Chemistry, The Central Science, 10th edition
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Chapter 5
Thermochemistry

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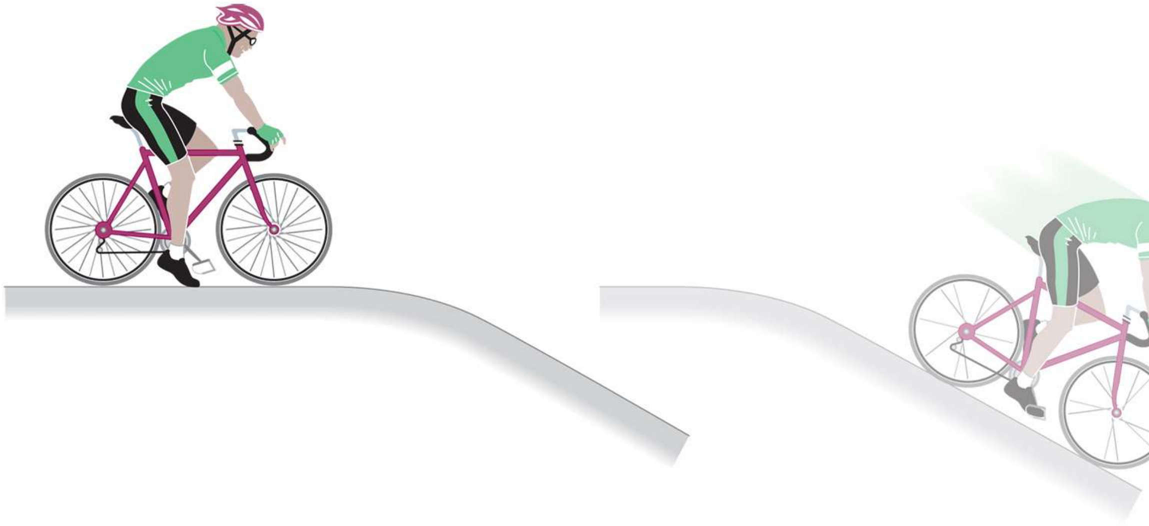
Energy

- The ability to do work or transfer heat.
    - Work: Energy used to cause an object that has mass to move.
    - Heat: Energy used to cause the temperature of an object to rise.

Potential Energy

Energy an object possesses by virtue of its position or chemical composition.



Kinetic Energy

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)**.

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

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).

Work

- Energy used to move an object over some distance.
- $w = F \cdot d$,

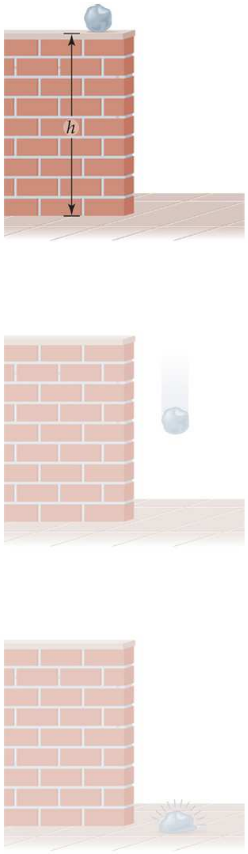
  where w is work, F is the force, and d is the distance over which the force is exerted.

Heat

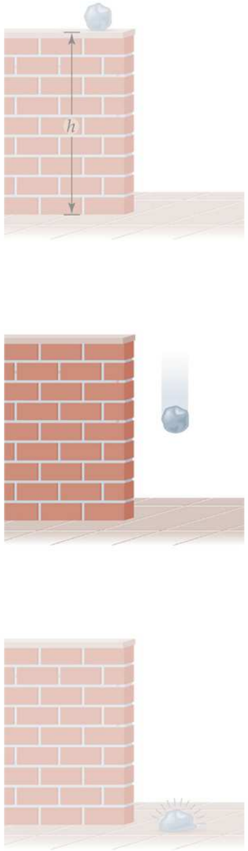
- Energy can also be transferred as heat.
- Heat flows from warmer objects to cooler objects.

Transferal of Energy

a) The potential energy of this ball of clay is increased when it is moved from the ground to the top of the wall.



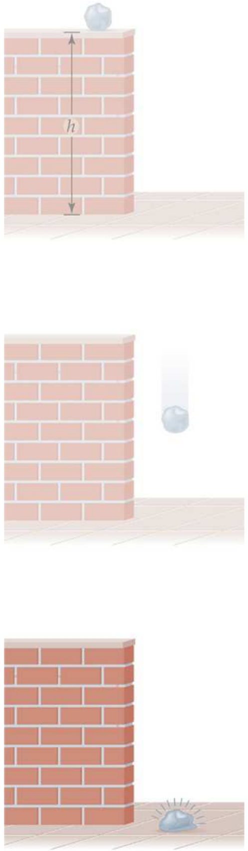
Transferal of Energy



a) The potential energy of this ball of clay is increased when it is moved from the ground to the top of the wall.

b) As the ball falls, its potential energy is converted to kinetic energy.

Transferal of Energy



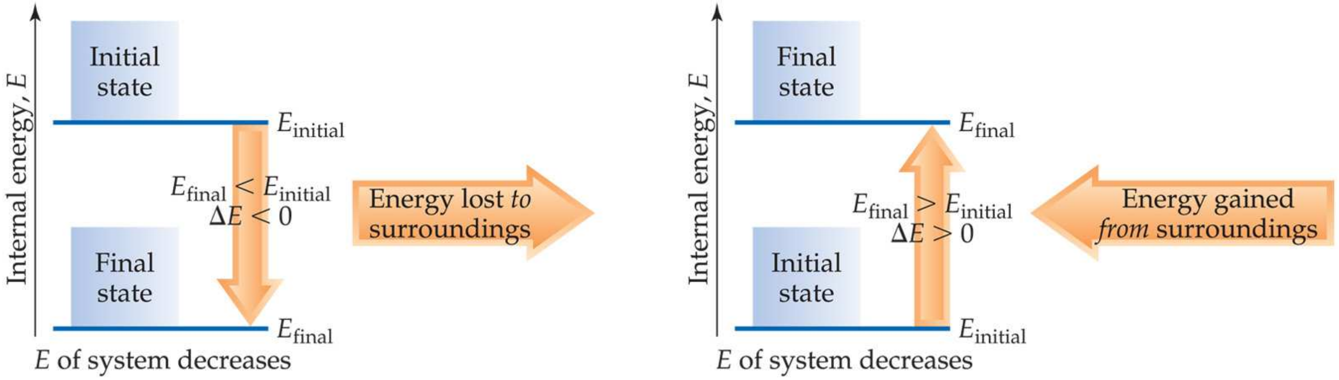
a) The potential energy of this ball of clay is increased when it is moved from the ground to the top of the wall.

b) As the ball falls, its potential energy is converted to kinetic energy.

c) When it hits the ground, its kinetic energy falls to zero (since it is no longer moving); some of the energy does work on the ball, the rest is dissipated as heat.

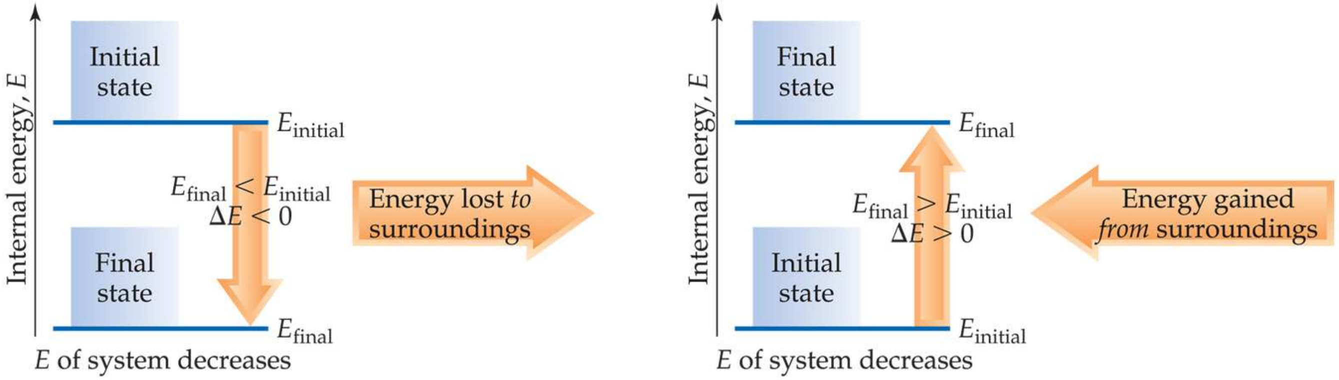
First Law of Thermodynamics

- 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*.

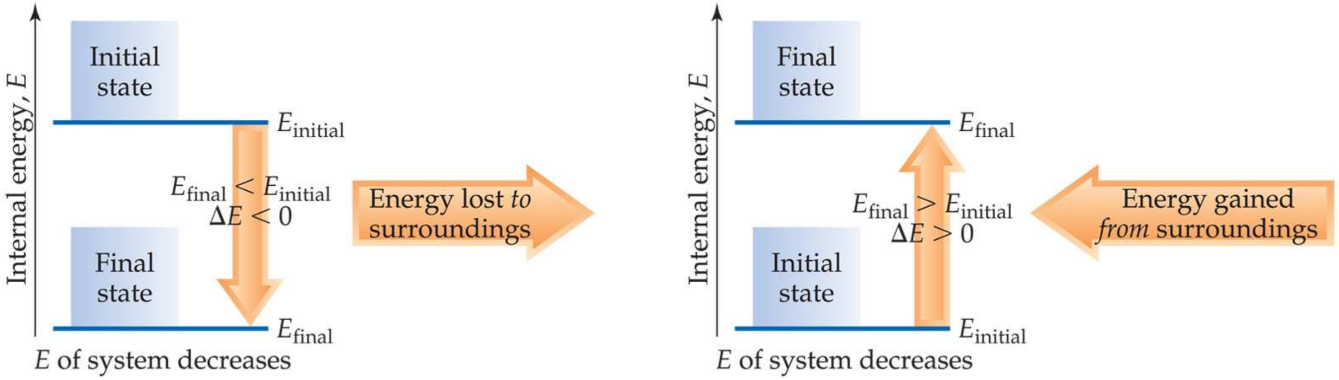


- In this system the internal energy includes the motion of the H_2 and O_2 molecules through space, their rotation and internal vibrations, the energies of the nuclei of each atom and of the component electrons.
- The internal energy is represented by E.

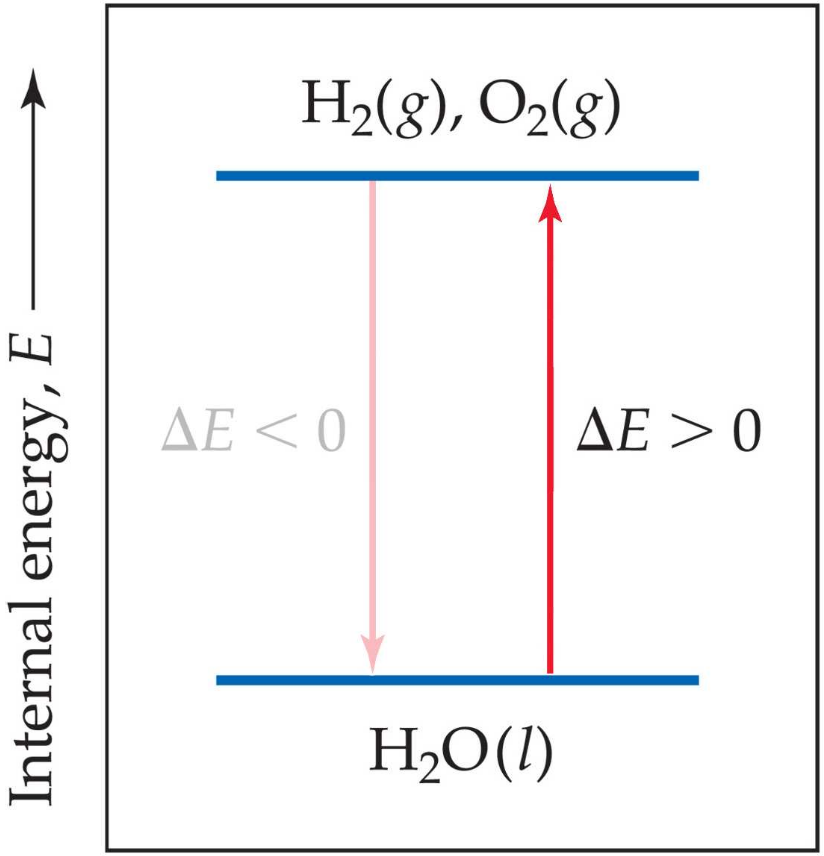
Internal Energy

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

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

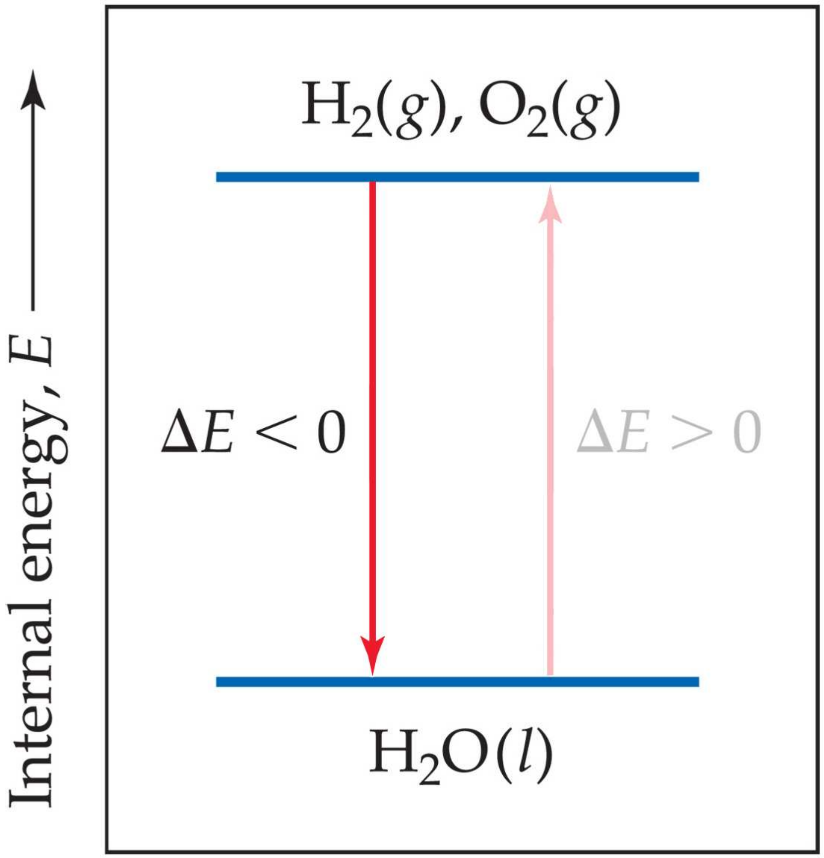


Changes in Internal Energy



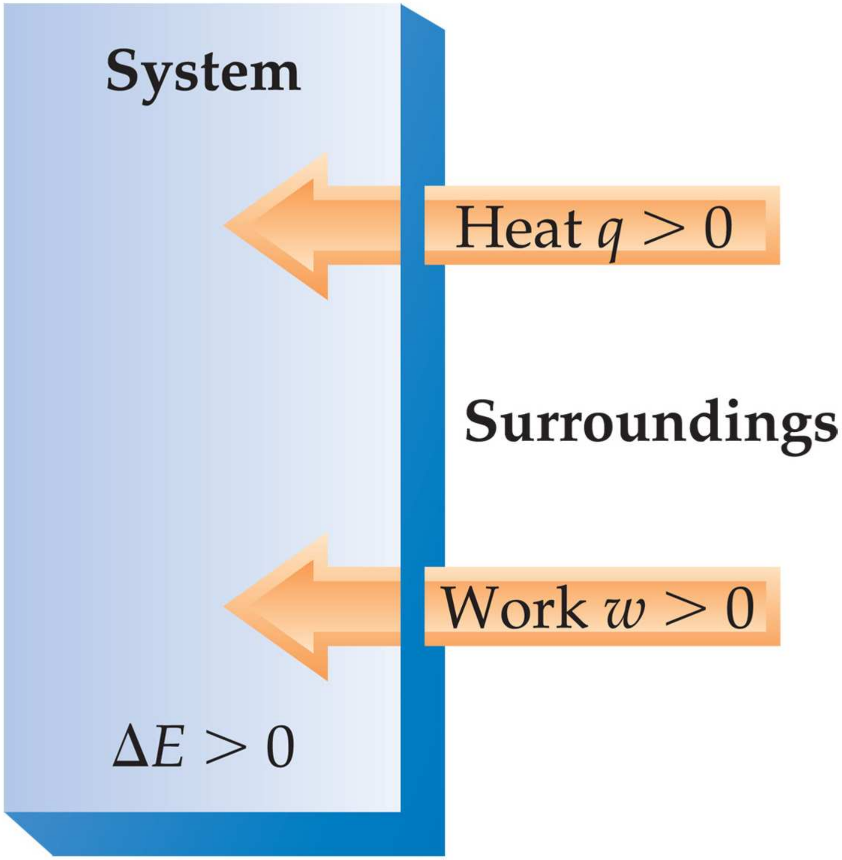
- If $\Delta E > 0$, $E_{\text{final}} > E_{\text{initial}}$
  - Therefore, the system *absorbed* energy from the surroundings.
  - This energy change is called endergonic.

Changes in Internal Energy



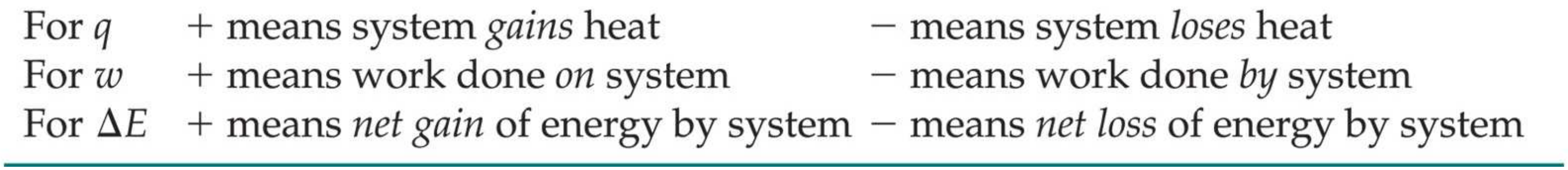
- If $\Delta E < 0$, $E_{\text{final}} < E_{\text{initial}}$
  - Therefore, the system *released* energy to the surroundings.
  - This energy change is called exergonic.

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, $\Delta E = q + w$.

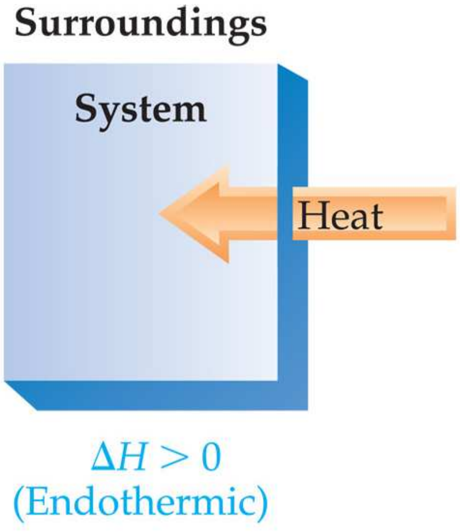
ΔE, q, w, and Their Signs



For q	+ means system *gains* heat	− means system *loses* heat
For w	+ means work done *on* system	− means work done *by* system
For ΔE	+ means *net gain* of energy by system	− means *net loss* of energy by system

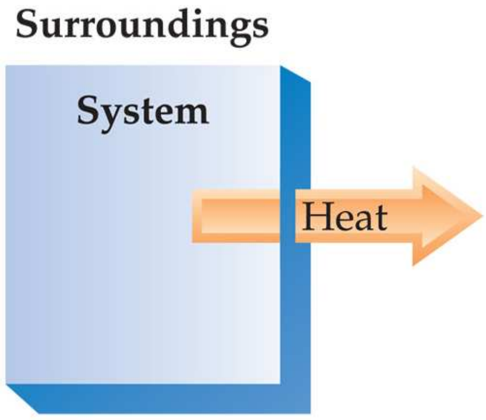
Exchange of Heat between System and Surroundings

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



Exchange of Heat between System and Surroundings

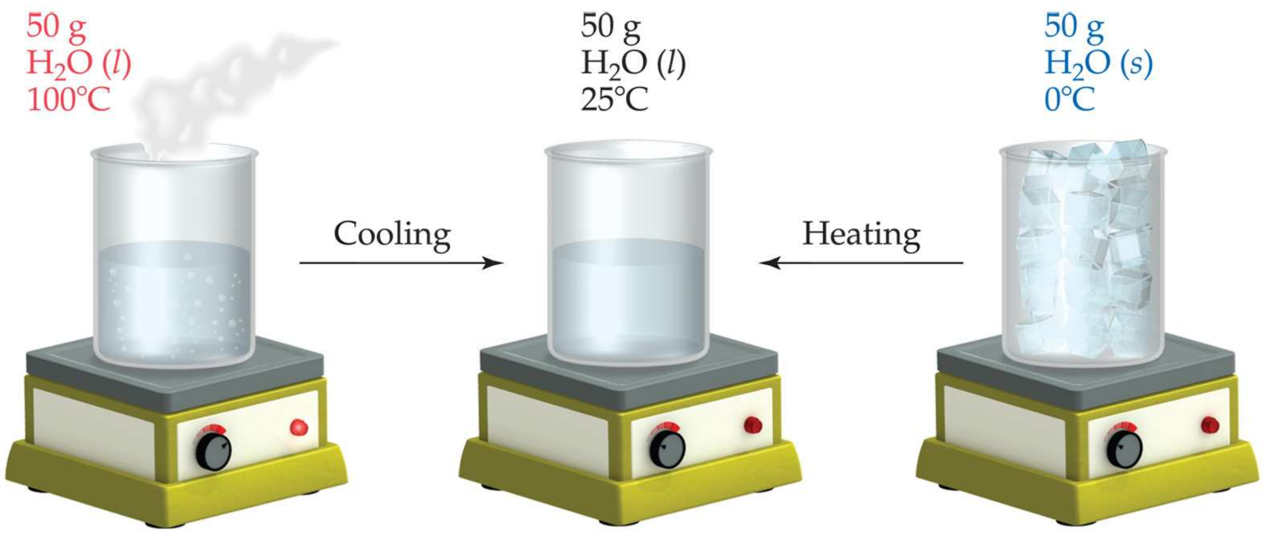
- When heat is absorbed by the system from the surroundings, the process is endothermic.
- When heat is released by the system to the surroundings, the process is exothermic.



$\Delta H < 0$
(Exothermic)

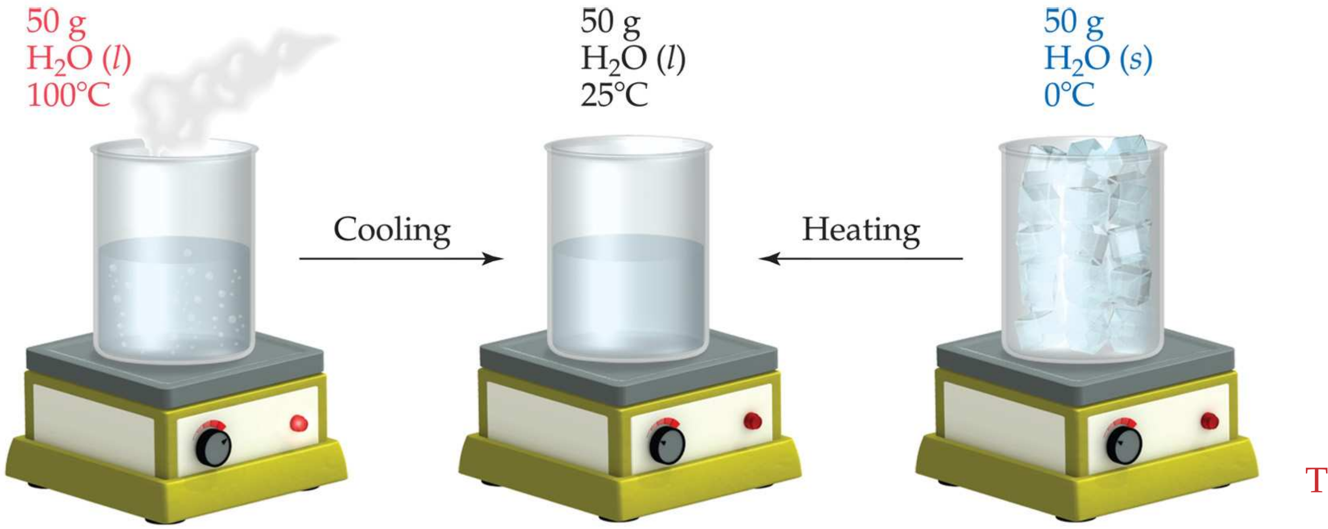
State Functions

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



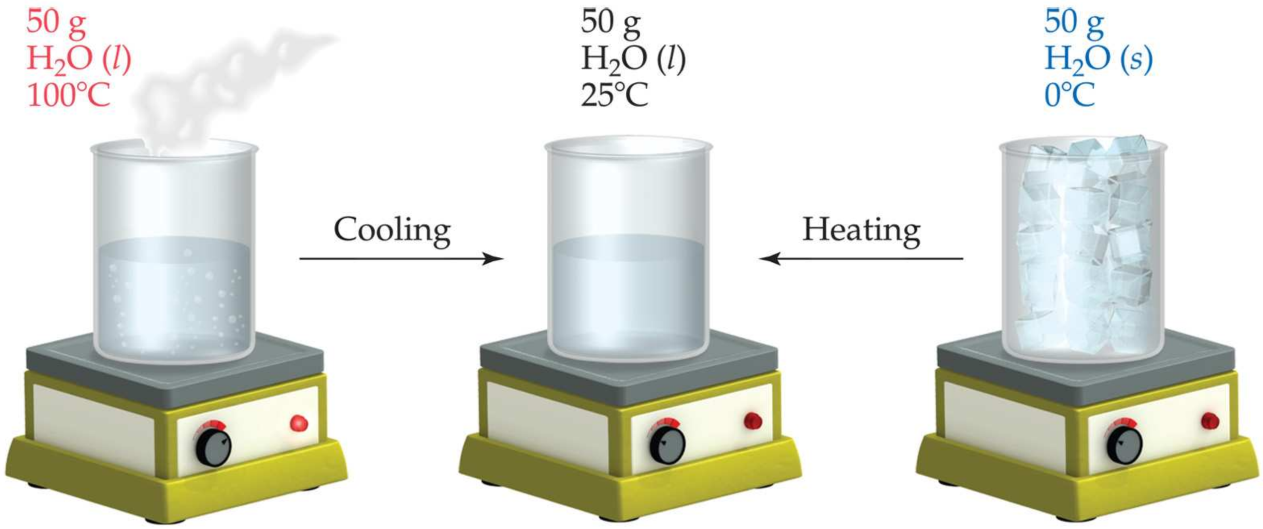
State Functions

- 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.

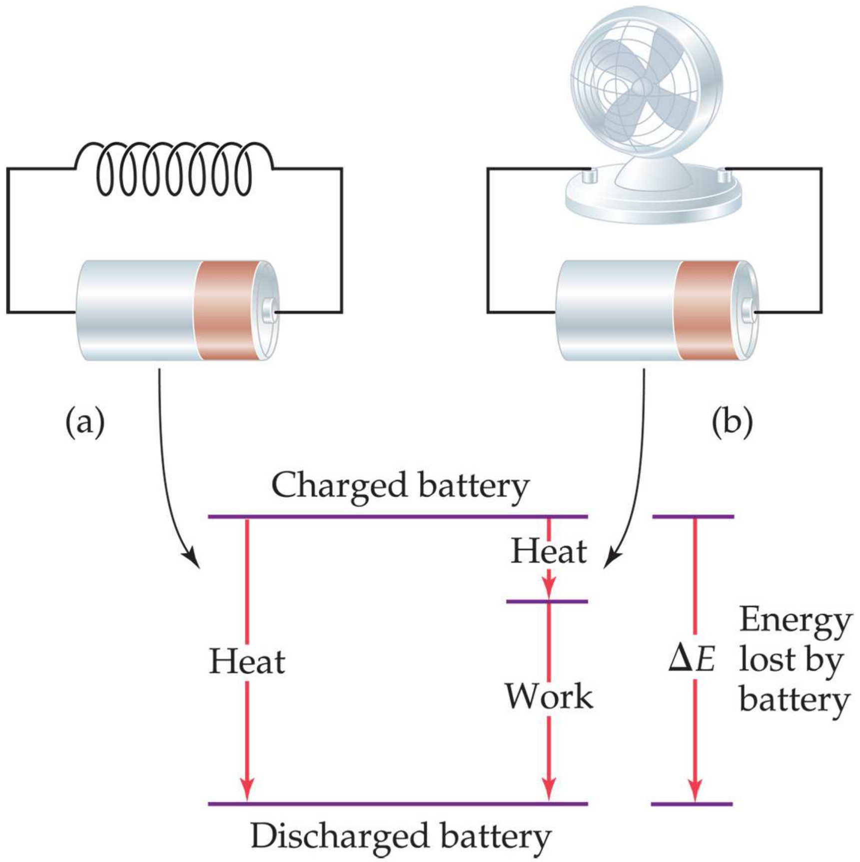


State Functions

- 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, Δ*E* depends only on E_{initial} and E_{final}.

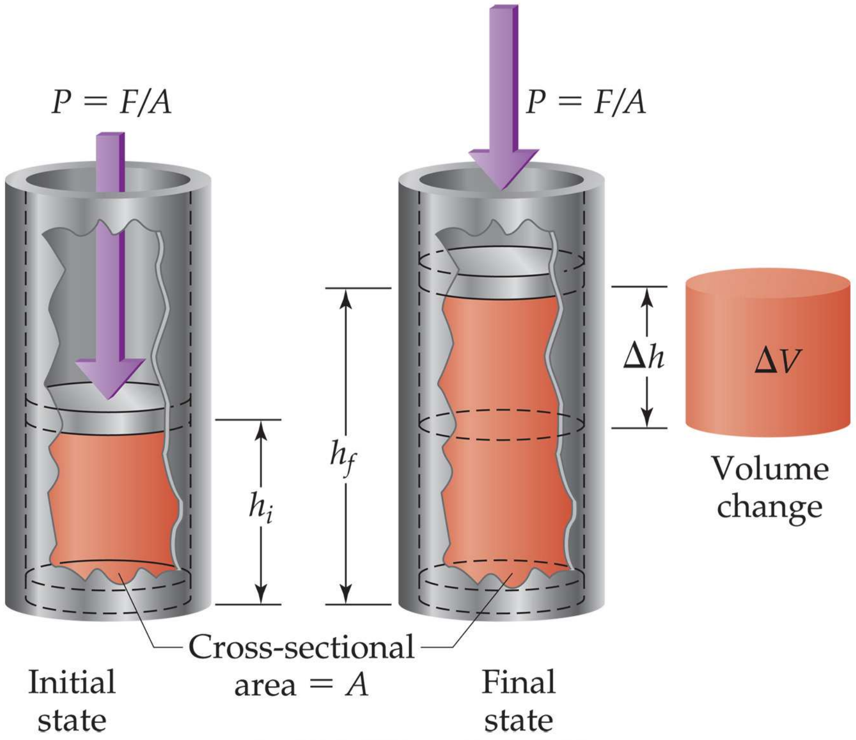


State Functions



- 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

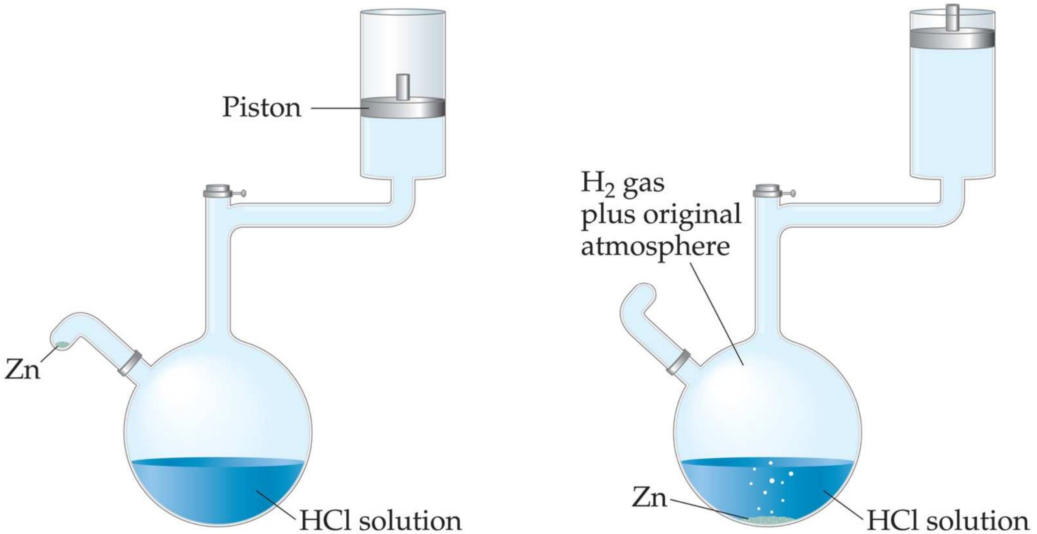


When a process occurs in an open container, commonly the only work done is a change in volume of a gas pushing on the surroundings (or being pushed on by the surroundings).

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 (Greek enthalpein- to warm) of the system.

- Enthalpy is an extensive property of a substance that can be used to obtain the heat absorbed or evolved in a chemical reaction.
- 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:

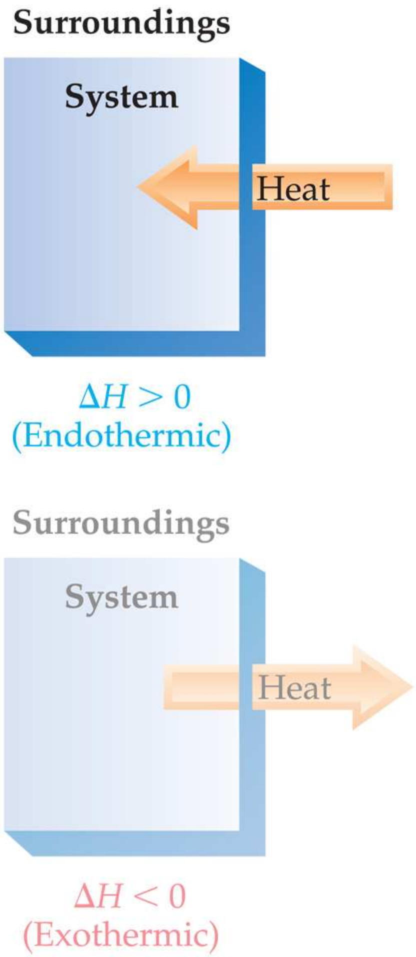
$$\Delta H = \Delta E + P\Delta V$$

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

$$\Delta H = q$$

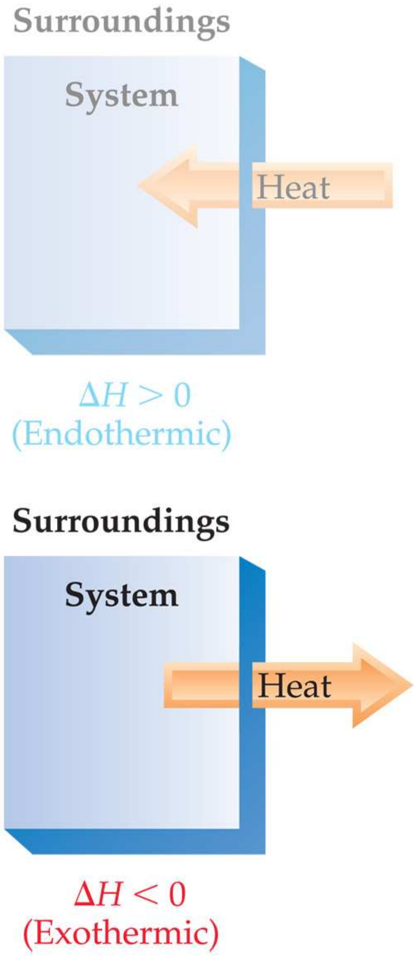
- So, at constant pressure the change in enthalpy *is* the heat gained or lost.

Endothermicity and Exothermicity



- A process is endothermic, then, when ΔH is positive.

Endothermicity and Exothermicity

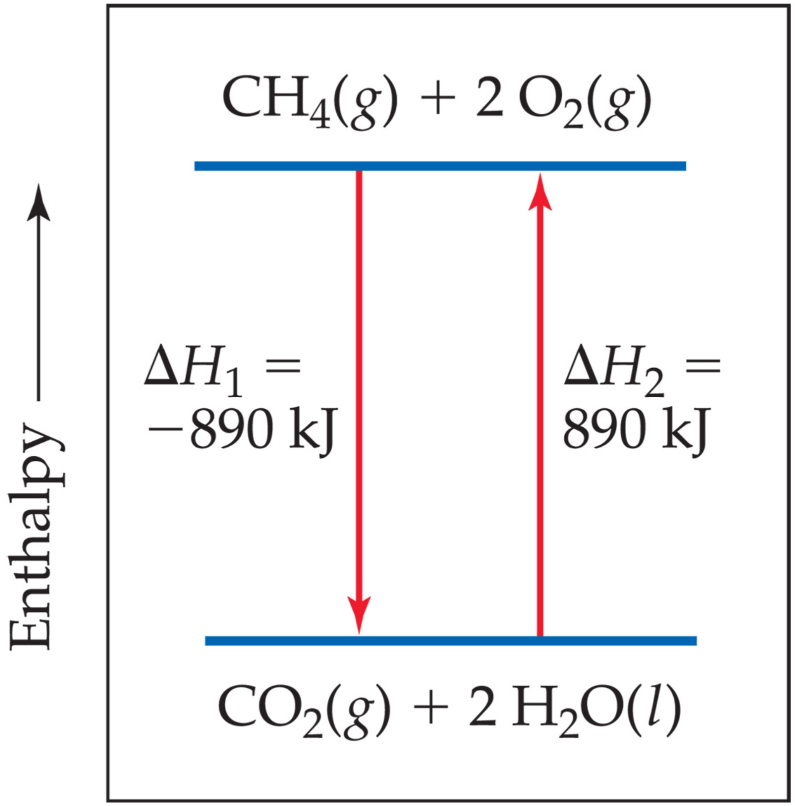


- A process is endothermic when ΔH is positive.
- A process is exothermic when ΔH is negative.

Enthalpies of Reaction

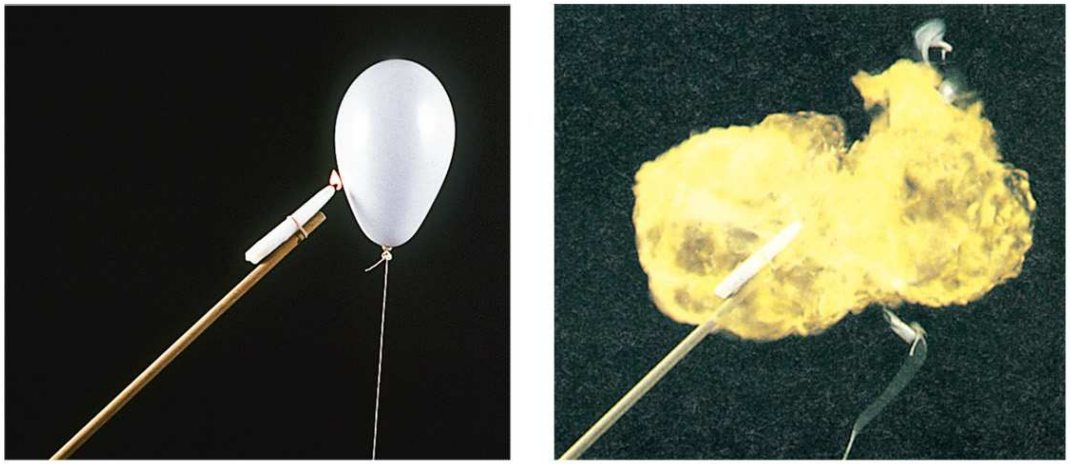
The *change* in enthalpy, Δ*H*, is the enthalpy of the products minus the enthalpy of the reactants:

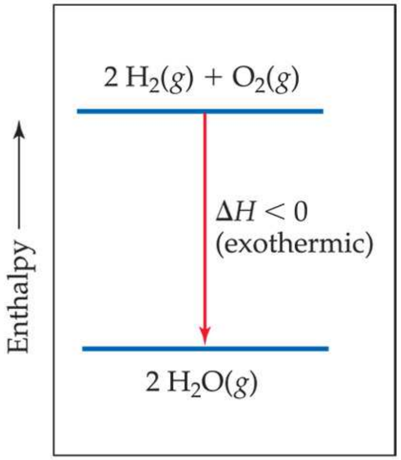
$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$



Enthalpies of Reaction

This quantity, Δ*H*, is called the enthalpy of reaction, or the heat of reaction.





The Truth about Enthalpy

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

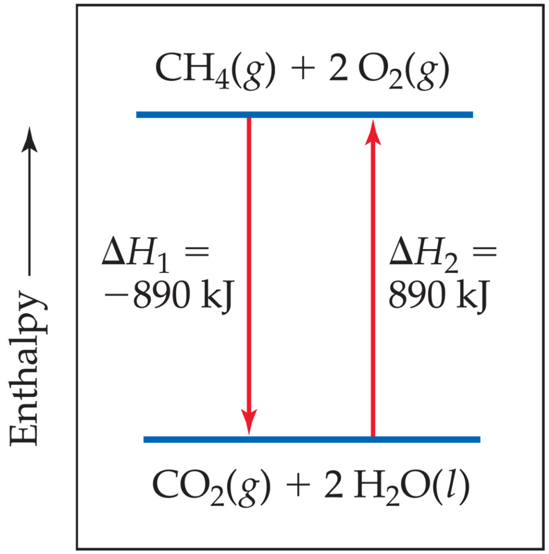
Therefore it is important to specify the states of the reactants and products in a thermochemical equation.

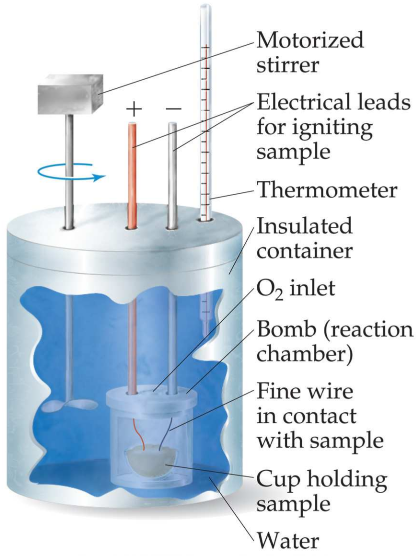
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H = -890\ \text{kJ}$$

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta H = +44\ \text{kJ}$$

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.
- 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.

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.

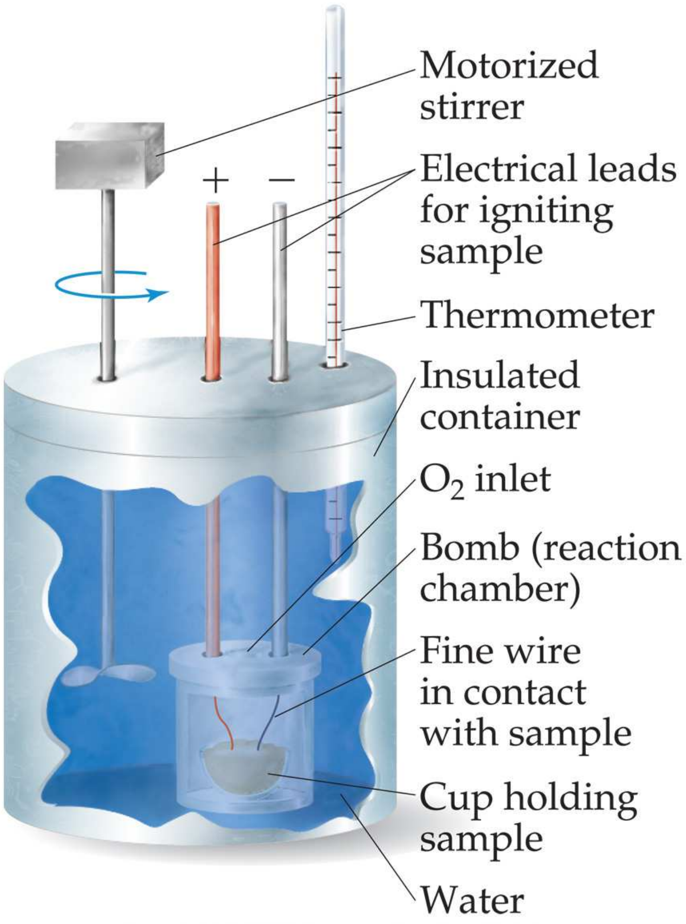
Constant Pressure Calorimetry

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

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

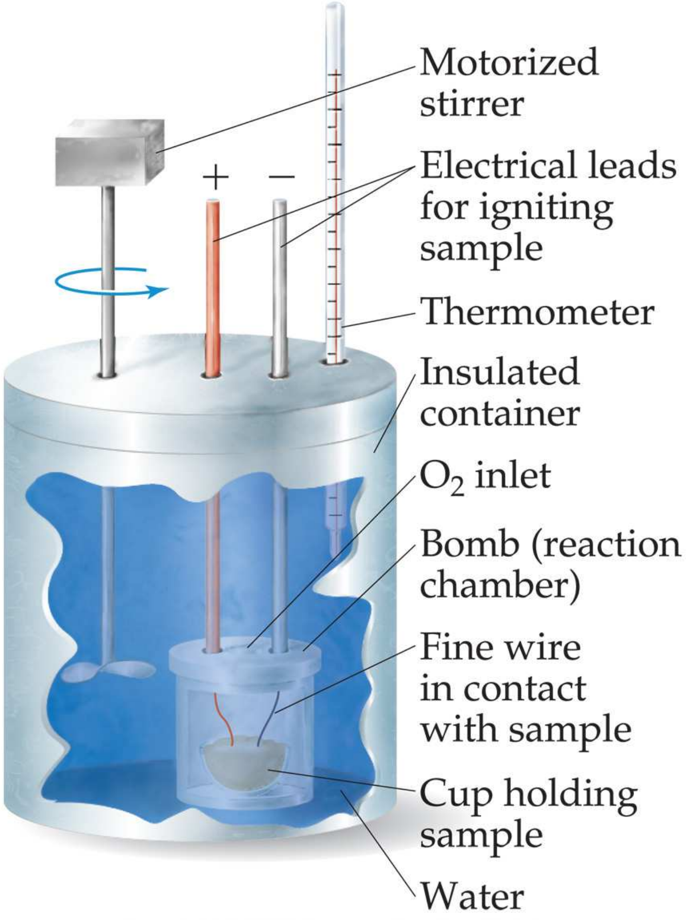
Bomb Calorimetry

Reactions can be carried out in a sealed “bomb,” such as this one, and measure the heat absorbed by the water.

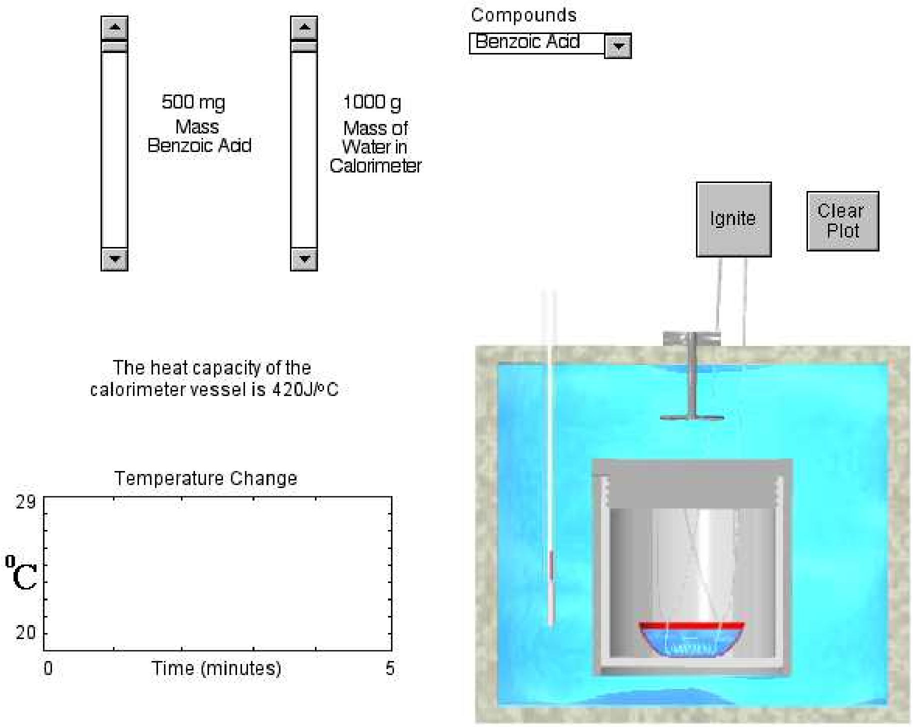


Bomb Calorimetry

- Because the volume in the bomb calorimeter is constant, what is measured is really the change in internal energy, ΔE, not ΔH.
- For most reactions, the difference is very small.



Bomb Calorimetry


Compounds: Benzoic Acid

500 mg Mass Benzoic Acid

1000 g Mass of Water in Calorimeter

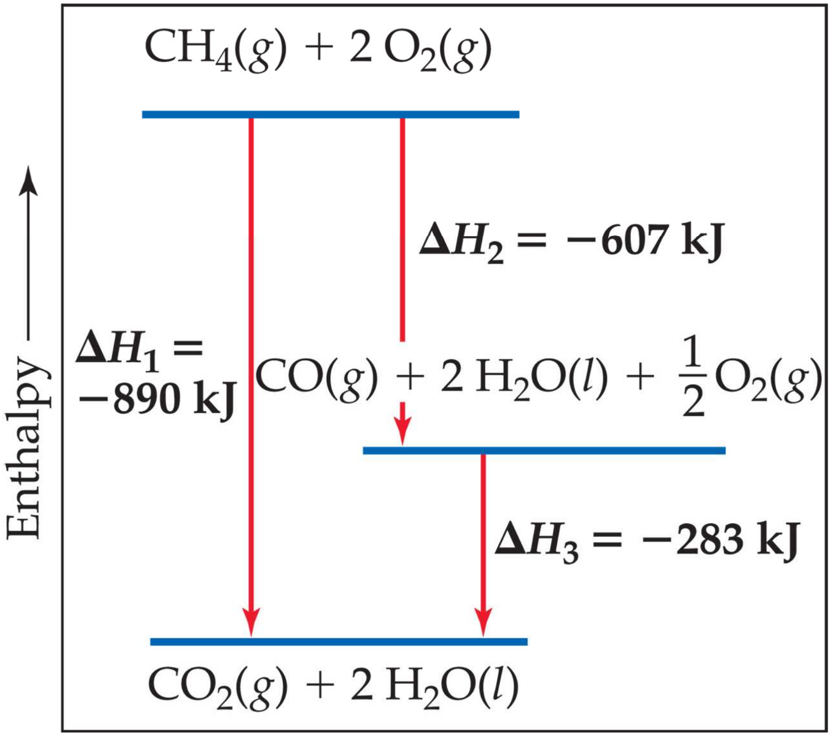
The heat capacity of the calorimeter vessel is 420J/°C

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.

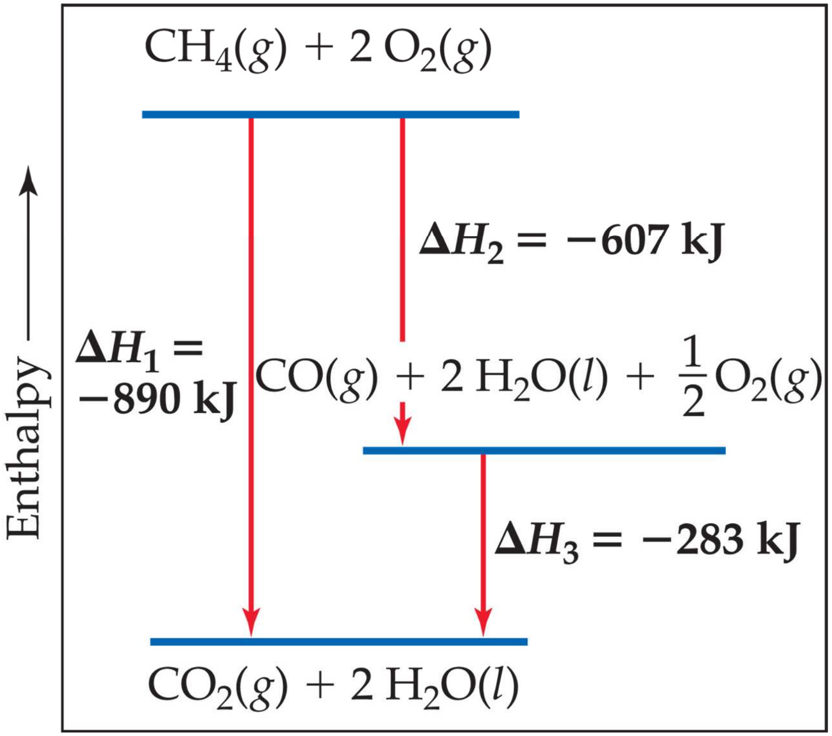
- However, we can estimate ΔH using ΔH values that are published and the properties of enthalpy.

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



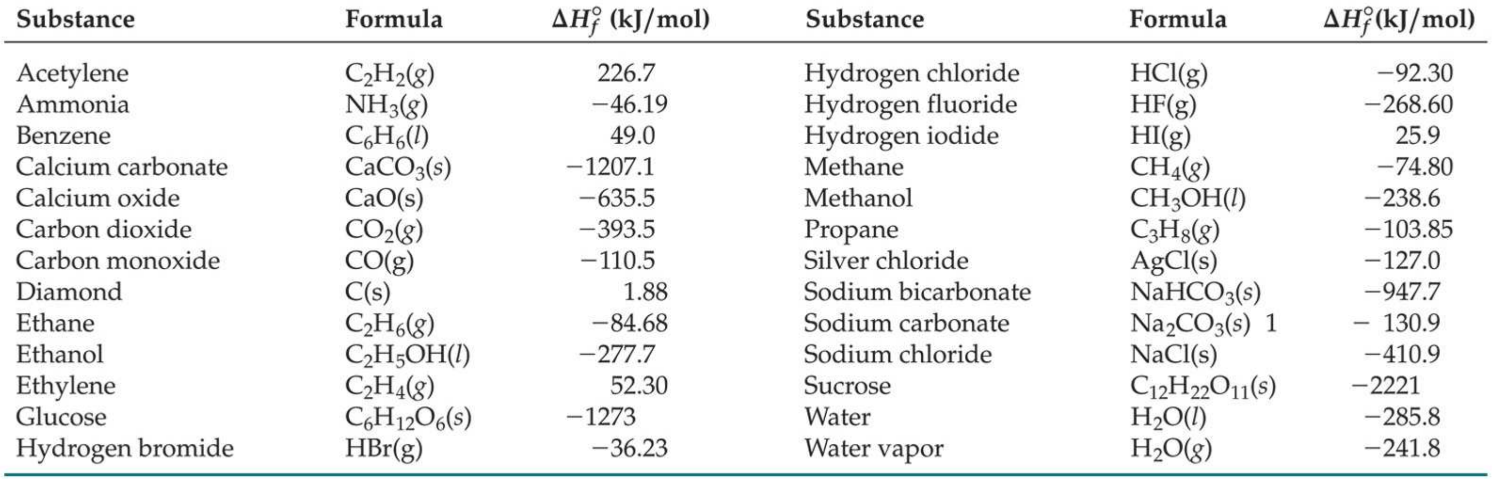
Because ΔH is a state function, the total enthalpy change depends only on the initial state of the reactants and the final state of the products.

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.

Standard Enthalpies of Formation

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



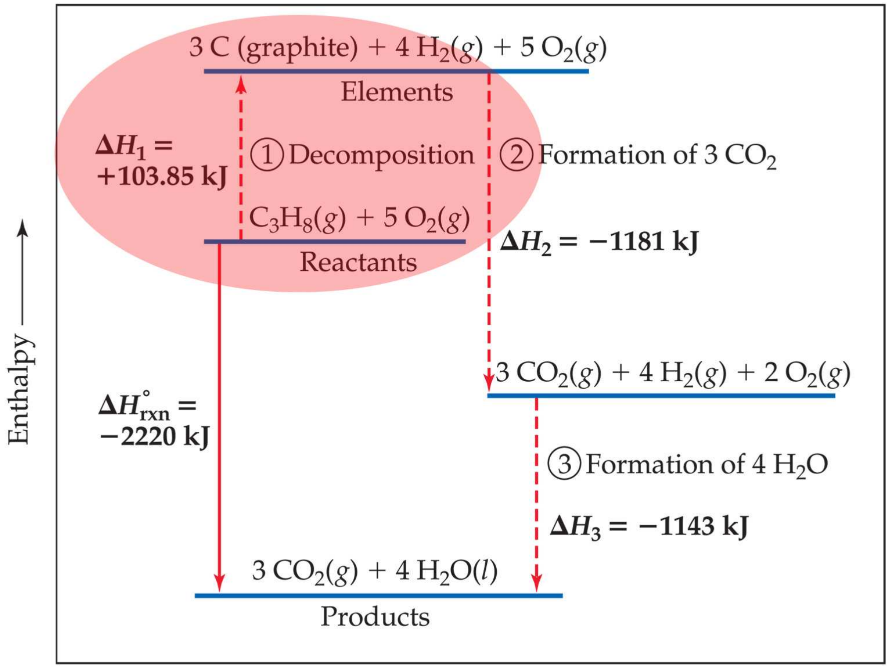
Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f°(kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
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	$Na_2CO_3(s)$ 1	− 130.9
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

Calculation of Δ*H*

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

- Imagine this as occurring in 3 steps:

$$C_3H_8\,(g) \longrightarrow 3\,C_{(graphite)} + 4\,H_2\,(g)$$



Calculation of Δ*H*

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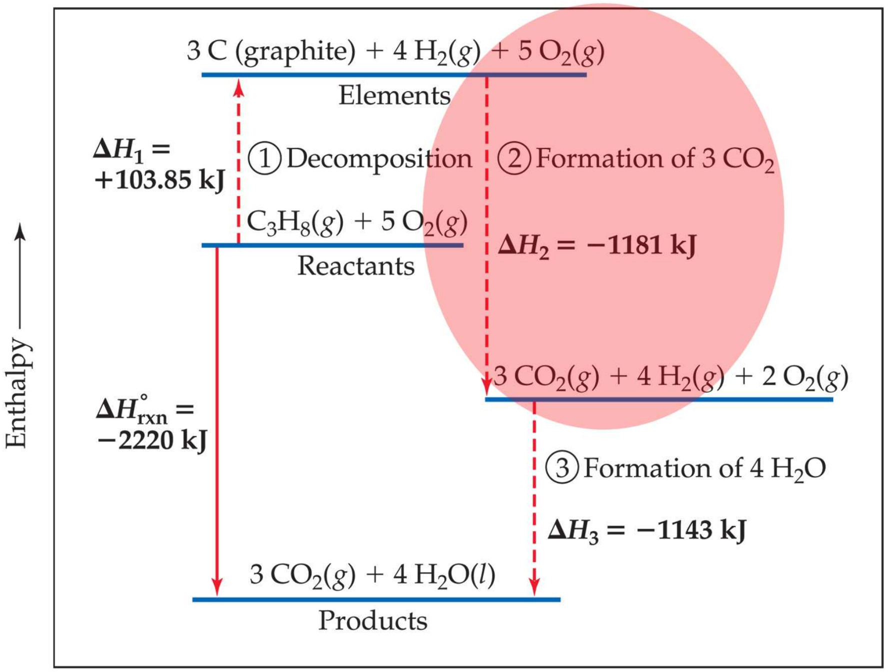
$$3\,C_{(graphite)} + 3\,O_2\,(g) \longrightarrow 3\,CO_2\,(g)$$

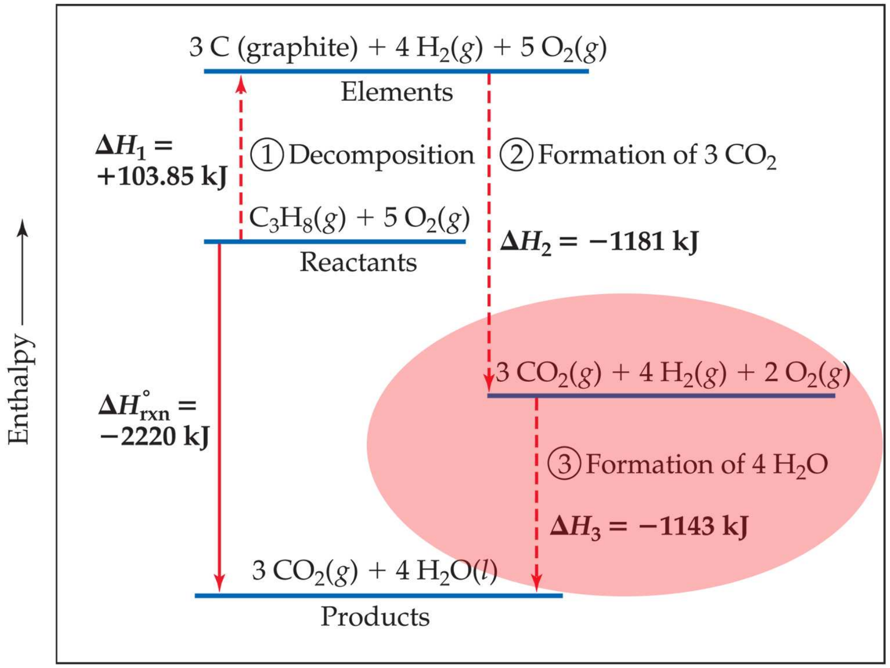


Calculation of Δ*H*

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

- Imagine this as occurring in 3 steps:

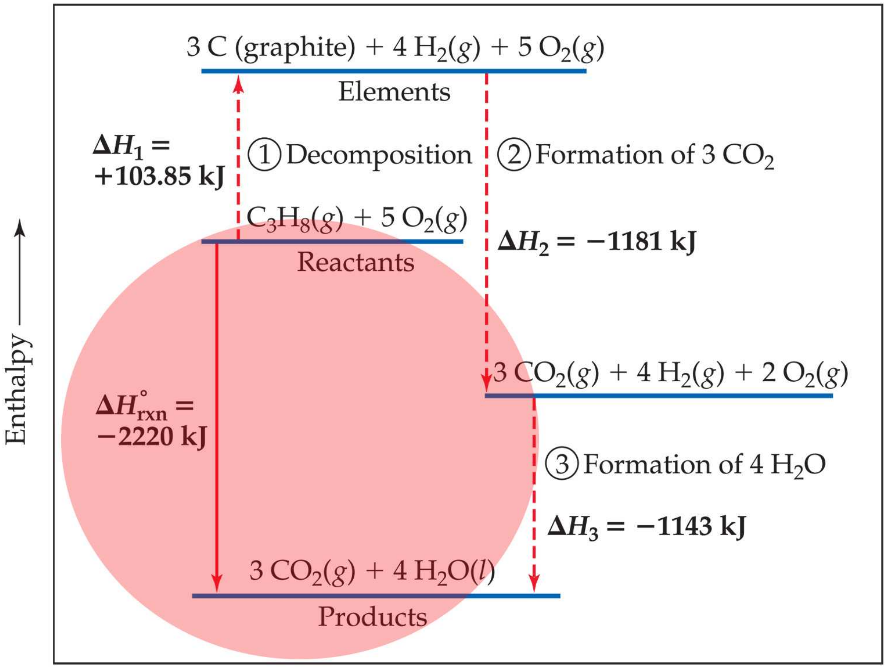
$$C_3H_8\,(g) \longrightarrow 3\,C_{(graphite)} + 4\,H_2\,(g)$$
$$3\,C_{(graphite)} + 3\,O_2\,(g) \longrightarrow 3\,CO_2\,(g)$$
$$4\,H_2\,(g) + 2\,O_2\,(g) \longrightarrow 4\,H_2O\,(l)$$



Calculation of Δ*H*

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

- The sum of these equations is:



$$C_3H_8\,(g) \longrightarrow 3\,C_{(graphite)} + 4\,H_2\,(g)$$
$$3\,C_{(graphite)} + 3\,O_2\,(g) \longrightarrow 3\,CO_2\,(g)$$
$$4\,H_2\,(g) + 2\,O_2\,(g) \longrightarrow 4\,H_2O\,(l)$$

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

Calculation of ΔH

We can use Hess's law in this way:

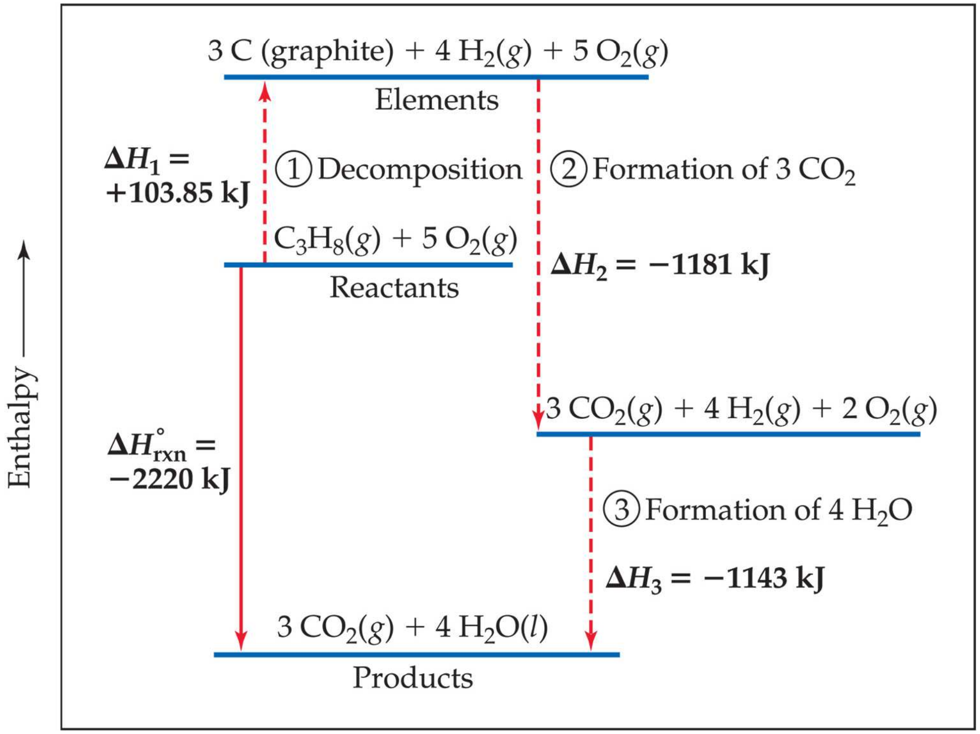
$$\Delta H = \Sigma\, n\, \Delta H^{\circ}_{f(\text{products})} - \Sigma\, m\, \Delta H^{\circ}_{f(\text{reactants})}$$

where *n* and *m* are the stoichiometric coefficients.

Calculation of ΔH

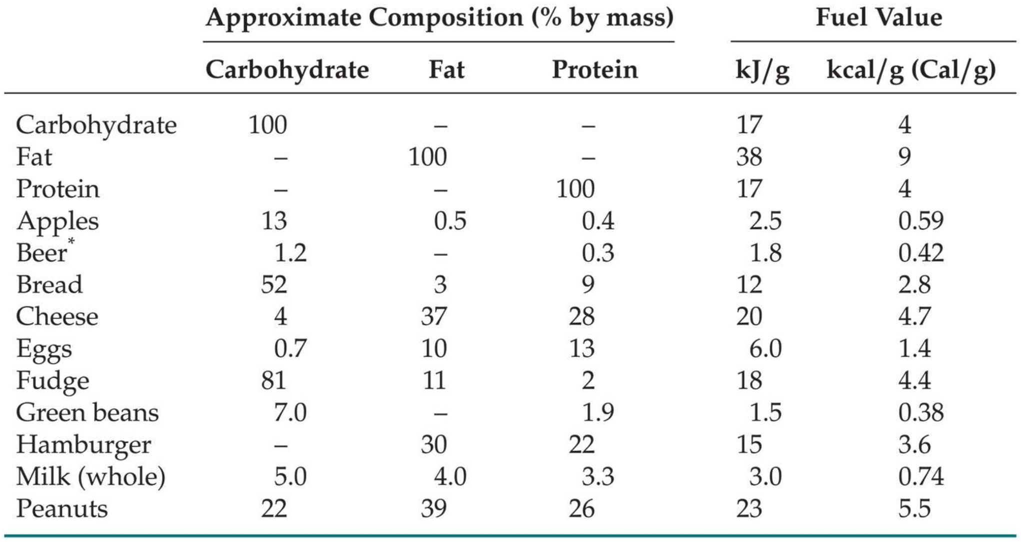
$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

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



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.

Fuels

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

	Approximate Elemental Composition (mass %)			
	C	**H**	**O**	**Fuel Value (kJ/g)**
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