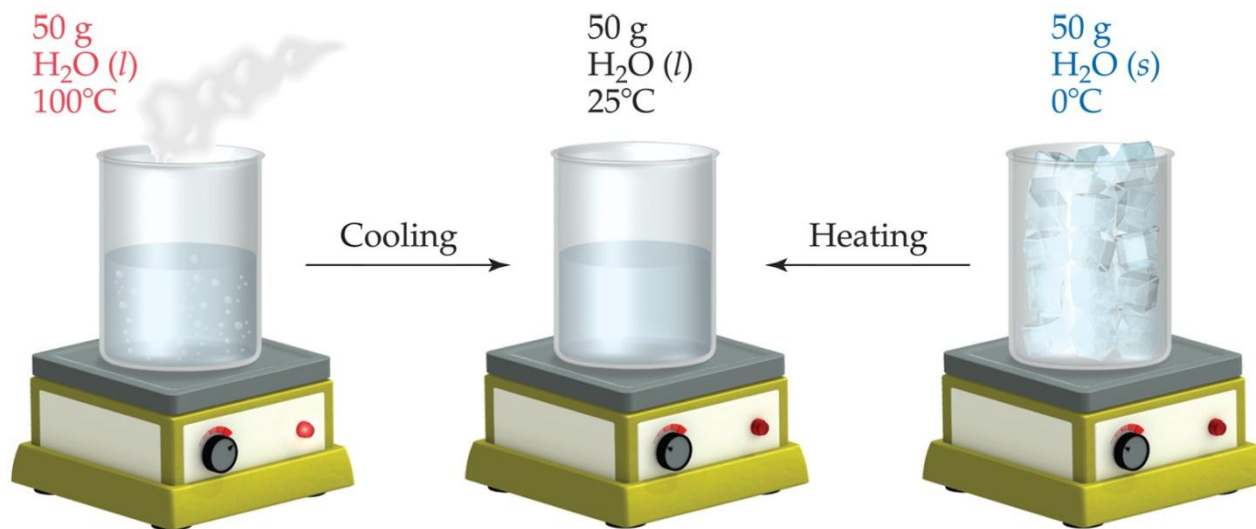
State Functions

- However, we do know that the internal energy of a system is independent of the path by which the system achieved that state.
 - In the system below, the water could have reached room temperature from either direction.

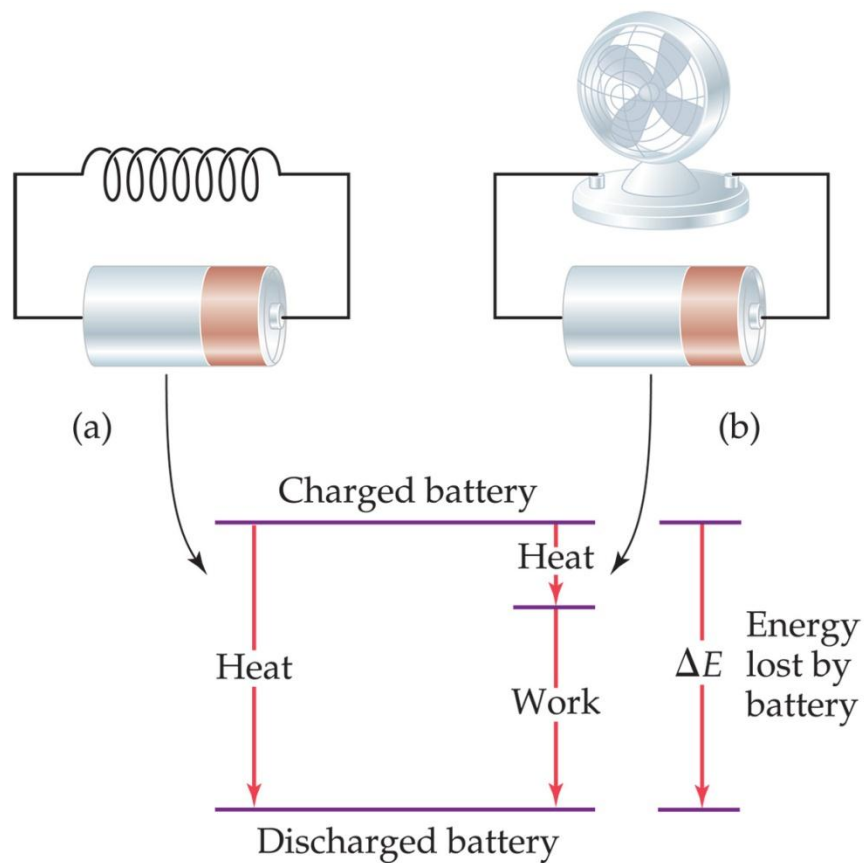


State Functions

- Therefore, internal energy is a state function.
- It depends only on the present state of the system, not on the path by which the system arrived at that state.
- And so, ΔE depends only on E_{initial} and E_{final} .

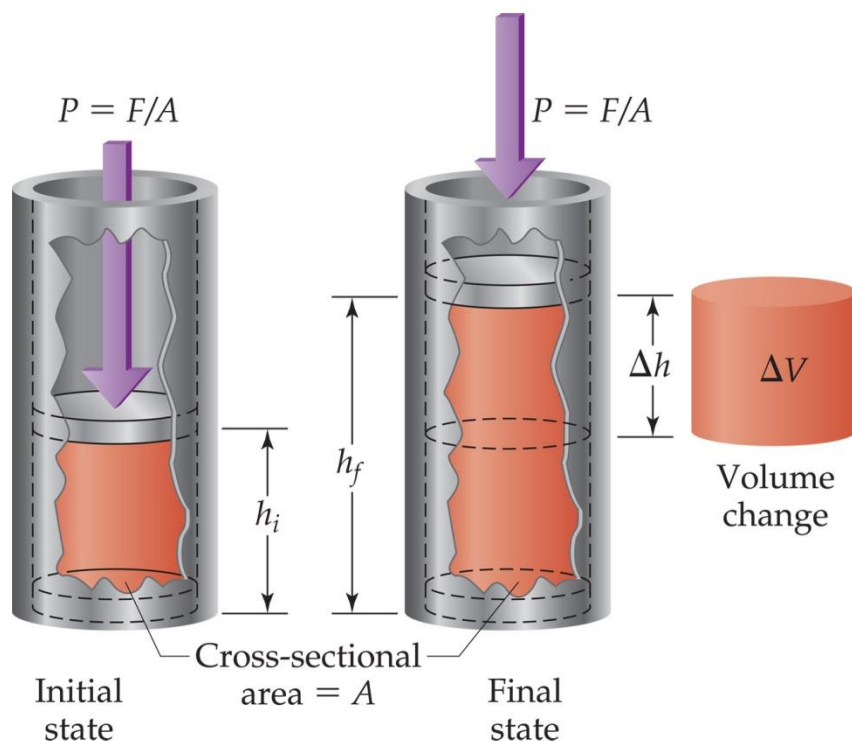


State Functions



- However, q and w are *not* state functions.
- Whether the battery is shorted out or is discharged by running the fan, its ΔE is the same.
 - But q and w are different in the two cases.

Work

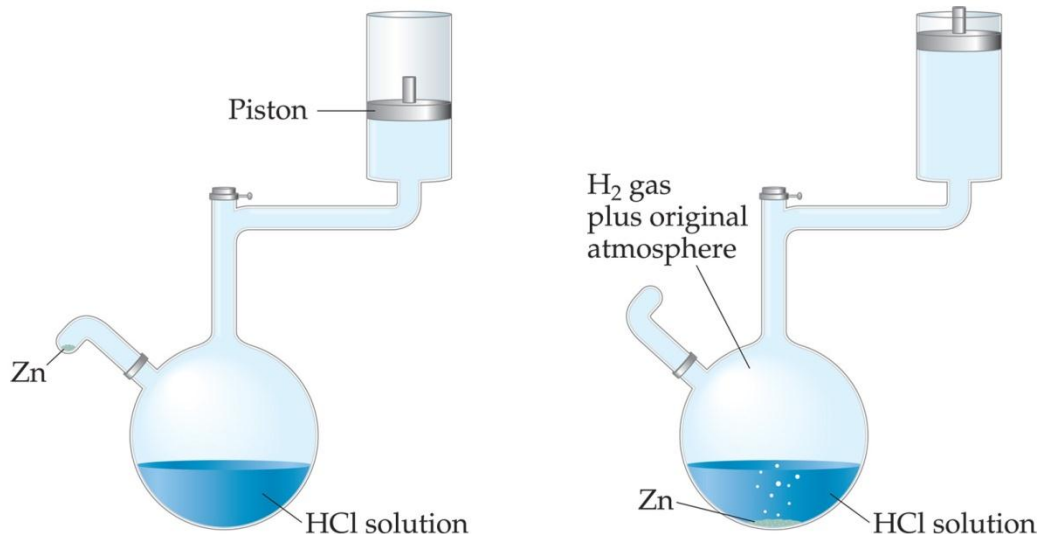


Usually in an open container the only work done is by a gas pushing on the surroundings (or by the surroundings pushing on the gas).

Work

We can measure the work done by the gas if the reaction is done in a vessel that has been fitted with a piston.

$$w = -P\Delta V$$



Enthalpy

- If a process takes place at constant pressure (as the majority of processes we study do) and the only work done is this pressure-volume work, we can account for heat flow during the process by measuring the **enthalpy** of the system.
- Enthalpy is the internal energy plus the product of pressure and volume:

$$H = E + PV$$



Enthalpy

- When the system changes at constant pressure, the change in enthalpy, ΔH , is

$$\Delta H = \Delta(E + PV)$$

- This can be written

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



Enthalpy

- Since $\Delta E = q + w$ and $w = -P\Delta V$, we can substitute these into the enthalpy expression:

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

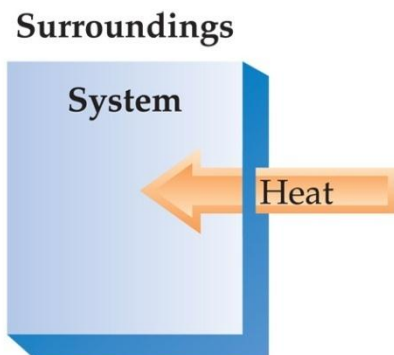
$$\Delta H = (q + w) - w$$

$$\Delta H = q$$

- So, at constant pressure, the change in enthalpy *is* the heat gained or lost.

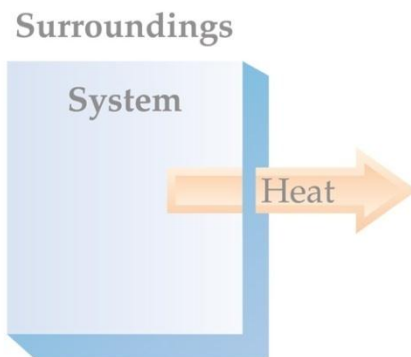


Endothermicity and Exothermicity



$\Delta H > 0$
(Endothermic)

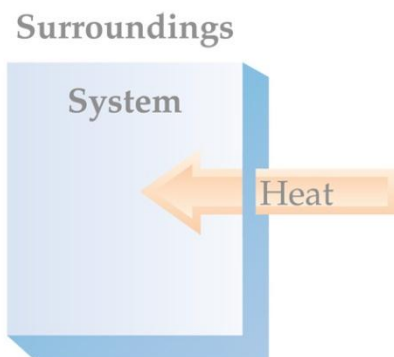
- A process is endothermic when ΔH is positive.



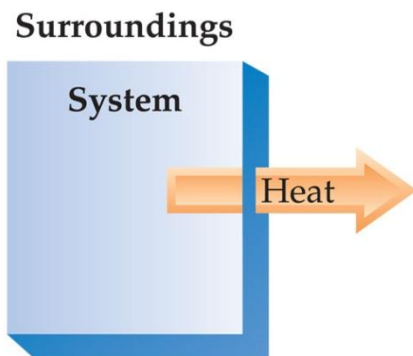
$\Delta H < 0$
(Exothermic)



Endothermicity and Exothermicity



$\Delta H > 0$
(Endothermic)



$\Delta H < 0$
(Exothermic)

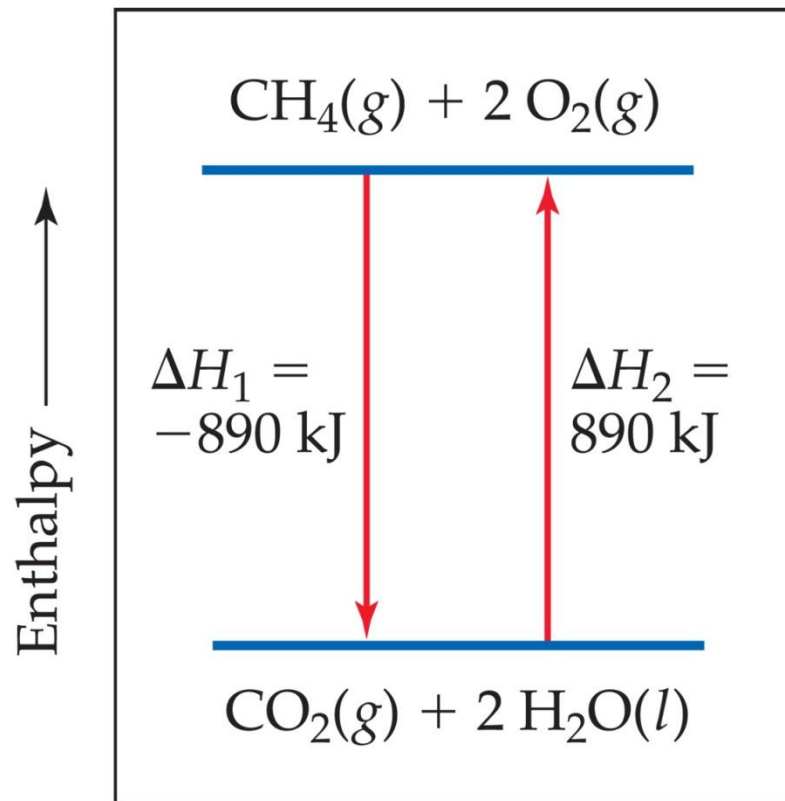
- A process is endothermic when ΔH is positive.
- A process is exothermic when ΔH is negative.



Enthalpy of Reaction

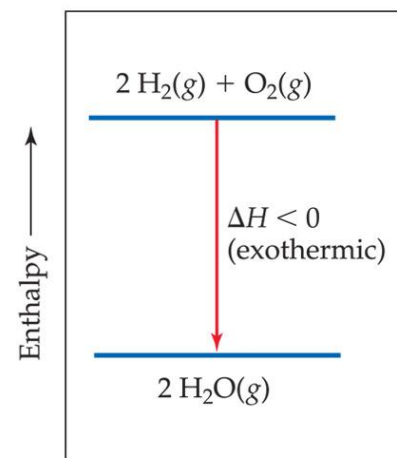
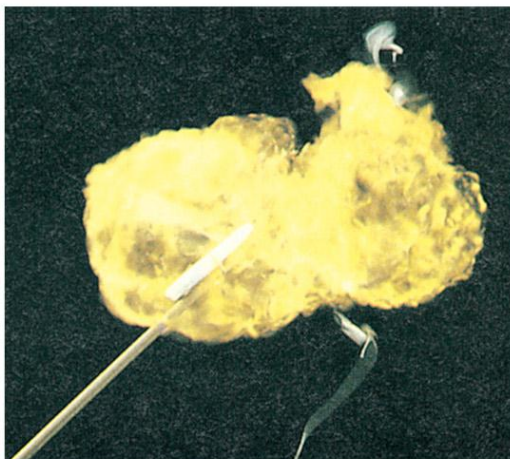
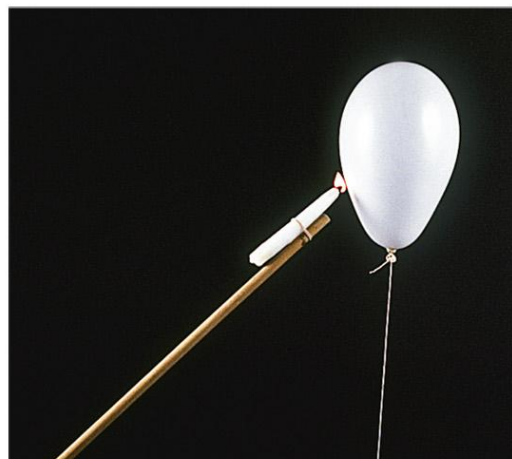
The *change* in enthalpy, ΔH , is the enthalpy of the products minus the enthalpy of the reactants:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$



Enthalpy of Reaction

This quantity, ΔH , is called the enthalpy of reaction, or the heat of reaction.



The Truth about Enthalpy

1. Enthalpy is an extensive property.
2. ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction.
3. ΔH for a reaction depends on the state of the products and the state of the reactants.



Exercise 5.2 Relating Heat and Work to Changes of Internal Energy

Substances A and B react to form a solid product: $A_{(g)} + B_{(g)} \rightarrow C_{(s)}$. As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

Solution

Analyze: The question asks us to determine ΔE , given information about q and w .

Plan: We first determine the signs of q and w (Table 5.1) and then use Equation $\Delta E = q + w$, to calculate ΔE .

Solve: Heat is transferred **from** the system to the surroundings, and work is **done on** the system by the surroundings, so q is **negative** and w is **positive**: $q = -1150 \text{ J}$ and $w = 480 \text{ kJ}$. Thus,

$$\Delta E = q + w = (-1150 \text{ J}) + (480 \text{ J}) = -670 \text{ J}$$

The negative value of ΔE tells us that a net quantity of 670 J of energy has been transferred from the system to the surroundings.



Determining the Sign of ΔH

Indicate the sign of the enthalpy change, ΔH , in each of the following processes carried out under atmospheric pressure, and indicate whether the process is endothermic or exothermic:

(a) An ice cube melts; (b) 1 g of butane (C_4H_{10}) is combusted in sufficient oxygen to give complete combustion to CO_2 and H_2O .

$$\Delta H = q$$

Plan: We must predict whether heat is absorbed or released by the system in each process.

Processes in which **heat** is **absorbed** are **endothermic** and have a **positive** sign for ΔH ;

Processes in which **heat** is **released** are **exothermic** and have a **negative** sign for ΔH .

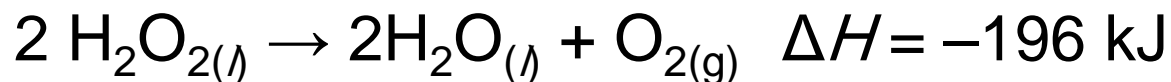
Solve: In (a) The ice cube absorbs heat from the surroundings as it melts, so ΔH is **positive** and the process is **endothermic**.

In (b) the system is the 1 g of butane and the oxygen required to combust it. The combustion of butane in oxygen gives off heat, so ΔH is **negative** and the process is **exothermic**.



Relating ΔH to Quantities of Reactants and Products

Hydrogen peroxide can decompose to water and oxygen by the following reaction:



Calculate the value of q when 5.00 g of $\text{H}_2\text{O}_{2(l)}$ decomposes at constant pressure.

First, we must convert moles to KJ of energy.

Second, we must convert grams of H_2O_2 to moles of H_2O_2 .

2 moles of H_2O_2 releases -196 KJ

1 mole gives -98 KJ

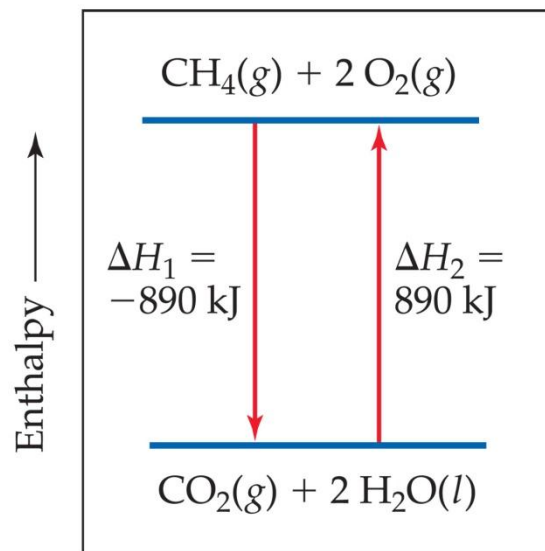
$$N = m/M_r$$

$$N = 5/34 \text{ ----- } x$$

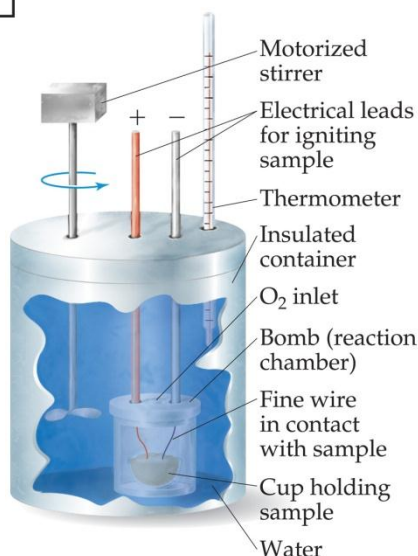
$$X = -14.4 \text{ KJ}$$



Calorimetry



Since we cannot know the exact enthalpy of the reactants and products, we measure ΔH through **calorimetry**, the measurement of heat flow.



Heat Capacity and Specific Heat

The amount of energy required to raise the temperature of a substance by 1 K (1°C) is its **heat capacity**.

| Elements | | Compounds | |
|--------------------|--------------------------|-----------------------|--------------------------|
| Substance | Specific Heat (J/g-K) | Substance | Specific Heat (J/g-K) |
| N ₂ (g) | 1.04 | H ₂ O(l) | 4.18 |
| Al(s) | 0.90 | CH ₄ (g) | 2.20 |
| Fe(s) | 0.45 | CO ₂ (g) | 0.84 |
| Hg(l) | 0.14 | CaCO ₃ (s) | 0.82 |



Heat Capacity and Specific Heat

We define **specific heat capacity** (or simply **specific heat**) as the amount of energy required to raise the temperature of 1 g of a substance by 1 K.

| Elements | | Compounds | |
|--------------------|--------------------------|-----------------------|--------------------------|
| Substance | Specific Heat (J/g-K) | Substance | Specific Heat (J/g-K) |
| N ₂ (g) | 1.04 | H ₂ O(l) | 4.18 |
| Al(s) | 0.90 | CH ₄ (g) | 2.20 |
| Fe(s) | 0.45 | CO ₂ (g) | 0.84 |
| Hg(l) | 0.14 | CaCO ₃ (s) | 0.82 |



Heat Capacity and Specific Heat

Specific heat, then, is

$$\text{Specific heat} = \frac{\text{heat transferred}}{\text{mass} \times \text{temperature change}}$$

$$s = \frac{q}{m \times \Delta T}$$



Constant Pressure Calorimetry



By carrying out a reaction in aqueous solution in a simple calorimeter such as this one, one can indirectly measure the heat change for the system by measuring the heat change for the water in the calorimeter.



Constant Pressure Calorimetry



Because the specific heat for water is well known (4.184 J/g-K), we can measure ΔH for the reaction with this equation:

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



Example: (a) How much heat is needed to warm 250 g of water (about 1 cup) from 22 ° C (about room temperature) to near its boiling point, 98 °C? The specific heat of water is 4.18 J/g-K.

(b) What is the molar heat capacity of water?

Analyze: In part **(a)** we must find the quantity of heat (q) needed to warm the water, given the mass of water (m), its temperature change (ΔT), and its specific heat (C_s). In part **(b)** we must calculate the molar heat capacity (heat capacity per mole, C_m) of water from its specific heat (heat capacity per gram).

Solve:

(a) The water undergoes a temperature change of

Using the equation

The heat needed is = 7.9×10^4 J

$$\Delta T = 98\text{ }^{\circ}\text{C} - 22\text{ }^{\circ}\text{C} = 76\text{ }^{\circ}\text{C} = 76\text{ K}$$

$$q = C_s \times m \times \Delta T \\ = (4.18\text{ J/g-K})(250\text{ g})(76\text{ K}) = 7.9 \times 10^4\text{ J}$$

(b) The molar heat capacity is the heat capacity of one mole of substance.

Using the equation $C_m = C_s \times m$

$$1\text{ mol H}_2\text{O} = 18.0\text{ g H}_2\text{O}$$

$$C_m = \left(4.18\frac{\text{J}}{\text{g-K}}\right)\left(\frac{18.0\text{ g}}{1\text{ mol}}\right) = 75.2\text{ J/mol-K}$$



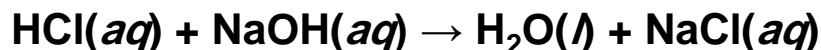
Exercise: Measuring ΔH Using a Coffee-Cup Calorimeter

When a student mixes 50 mL of 1.0 *M* HCl and 50 mL of 1.0 *M* NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 °C to 27.5 °C.

Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming that the total volume of the solution is 100 mL, its density is 1.0 g/mL, and specific heat is 4.18 J/g-K.

Analyze:

Mixing solutions of HCl and NaOH results in an acid–base reaction:



We need to calculate the heat produced per mole of HCl, given the temperature increase of the solution, the number of moles of HCl and NaOH involved, and the density and specific heat of the solution.

Because the total volume of the solution is 100 mL, its mass is

$$(100 \text{ mL})(1.0 \text{ g/mL}) = 100 \text{ g}$$

$$\Delta T = 27.5 \text{ }^{\circ}\text{C} - 21.0 \text{ }^{\circ}\text{C} = 6.5 \text{ }^{\circ}\text{C} = 6.5 \text{ K}$$

$$q_{\text{rxn}} = -C_s \times m \times \Delta T$$

$$= -(4.18 \text{ J/g-K})(100 \text{ g})(6.5 \text{ K}) = -2.7 \times 10^3 \text{ J} = -2.7 \text{ kJ}$$

$$\Delta H = q_p = -2.7 \text{ kJ}$$

The temperature change is

Using the equation, we have



To express the enthalpy change on a molar basis, we use the fact that the number of moles of HCl is given by the product of the respective solution volumes (50 mL = 0.050 L) and concentrations (1.0 M = 1.0 mol/L):

Thus, the enthalpy change per mole of HCl is

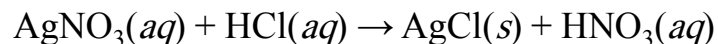
$$(0.050 \text{ L})(1.0 \text{ mol/L}) = 0.050 \text{ mol}$$

$$\Delta H = -2.7 \text{ kJ}/0.050 \text{ mol} = -54 \text{ kJ/mol}$$

Check: ΔH is negative (exothermic), which is expected for the reaction of an acid with a base and evidenced by the fact that the reaction causes the temperature of the solution to increase.

Practice Exercise

When 50.0 mL of 0.100 M AgNO₃ and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30 °C to 23.11 °C. The temperature increase is caused by the following reaction:



Calculate ΔH for this reaction in kJ/mol AgNO₃, assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g °C.

Answer: -68,000 J/mol = -68 kJ/mol

$$q = -C_s \times m \times \Delta t$$

$$q = -(4.18 \text{ J/g}\cdot\text{K})(100 \text{ g})(23.11-22.30)$$

$$q = -338.58 \text{ J}$$

$$q = -0.3386 \text{ KJ}$$

$$\begin{aligned} (n) \text{ Moles of AgNO}_3 &= M \times V \\ &= 0.1 \times 50 \text{ mL}/1000 \text{ mL} \\ \text{Then } n &= 0.005 \text{ mol} \end{aligned}$$

$$\begin{aligned} \Delta H &= -0.3386 \text{ KJ}/0.005 \text{ mol} \\ &= -67.716 \text{ KJ/mol} \\ &= -68 \text{ KJ/mol} \end{aligned}$$

Thermochemistry



Exercise 5.7 Measuring q_{rxn} Using a Bomb Calorimeter

Methylhydrazine (CH_6N_2) is used as a liquid rocket fuel. The combustion of methylhydrazine with oxygen produces $\text{N}_2(\text{g})$, $\text{CO}_2(\text{g})$, and $\text{H}_2\text{O}(\text{l})$:



When 4.00 g of methylhydrazine is combusted in a **bomb calorimeter**, the temperature of the calorimeter increases from 25.00°C to 39.50°C . In a separate experiment the heat capacity of the calorimeter is measured to be $7.794 \text{ kJ}/^\circ \text{C}$. Calculate the heat of reaction for the combustion of a mole of CH_6N_2 .

Solution

Analyze: We are given a temperature change and the total heat capacity of the calorimeter. We are also given the amount of reactant combusted. **Our goal is to calculate the enthalpy change per mole for combustion of the reactant.**

Plan: We will first calculate the heat evolved for the combustion of the 4.00-g sample. We will then convert this heat to a molar quantity.

Solve:

For combustion of the 4.00-g sample of methylhydrazine, the temperature change of the calorimeter is

We can use ΔT and the value for C_{cal} to calculate the heat of reaction (Equation 5.24):

We can readily convert this value to the heat of reaction for a mole of CH_6N_2 :

$$\Delta T = (39.50^\circ \text{C} - 25.00^\circ \text{C}) = 14.50^\circ \text{C}$$

$$q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T = -(7.794 \text{ kJ}/^\circ \text{C})(14.50^\circ \text{C}) = -113.0 \text{ kJ}$$

$$\left(\frac{-113.0 \text{ kJ}}{4.00 \text{ g CH}_6\text{N}_2} \right) \times \left(\frac{46.1 \text{ g CH}_6\text{N}_2}{1 \text{ mol CH}_6\text{N}_2} \right) = -1.30 \times 10^3 \text{ kJ/mol CH}_6\text{N}_2$$

$$4 \text{ g (CH}_6\text{N}_2) \longrightarrow -113 \text{ kJ} \quad X = (46.1 \times -113)/4$$

$$1 \text{ mole} = 46.1 \text{ g} \longrightarrow x \quad = -1.3 \times 10^3 \text{ kJ/mol}$$



Practice Exercise

A 0.5865-g sample of lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) is burned in a calorimeter whose heat capacity is $4.812 \text{ kJ}^\circ\text{C}$. The temperature increases from 23.10°C to 24.95°C . Calculate the heat of combustion of lactic acid (a) per gram and (b) per mole.

Answers: (a) -15.2 kJ/g , (b) -1370 kJ/mol .

For Bomb Calorimeter **$q = -C_s \times \Delta t$**

$$q = -(4.18 \text{ J/g}\cdot\text{C})(24.95 - 23.10)$$

$$q = -8.90 \text{ J} \longrightarrow 0.5865 \text{ g}$$

The heat evolved for the combustion of the 0.5865g sample

$$q = \text{ } \times \longrightarrow 1 \text{ g}$$

(a) The heat of combustion per g of lactic acid

$$q = X = 8.90/0.586 = -15.2 \text{ kJ/g}$$

(b) The heat of combustion per mol of lactic acid

Mr of ($\text{HC}_3\text{H}_5\text{O}_3$) = 90 then 1 mol contains 90 g

$$q = 90 \times 15.2 = 1366 = 1370 \text{ kJ/mol}$$



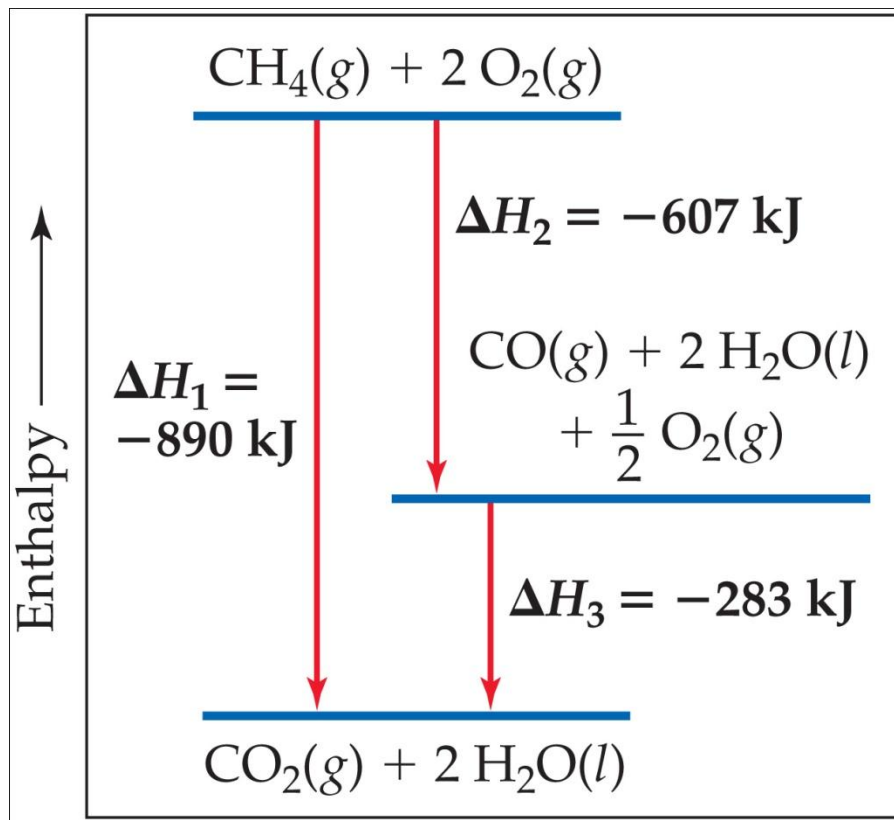
Hess's Law

- ΔH is well known for many reactions, and it is inconvenient to measure ΔH for every reaction in which we are interested.
- However, we can estimate ΔH using published ΔH values and the properties of enthalpy.

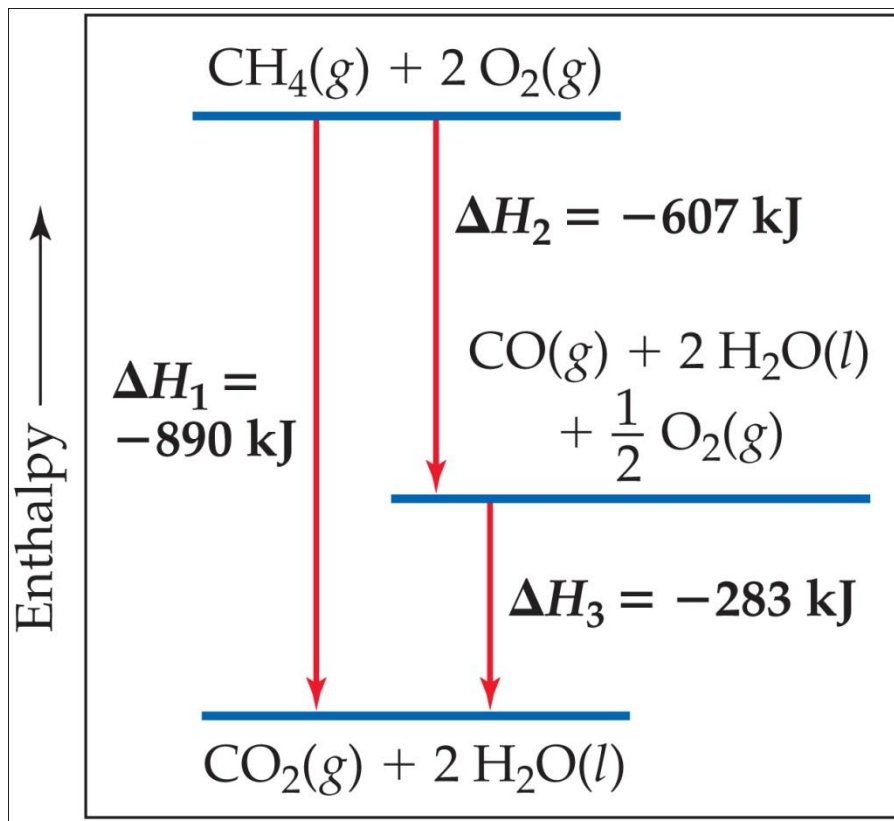


Hess's Law

Hess's law states that "if a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps."



Hess's Law



Because ΔH is a state function, the total enthalpy change depends only on the initial state of the reactants and the final state of the products.

The total enthalpy change does not rely on the path taken from beginning to end.

Thermochemistry



Enthalpies of Formation

An enthalpy of formation, ΔH_f , is defined as the enthalpy change for the reaction in which a compound is made from its constituent elements in their elemental forms.

There are a few rules that must be followed when manipulating a reaction.

- (I) The reaction can be reversed. This will change the sign of ΔH_f .
- (II) The reaction can be multiplied by a constant.
- (III) The value of ΔH_f must be multiplied by the same constant.

Any combination of the first two rules may be used.



Standard Enthalpies of Formation

Standard enthalpies of formation, ΔH_f° , are measured under standard conditions (25 ° C and 1.00 atm pressure).

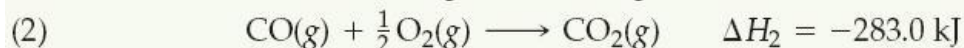
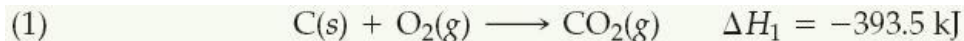
TABLE 5.3 ■ Standard Enthalpies of Formation, ΔH_f° , at 298 K

| Substance | Formula | ΔH_f° (kJ/mol) | Substance | Formula | ΔH_f° (kJ/mol) |
|-------------------|-------------------|-----------------------------|--------------------|-------------------------|-----------------------------|
| Acetylene | $C_2H_2(g)$ | 226.7 | Hydrogen chloride | $HCl(g)$ | -92.30 |
| Ammonia | $NH_3(g)$ | -46.19 | Hydrogen fluoride | $HF(g)$ | -268.60 |
| Benzene | $C_6H_6(l)$ | 49.0 | Hydrogen iodide | $HI(g)$ | 25.9 |
| Calcium carbonate | $CaCO_3(s)$ | -1207.1 | Methane | $CH_4(g)$ | -74.80 |
| Calcium oxide | $CaO(s)$ | -635.5 | Methanol | $CH_3OH(l)$ | -238.6 |
| Carbon dioxide | $CO_2(g)$ | -393.5 | Propane | $C_3H_8(g)$ | -103.85 |
| Carbon monoxide | $CO(g)$ | -110.5 | Silver chloride | $AgCl(s)$ | -127.0 |
| Diamond | $C(s)$ | 1.88 | Sodium bicarbonate | $NaHCO_3(s)$ | -947.7 |
| Ethane | $C_2H_6(g)$ | -84.68 | Sodium carbonate | $Na_2CO_3(s)$ | -1130.9 |
| Ethanol | $C_2H_5OH(l)$ | -277.7 | Sodium chloride | $NaCl(s)$ | -410.9 |
| Ethylene | $C_2H_4(g)$ | 52.30 | Sucrose | $C_{12}H_{22}O_{11}(s)$ | -2221 |
| Glucose | $C_6H_{12}O_6(s)$ | -1273 | Water | $H_2O(l)$ | -285.8 |
| Hydrogen bromide | $HBr(g)$ | -36.23 | Water vapor | $H_2O(g)$ | -241.8 |

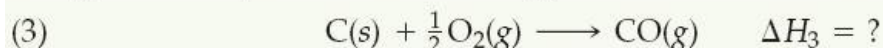


Sample Exercise 5.8 Using Hess's Law to Calculate ΔH

The enthalpy of reaction for the combustion of C to CO_2 is -393.5 kJ/mol C , and the enthalpy for the combustion of CO to CO_2 is -283.0 kJ/mol CO :



Using these data, calculate the enthalpy for the combustion of C to CO:

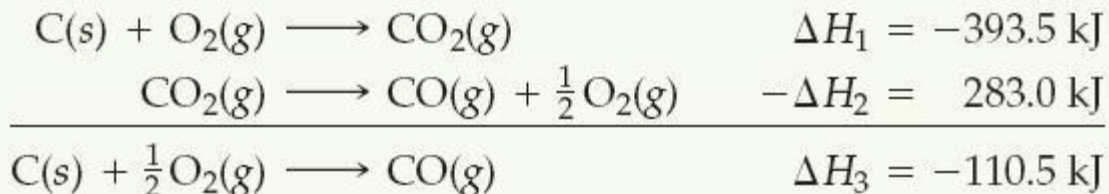


Solution

Analyze: We are given two thermochemical equations, and our goal is to combine them in such a way as to obtain the third equation and its enthalpy change.

Plan: We will use Hess's law. In doing so, we first note the numbers of moles of substances among the reactants and products in the target equation, (3). We then manipulate equations (1) and (2) to give the same number of moles of these substances, so that when the resulting equations are added, we obtain the target equation. At the same time, we keep track of the enthalpy changes, which we add.

Solve: To use equations (1) and (2), we arrange them so that $\text{C}(s)$ is on the reactant side and $\text{CO}(g)$ is on the product side of the arrow, as in the target reaction, equation (3). Because equation (1) has $\text{C}(s)$ as a reactant, we can use that equation just as it is. We need to turn equation (2) around, however, so that $\text{CO}(g)$ is a product. Remember that when reactions are turned around, the sign of ΔH is reversed. We arrange the two equations so that they can be added to give the desired equation:



Sample Exercise 5.8 Using Hess's Law to Calculate ΔH

Solution (continued)

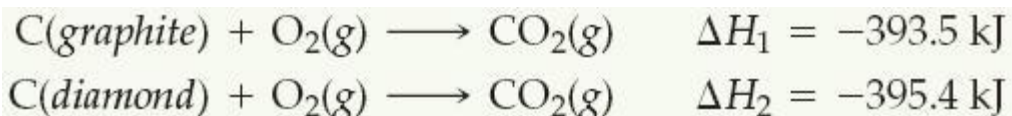
When we add the two equations, $\text{CO}_2(g)$ appears on both sides of the arrow and therefore cancels out.

Likewise, $\frac{1}{2}\text{O}_2(g)$ is eliminated from each side.

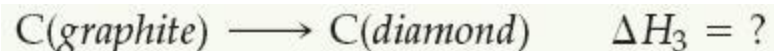
Comment: It is sometimes useful to add subscripts to the enthalpy changes, as we have done here, to keep track of the associations between the chemical reactions and their ΔH values.

Practice Exercise

Carbon occurs in two forms, graphite and diamond. The enthalpy of the combustion of graphite is -393.5 kJ/mol and that of diamond is -395.4 kJ/mol :



Calculate for the conversion of graphite to diamond:

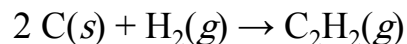


Answer: $\Delta H_3 = +1.9 \text{ kJ}$

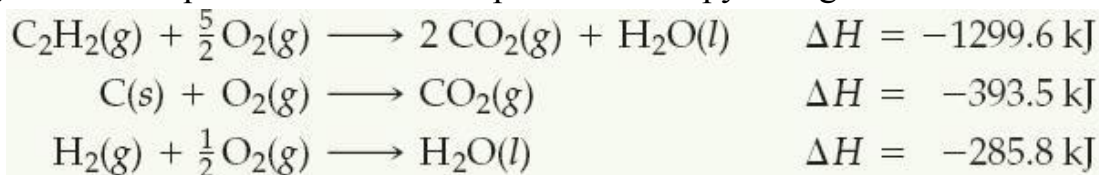


Sample Exercise 5.9 Using Three Equations with Hess's Law to Calculate ΔH

Calculate ΔH for the reaction



given the following chemical equations and their respective enthalpy changes

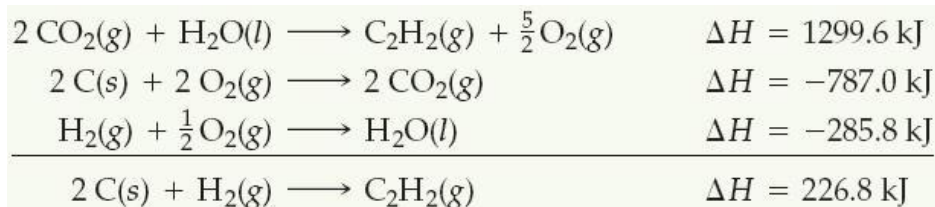


Solution

Analyze: We are given a chemical equation and asked to calculate its ΔH using three chemical equations and their associated enthalpy changes.

Plan: We will use Hess's law, summing the three equations or their reverses and multiplying each by an appropriate coefficient so that they add to give the net equation for the reaction of interest. At the same time, we keep track of the ΔH values, reversing their signs if the reactions are reversed and multiplying them by whatever coefficient is employed in the equation.

Solve: Because the target equation has C_2H_2 as a product, we turn the first equation around; the sign of ΔH is therefore changed. The desired equation has $2 \text{C}(s)$ as a reactant, so we multiply the second equation and its ΔH by 2. Because the target equation has H_2 as a reactant, we keep the third equation as it is. We then add the three equations and their enthalpy changes in accordance with Hess's law:

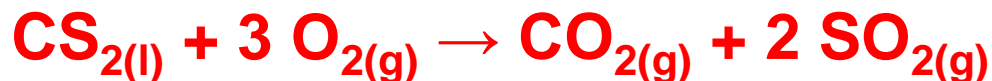
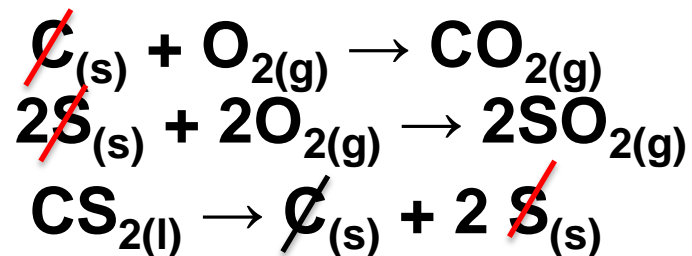
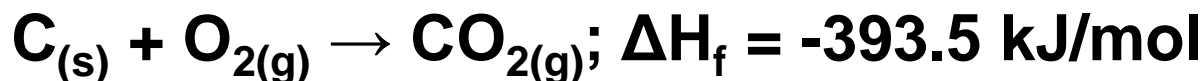


Calculation of ΔH

What is the value for ΔH for the following reaction?



Given:



$$\Delta H = -393.5 \text{ kJ/mol} + 2(-296.8 \text{ kJ/mol}) + (-87.9 \text{ kJ/mol})$$

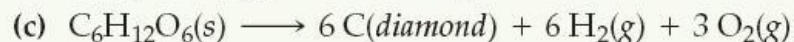
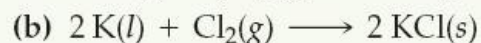
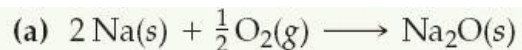
$$\Delta H = -393.5 \text{ kJ/mol} - 593.6 \text{ kJ/mol} - 87.9 \text{ kJ/mol}$$

$$\Delta H = -1075.0 \text{ kJ/mol}$$



Identifying Equations Associates with Enthalpies of Formation

For which of the following reactions at 25° C would the enthalpy change represent a standard enthalpy of formation? For each that does not, what changes are needed to make it an equation whose ΔH is an enthalpy of formation?

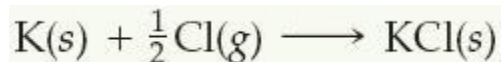


Solution

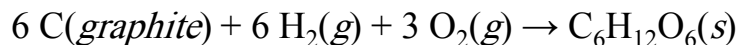
Analyze: The standard enthalpy of formation is represented by a reaction in which each reactant is an element in its standard state and the product is one mole of the compound.

Plan: We need to examine each equation to determine, first, whether the reaction is one in which one mole of substance is formed from the elements. Next, we need to determine whether the reactant elements are in their standard states.

Solve: In (a) 1 mol Na_2O is formed from the elements sodium and oxygen in their proper states, solid Na and O_2 gas, respectively. Therefore, the enthalpy change for reaction (a) corresponds to a standard enthalpy of formation. In (b) potassium is given as a liquid. It must be changed to the solid form, its standard state at room temperature. Furthermore, two moles of product are formed, so the enthalpy change for the reaction as written is twice the standard enthalpy of formation of $\text{KCl}(s)$. The equation for the formation reaction of 1 mol of $\text{KCl}(s)$ is



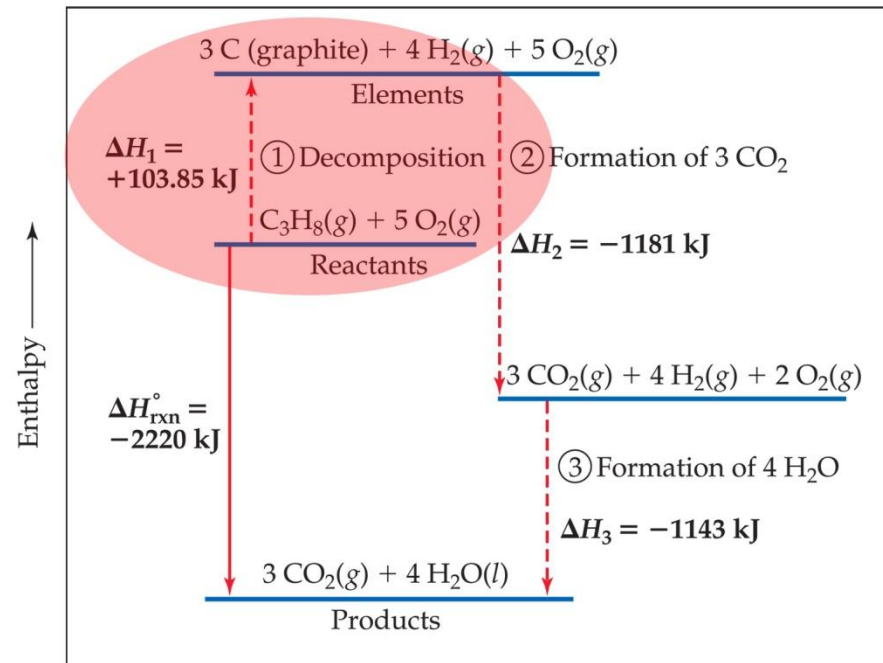
Reaction (c) does not form a substance from its elements. Instead, a substance decomposes to its elements, so this reaction must be reversed. Next, the element carbon is given as diamond, whereas graphite is the standard state of carbon at room temperature and 1 atm pressure. The equation that correctly represents the enthalpy of formation of glucose from its elements is



Calculation of ΔH



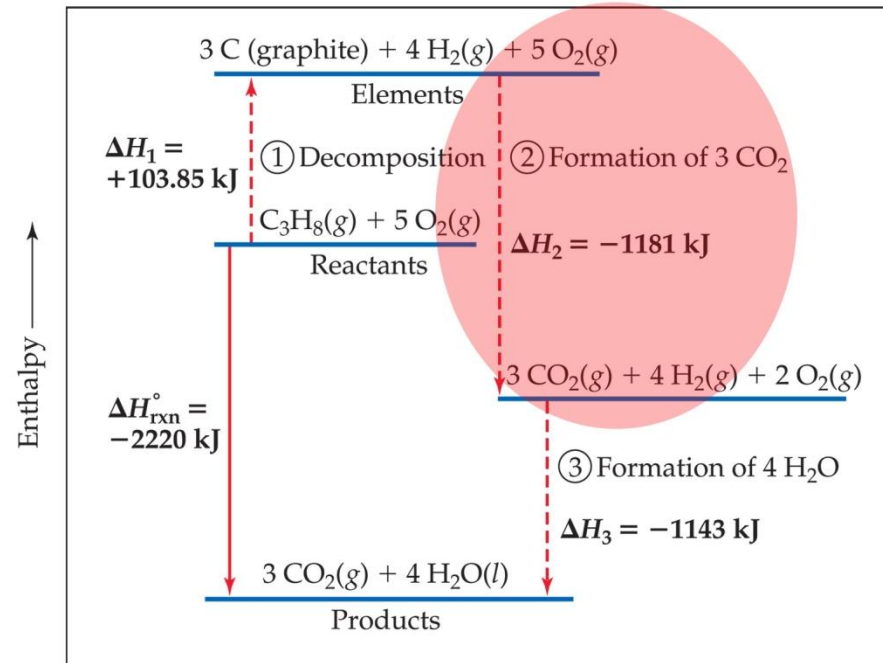
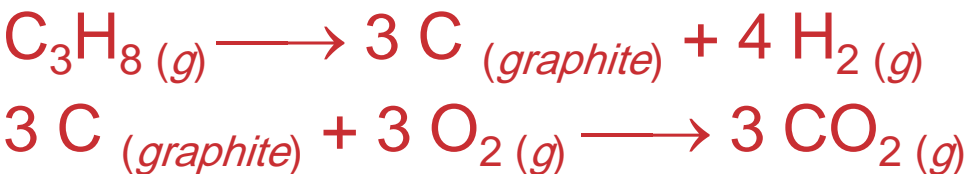
- Imagine this as occurring in three steps:



Calculation of ΔH



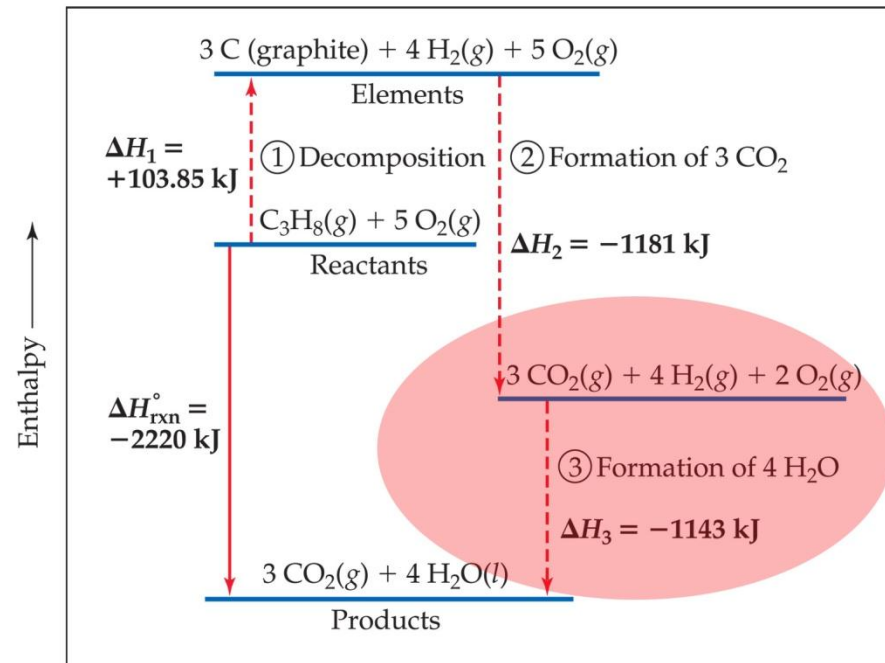
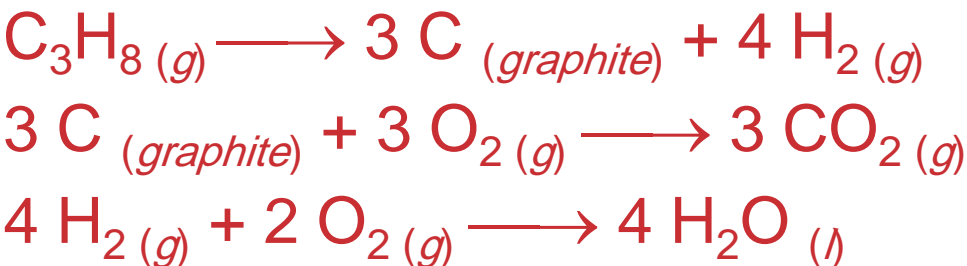
- Imagine this as occurring in three steps:



Calculation of ΔH



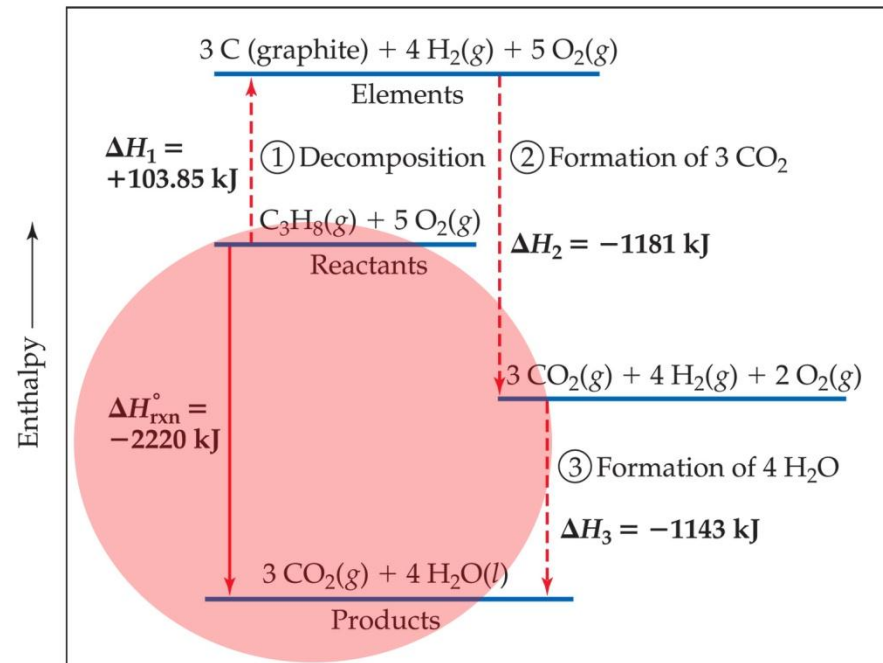
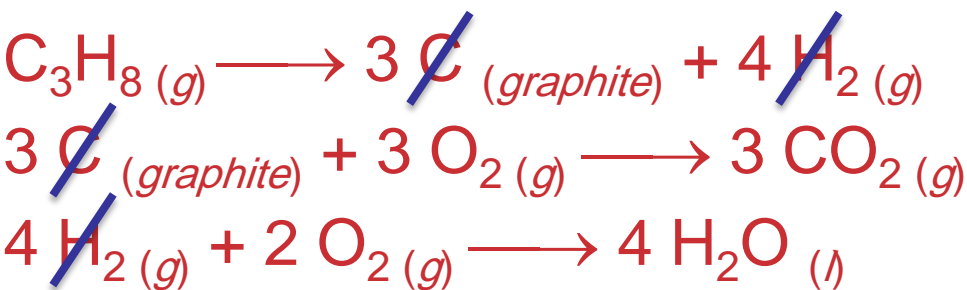
- Imagine this as occurring in three steps:



Calculation of ΔH



- The sum of these equations is:



Calculation of ΔH

We can use Hess's law in this way:

$$\Delta H = \sum n \Delta H_f^\circ \text{ products} - \sum m \Delta H_f^\circ \text{ reactants}$$

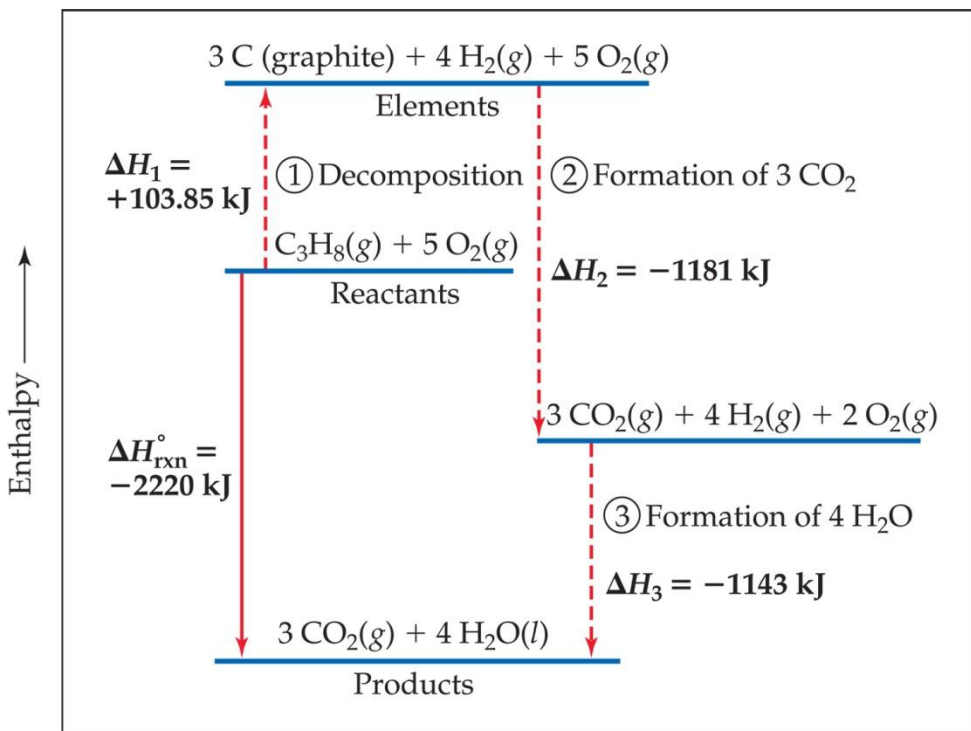
where n and m are the stoichiometric coefficients.



Calculation of ΔH



$$\Delta H = [3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ})] - [1(-103.85 \text{ kJ}) + 5(0 \text{ kJ})]$$



Energy in Foods

Most of the fuel in the food we eat comes from carbohydrates and fats.

| | Approximate Composition (% by mass) | | | Fuel Value | |
|--------------|-------------------------------------|-----|---------|------------|----------------|
| | Carbohydrate | Fat | Protein | kJ/g | kcal/g (Cal/g) |
| Carbohydrate | 100 | – | – | 17 | 4 |
| Fat | – | 100 | – | 38 | 9 |
| Protein | – | – | 100 | 17 | 4 |
| Apples | 13 | 0.5 | 0.4 | 2.5 | 0.59 |
| Beer* | 1.2 | – | 0.3 | 1.8 | 0.42 |
| Bread | 52 | 3 | 9 | 12 | 2.8 |
| Cheese | 4 | 37 | 28 | 20 | 4.7 |
| Eggs | 0.7 | 10 | 13 | 6.0 | 1.4 |
| Fudge | 81 | 11 | 2 | 18 | 4.4 |
| Green beans | 7.0 | – | 1.9 | 1.5 | 0.38 |
| Hamburger | – | 30 | 22 | 15 | 3.6 |
| Milk (whole) | 5.0 | 4.0 | 3.3 | 3.0 | 0.74 |
| Peanuts | 22 | 39 | 26 | 23 | 5.5 |

*Beers typically contain 3.5% ethanol, which has fuel value.



Energy in Fuels

The vast majority of the energy consumed in this country comes from fossil fuels.

| | Approximate Elemental Composition (mass %) | | | Fuel Value (kJ/g) |
|--------------------------------|--|-----|----|-------------------|
| | C | H | O | |
| Wood (pine) | 50 | 6 | 44 | 18 |
| Anthracite coal (Pennsylvania) | 82 | 1 | 2 | 31 |
| Bituminous coal (Pennsylvania) | 77 | 5 | 7 | 32 |
| Charcoal | 100 | 0 | 0 | 34 |
| Crude oil (Texas) | 85 | 12 | 0 | 45 |
| Gasoline | 85 | 15 | 0 | 48 |
| Natural gas | 70 | 23 | 0 | 49 |
| Hydrogen | 0 | 100 | 0 | 142 |

