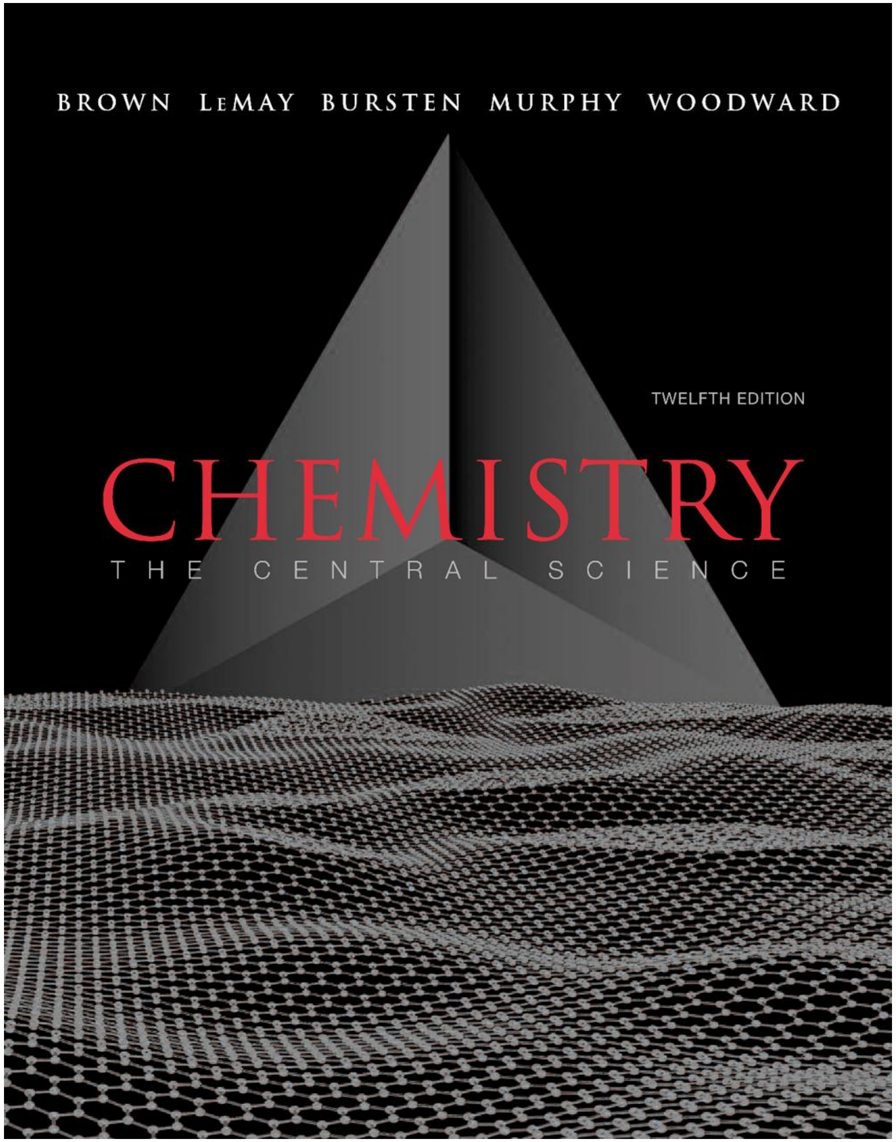

Lecture Presentation

Chapter 5

Thermochemistry

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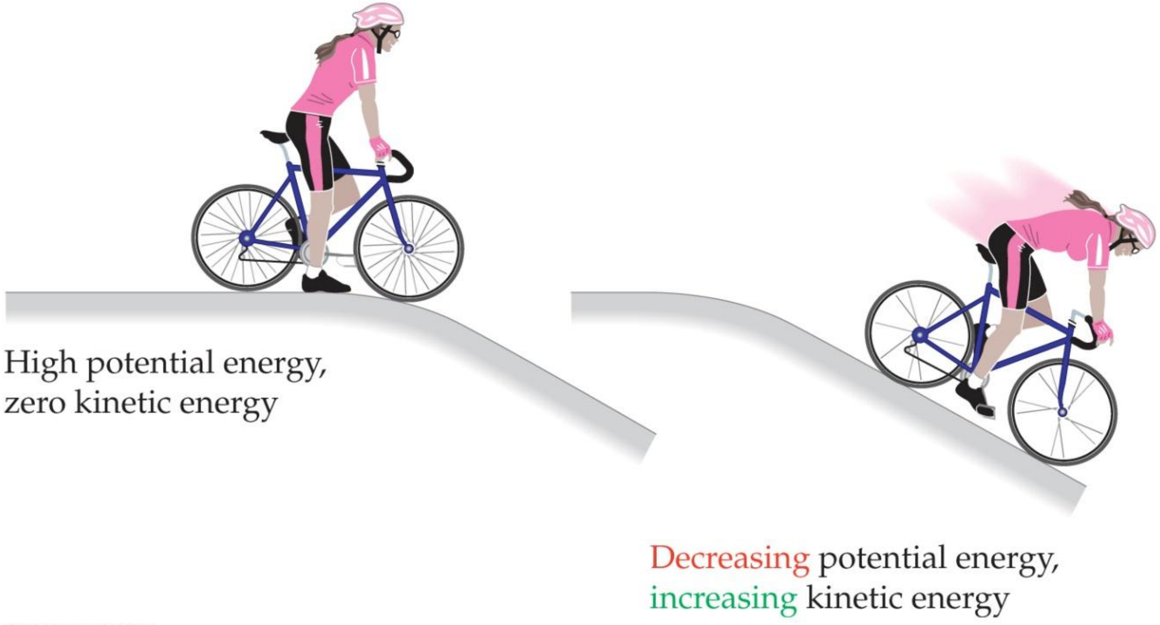
Energy

- **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**.

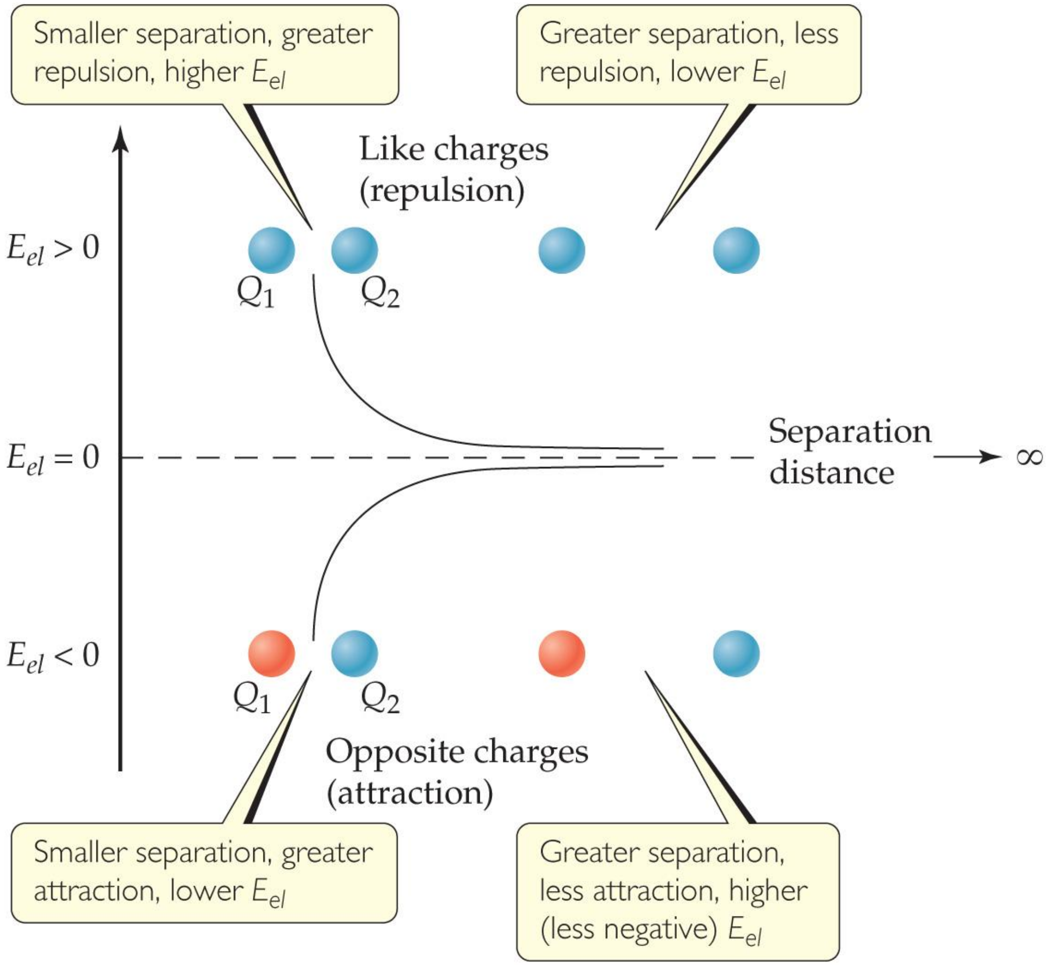
Kinetic Energy

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

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



Potential Energy



- **Potential energy** is energy an object possesses by virtue of its position or chemical composition.
- The most important form of potential energy in molecules is electrostatic potential energy, E_{el}:

$$E_{\text{el}} = \frac{\kappa Q_1 Q_2}{d}$$

Units of Energy

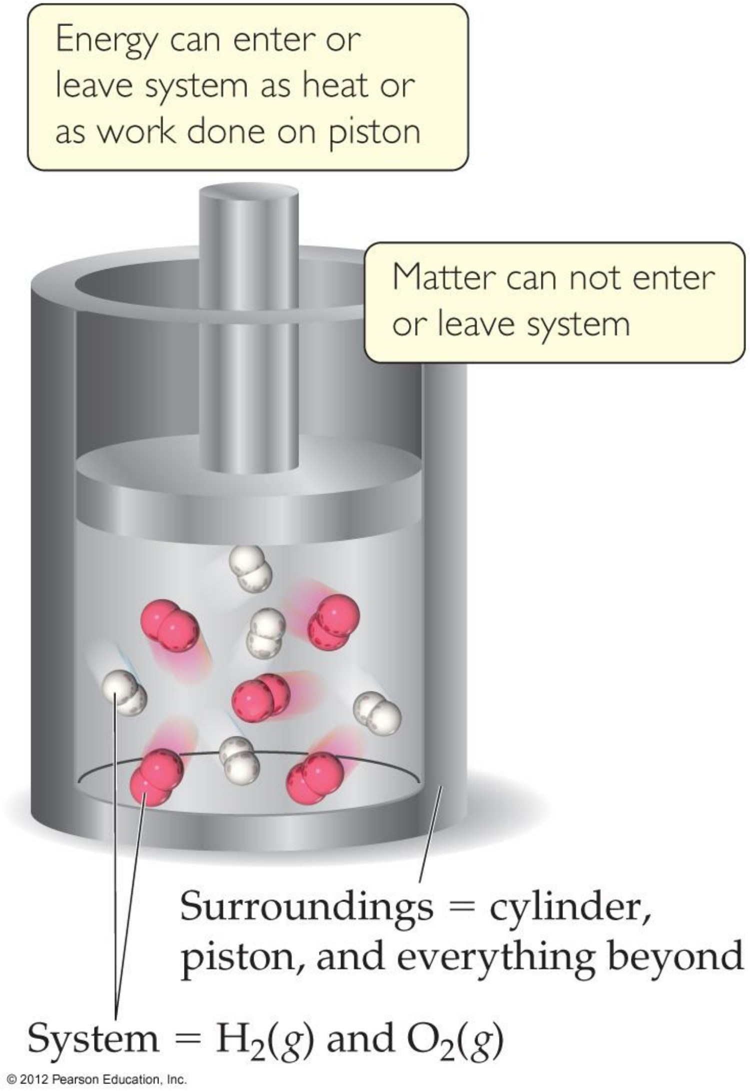
- The SI unit of energy is the **joule (*J*)**:

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

- 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).

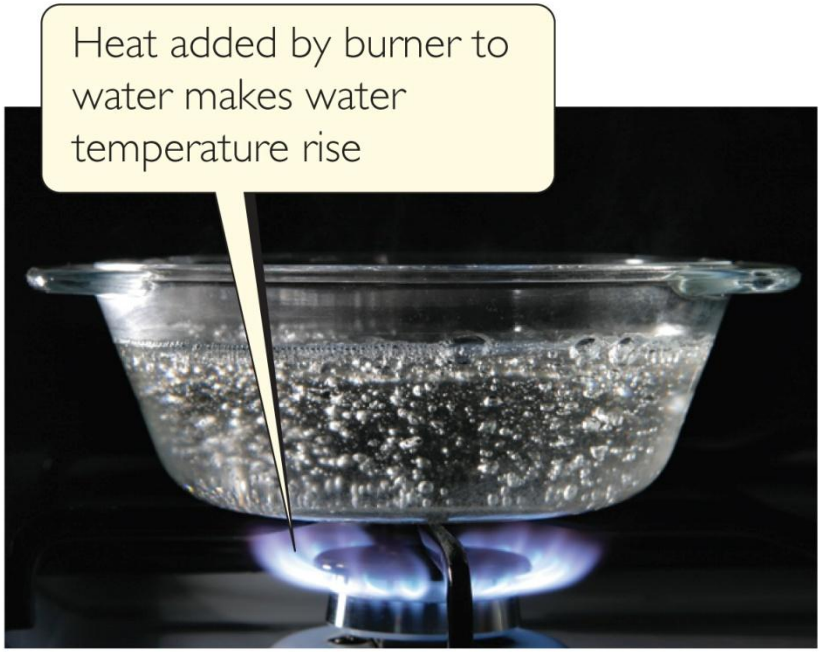
Definitions: Work

- 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.

(a)

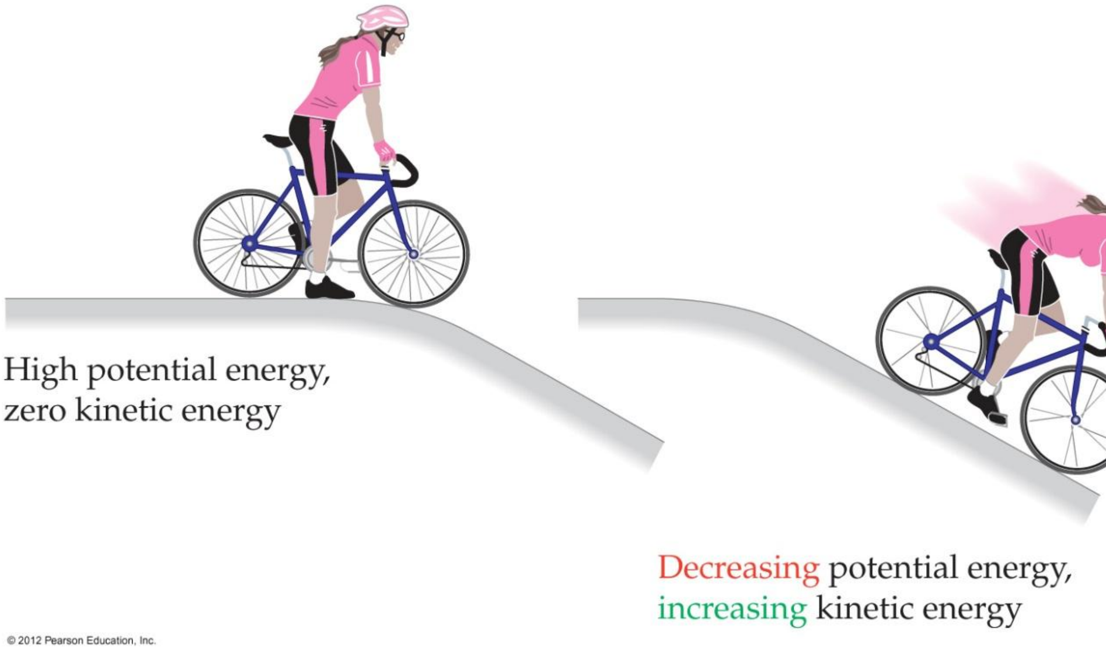
Heat



(b)

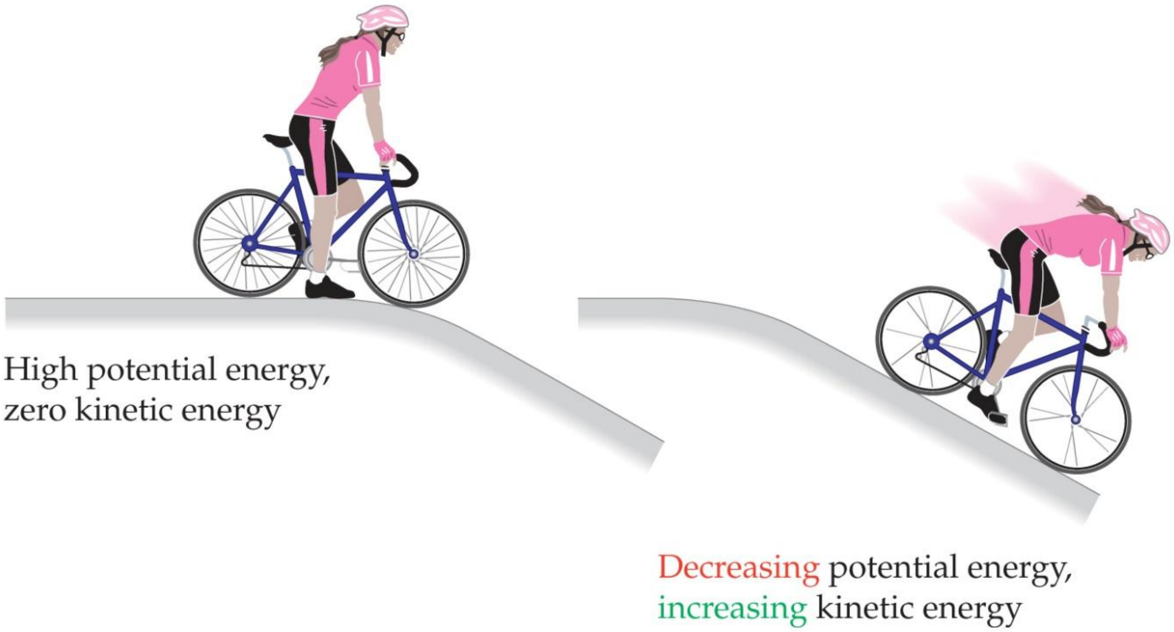
- Energy can also be transferred as heat.
- Heat flows from warmer objects to cooler objects.

Conversion of Energy



- Energy can be converted from one type to another.
- For example, the cyclist in Figure 5.2 has potential energy as she sits on top of the hill.

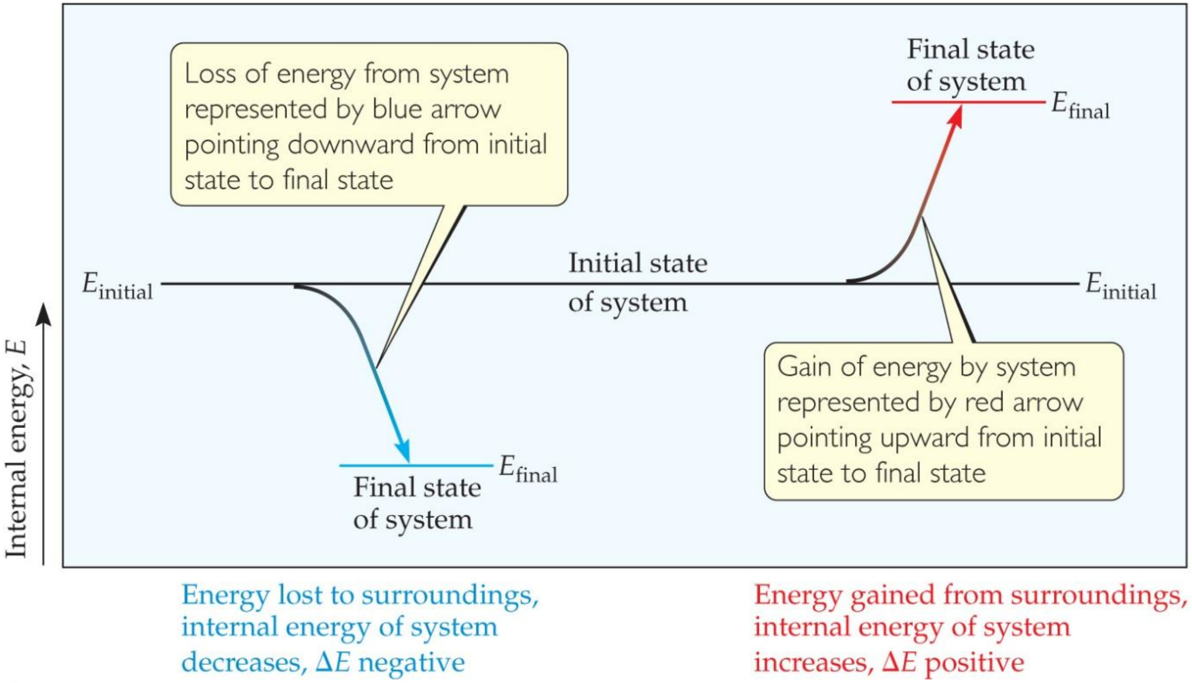
Conversion of Energy



- 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.

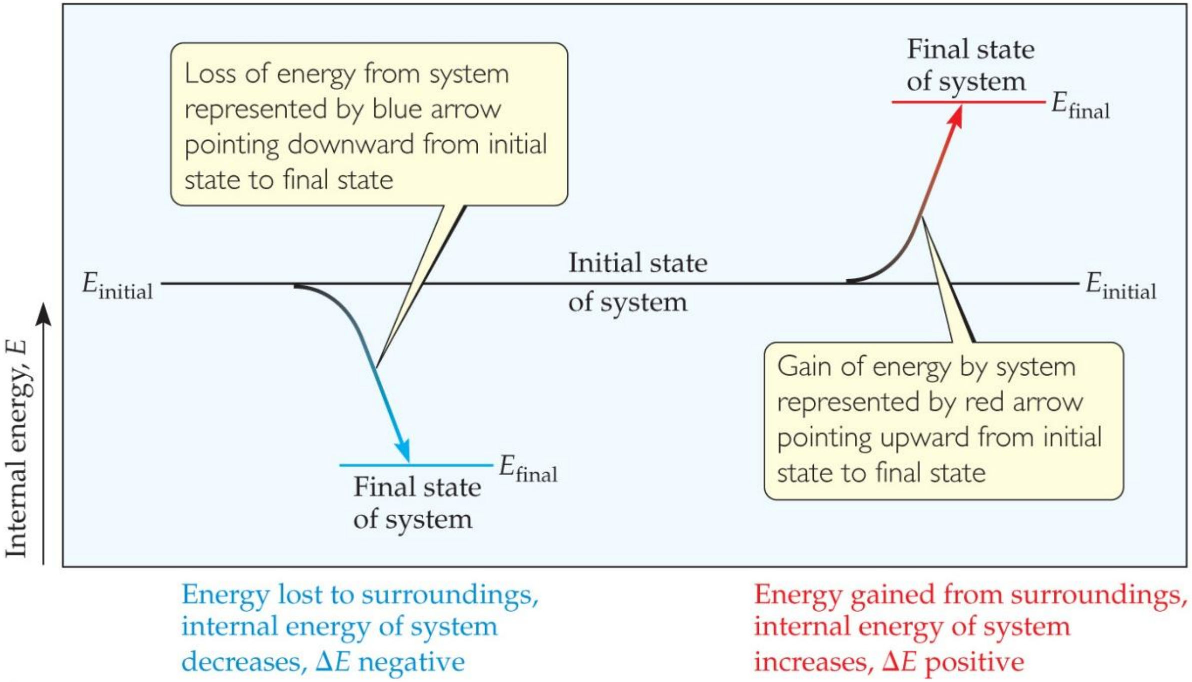
First Law of Thermodynamics

- 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

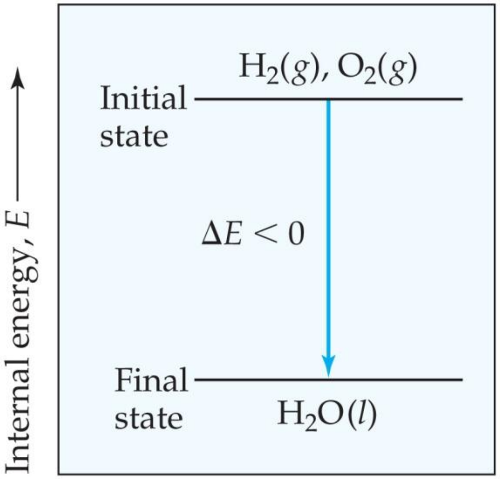
The **internal energy** of a system is the sum of all kinetic and potential energies of all components of the system; we call it *E.*



Internal Energy

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

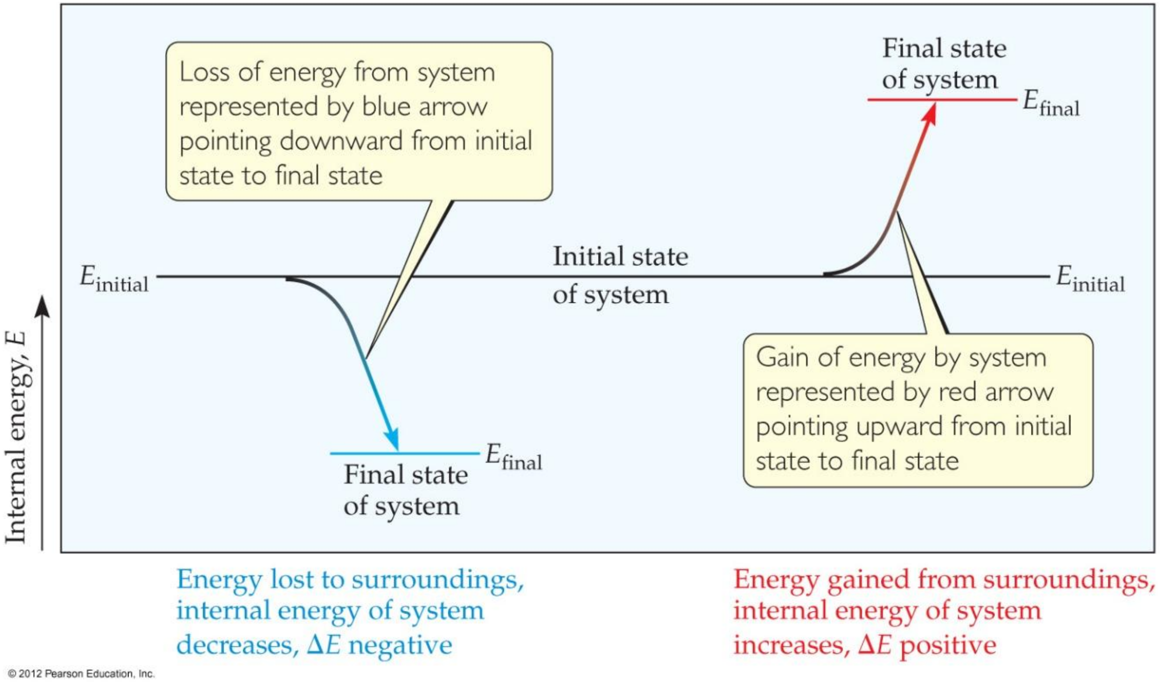
$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$



E_{initial} greater than E_{final}, energy released from system to surroundings during reaction, $\Delta E < 0$

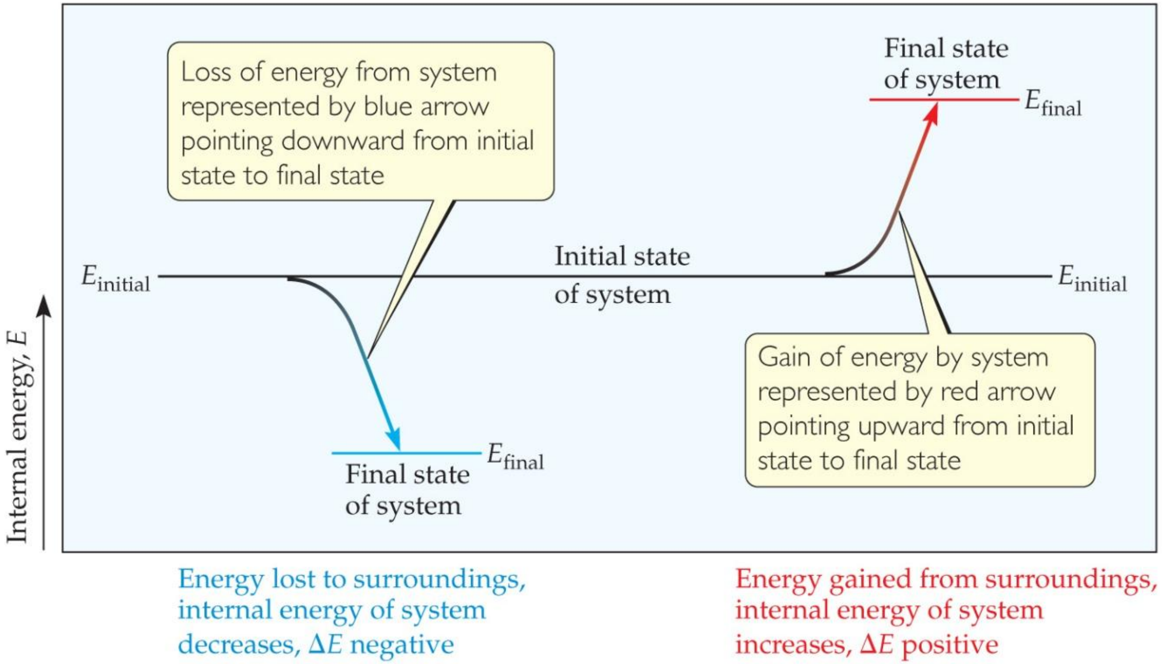
Changes in Internal Energy

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

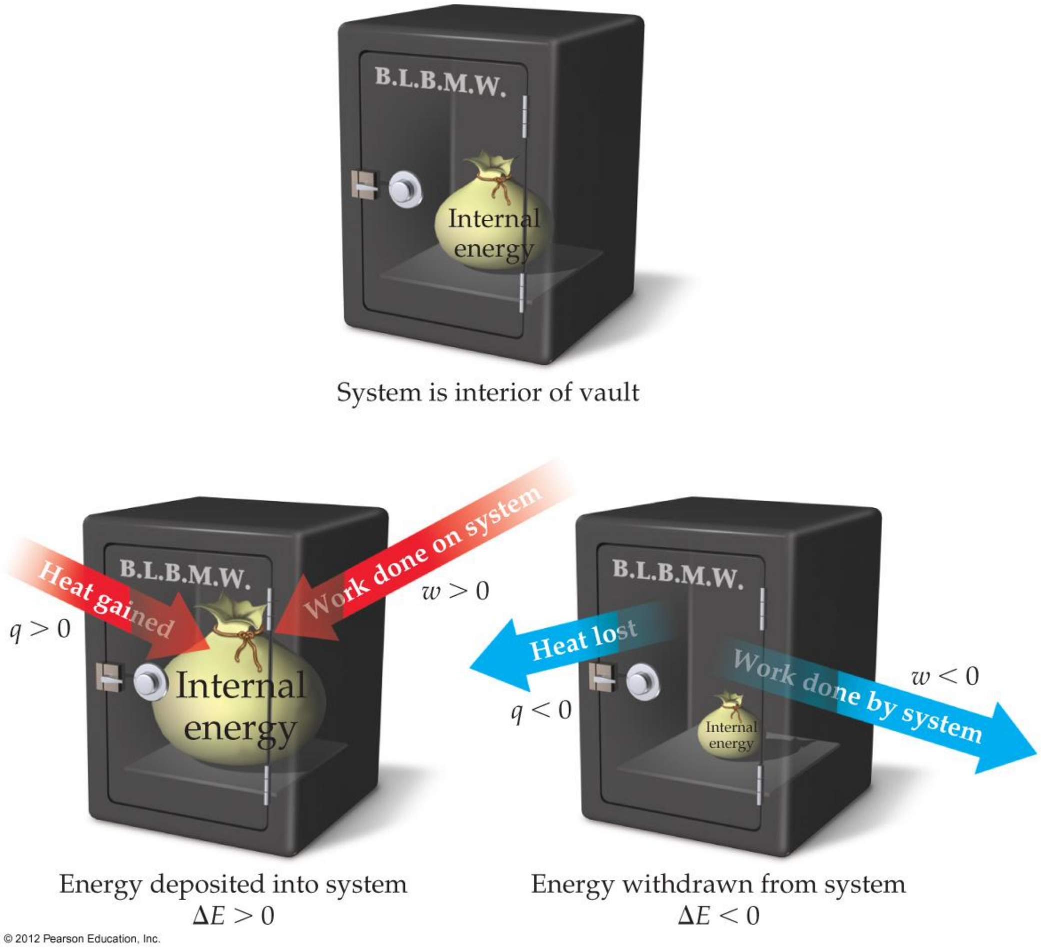


Changes in Internal Energy

- 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



System is interior of vault

Energy deposited into system
$\Delta E > 0$

Energy withdrawn from system
$\Delta E < 0$

- 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

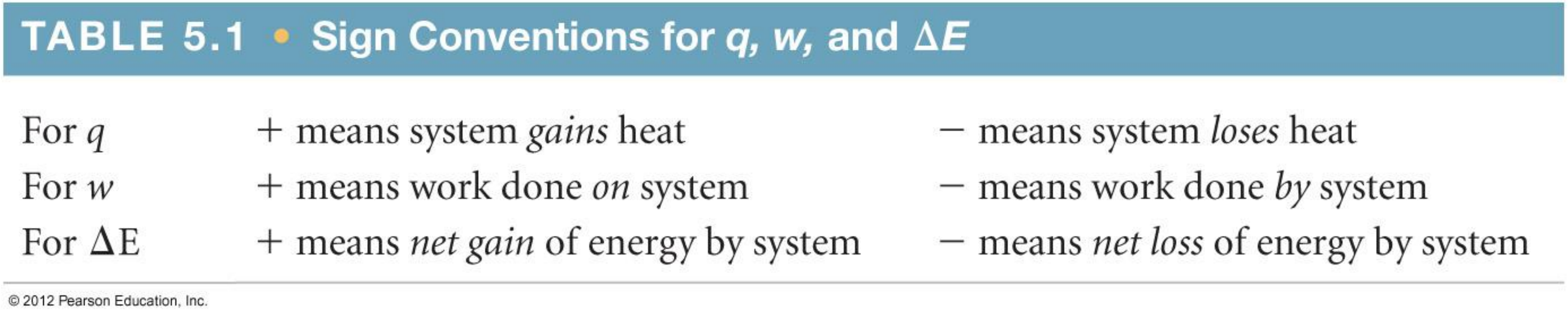


TABLE 5.1 • Sign Conventions for q, w, and ΔE

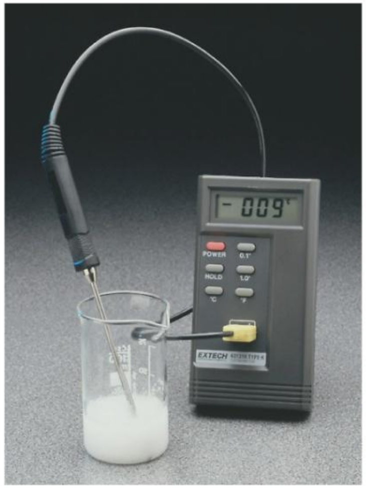
For q	+ means system *gains* heat	− means system *loses* heat
For w	+ means work done *on* system	− means work done *by* system
For ΔE	+ means *net gain* of energy by system	− means *net loss* of energy by system

Exchange of Heat between System and Surroundings

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

System: reactants + products

Surroundings: solvent,
initially at room temperature



Heat flows from surroundings into system (endothermic reaction), temperature of surroundings drops, thermometer reads temperature well below room temperature

(a)

Exchange of Heat between System and Surroundings

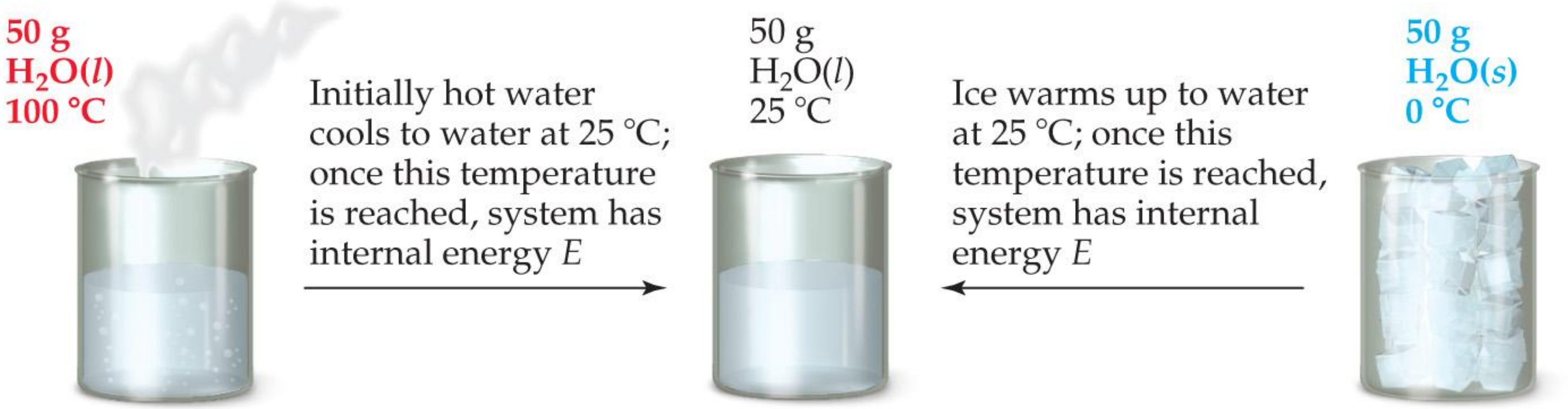
- When heat is absorbed by the system from the surroundings, the process is **endothermic**.
- When heat is released by the system into the surroundings, the process is **exothermic**.

Heat flows (violently) from system into surroundings (exothermic reaction), temperature of surroundings increases

(b)

State Functions

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

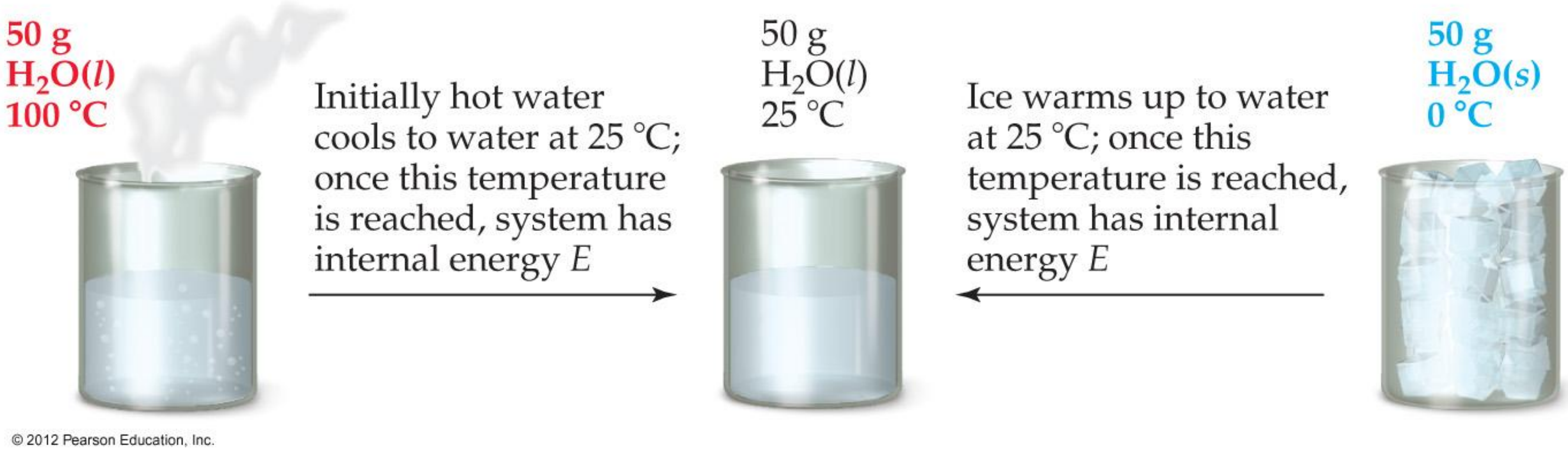


Initially hot water cools to water at 25 °C; once this temperature is reached, system has internal energy *E*

Ice warms up to water at 25 °C; once this temperature is reached, system has internal energy *E*

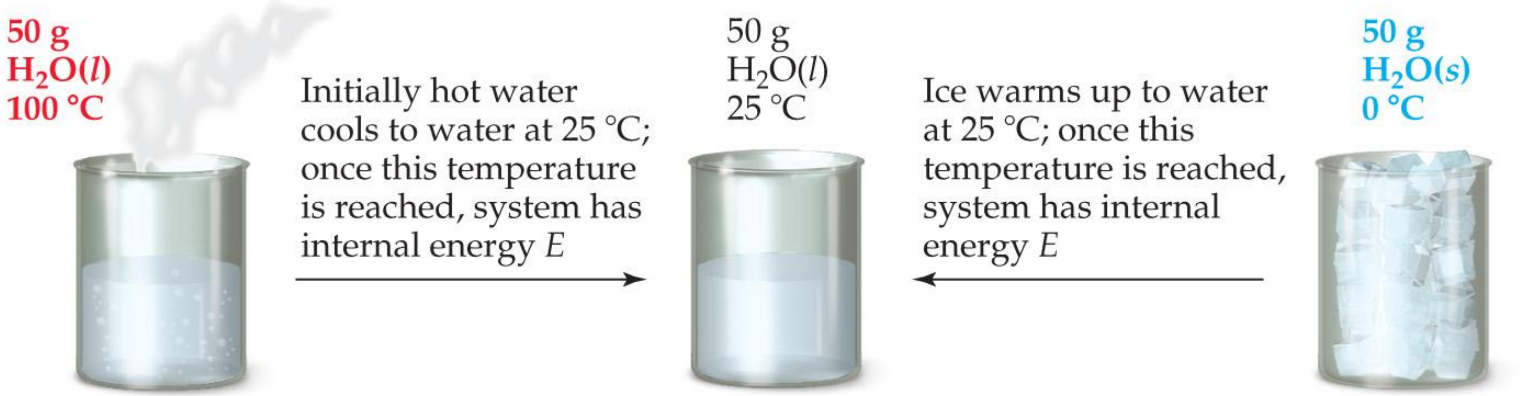
State Functions

- 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 depicted in Figure 5.9, 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}.



Initially hot water cools to water at 25 °C; once this temperature is reached, system has internal energy *E*

Ice warms up to water at 25 °C; once this temperature is reached, system has internal energy *E*

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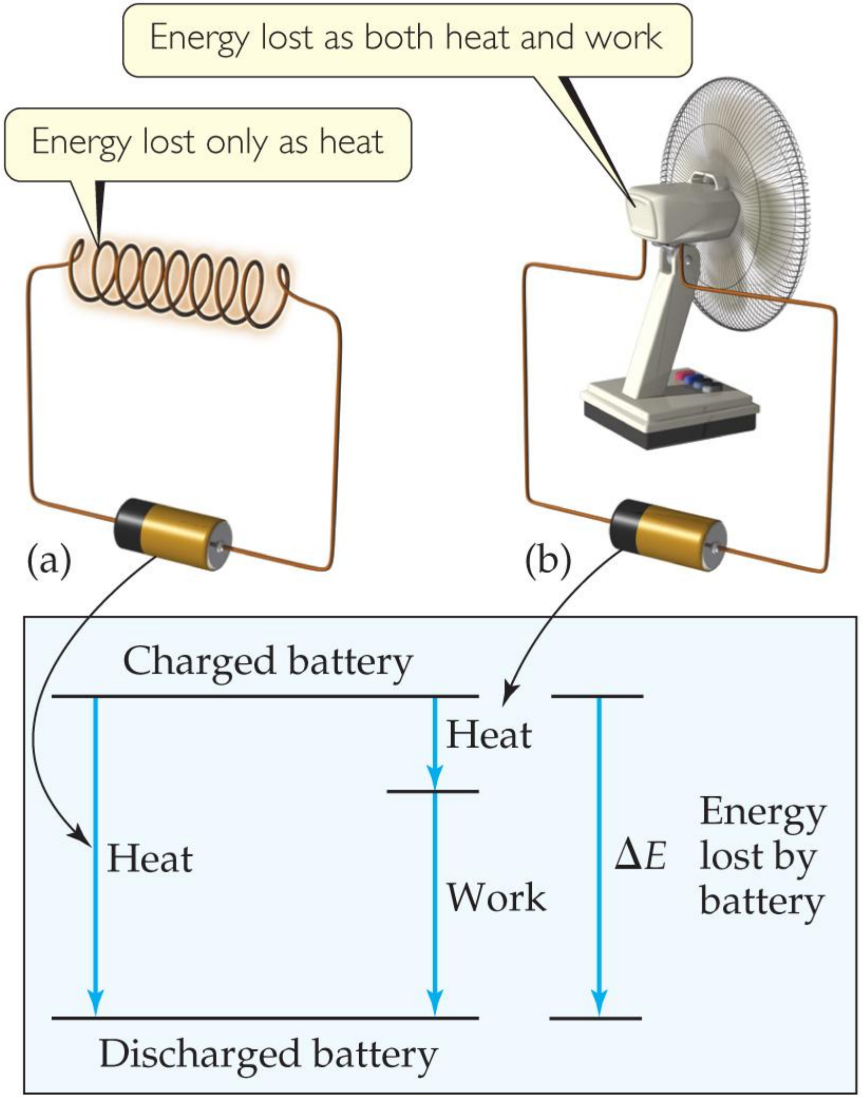
State Functions



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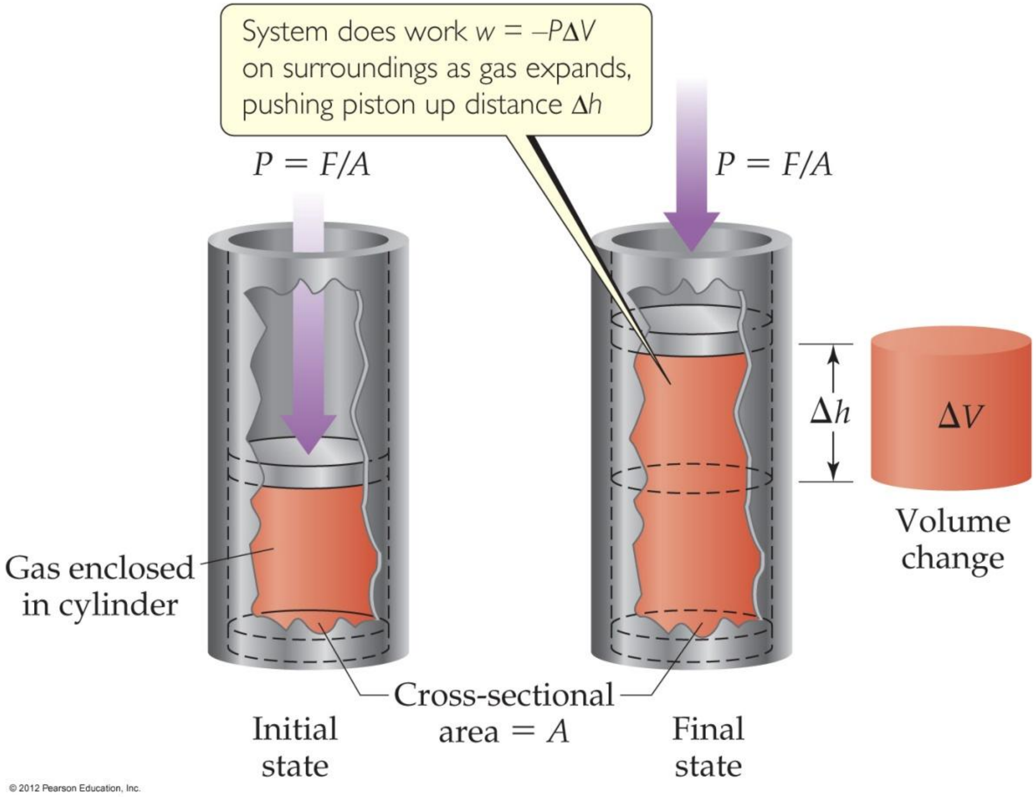
- However, *q* and *w* are *not* state functions.
- Whether the battery is shorted out or is discharged by running the fan, its Δ*E* is the same.
  - But *q* and *w* are different in the two cases.

Work

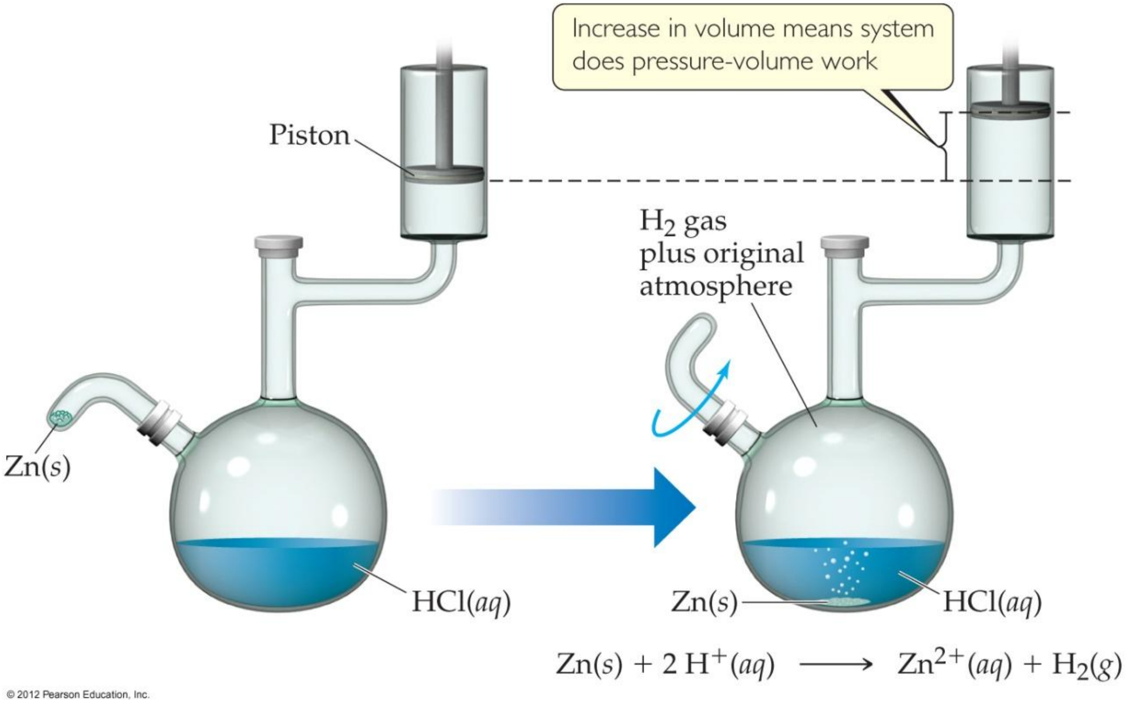


Usually in an open container the only work done is by a gas pushing on the surroundings (or by the surroundings pushing on the gas).

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:

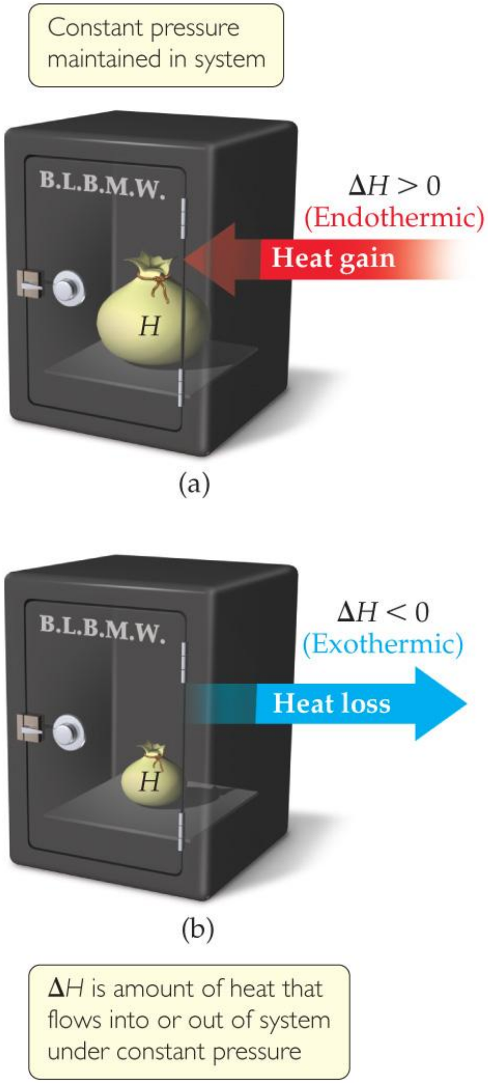
$$\Delta H = \Delta E + P\Delta V$$

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

$$\Delta H = q$$

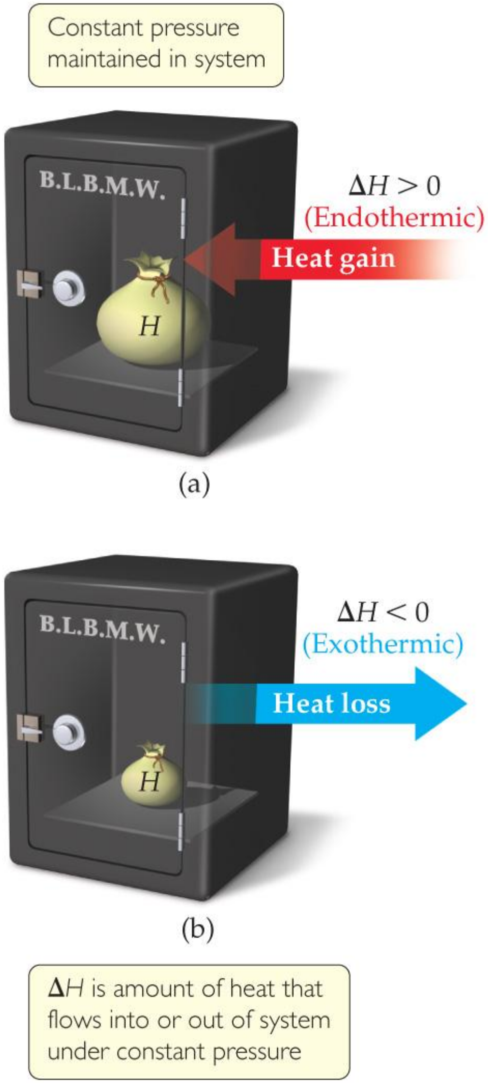
- So, at constant pressure, the change in enthalpy *is* the heat gained or lost.

Endothermicity and Exothermicity



- A process is endothermic when ΔH is positive.

Endothermicity and Exothermicity



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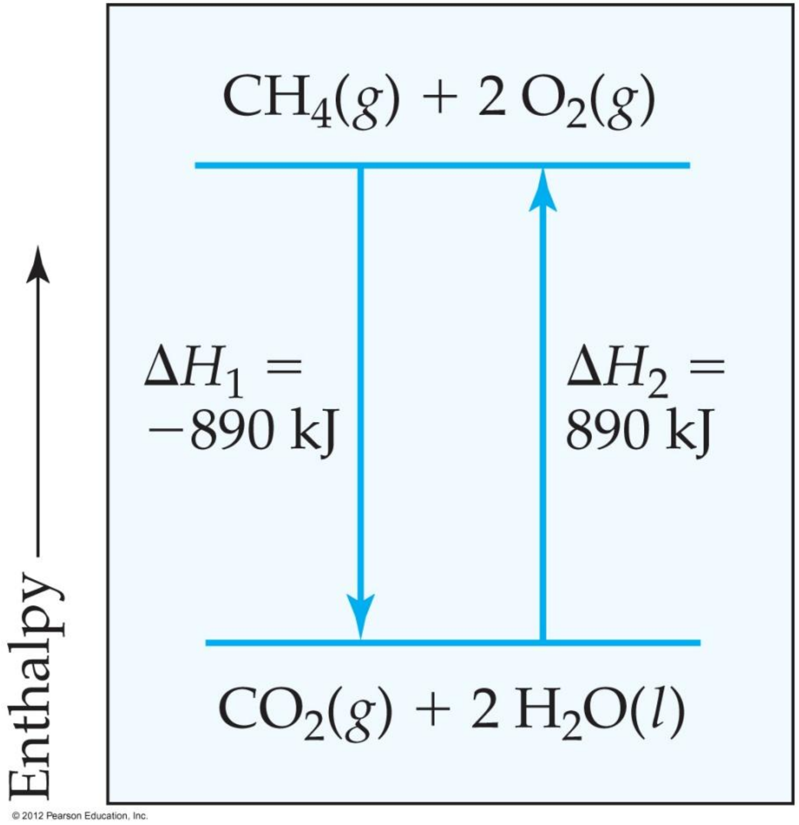
- A process is endothermic when ΔH is positive.
- A process is exothermic when ΔH is negative.

Enthalpy of Reaction

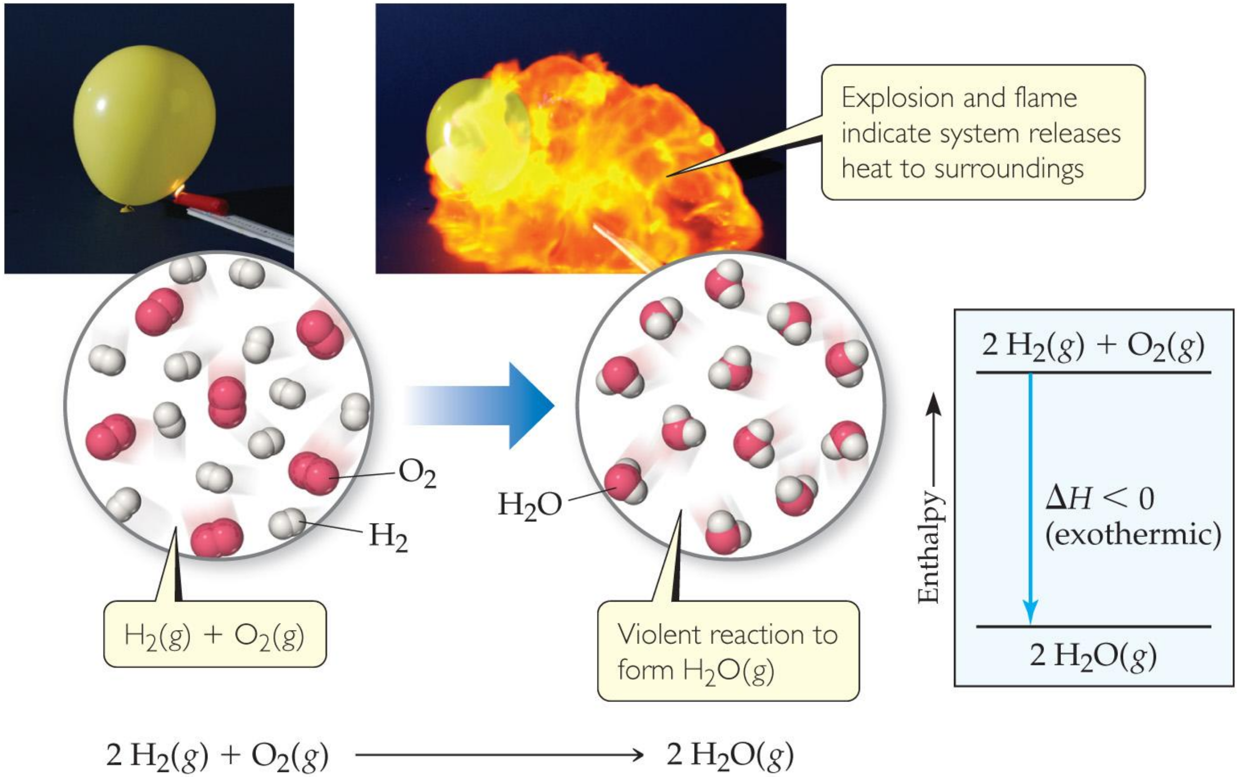
The *change* in enthalpy, ΔH, is the enthalpy of the products minus the enthalpy of the reactants:

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



Enthalpy of Reaction

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



Explosion and flame indicate system releases heat to surroundings

$H_2(g) + O_2(g)$

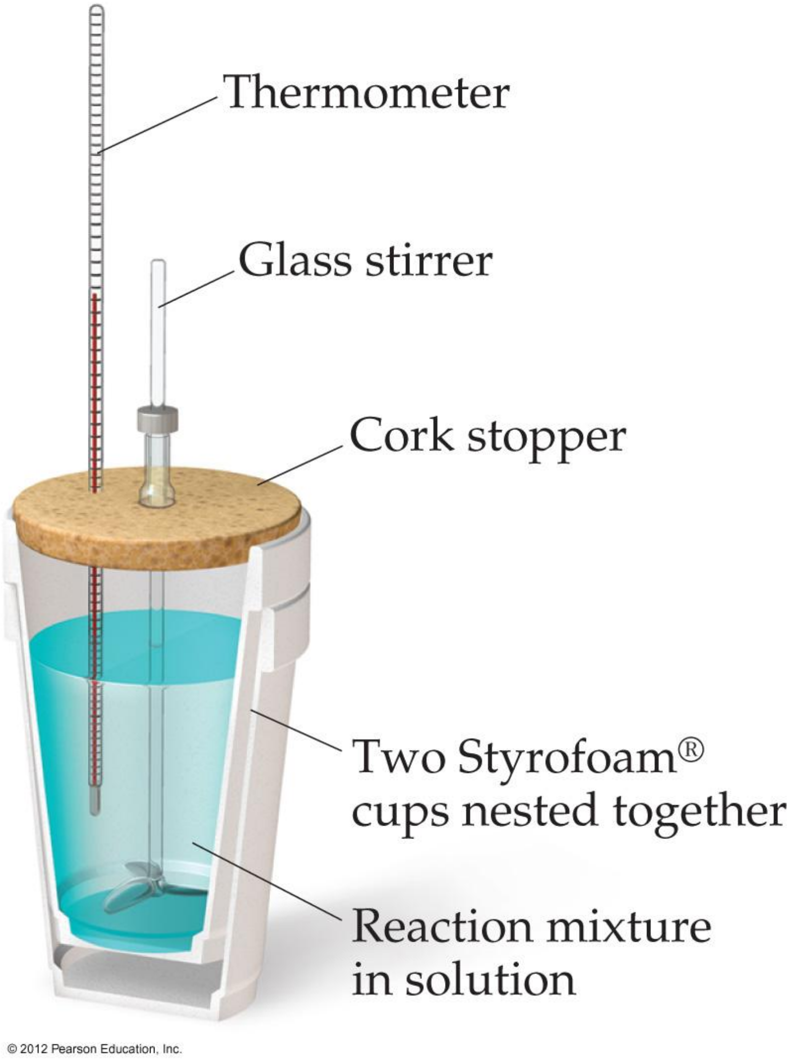
Violent reaction to form $H_2O(g)$

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

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.

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**.

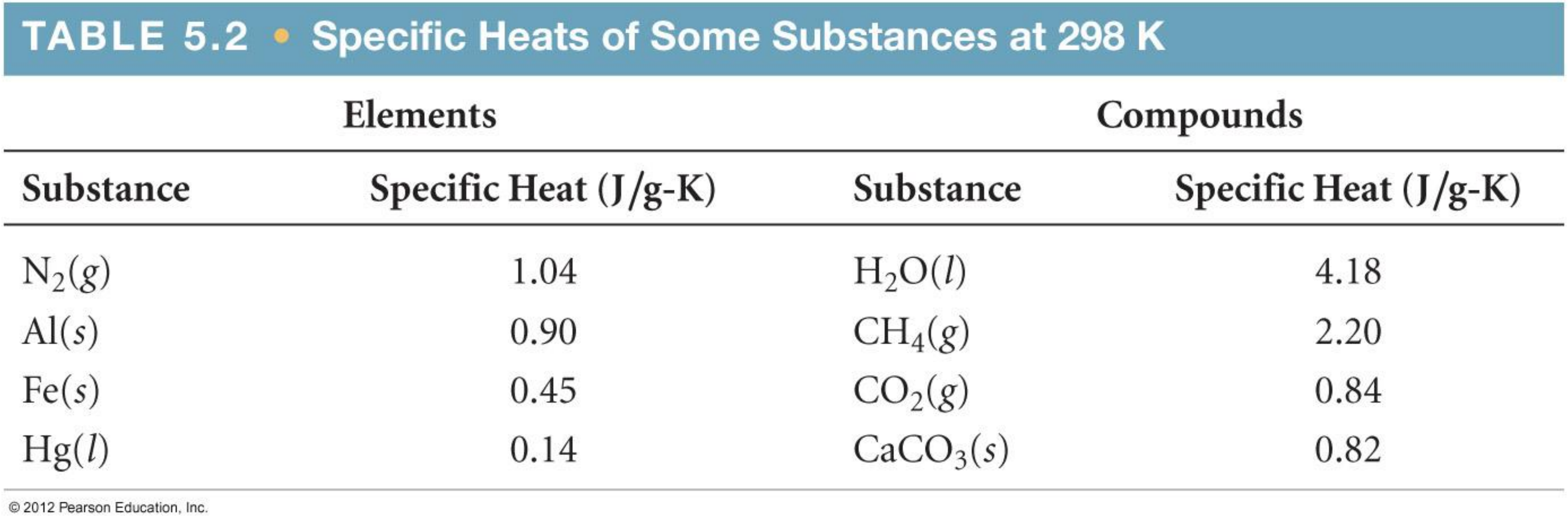
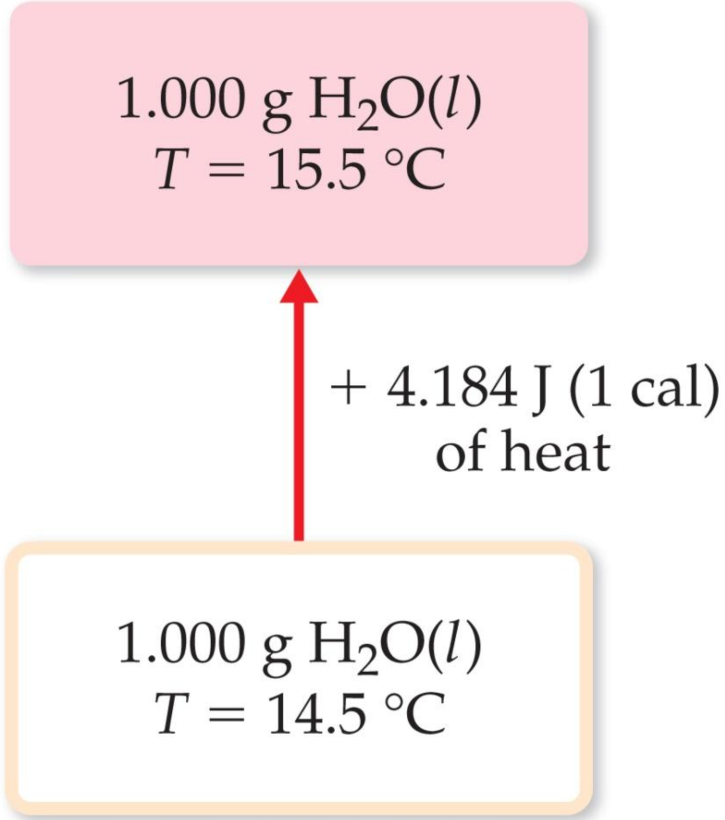


TABLE 5.2 • Specific Heats of Some Substances at 298 K

Elements		Compounds	
Substance	**Specific Heat (J/g-K)**	**Substance**	**Specific Heat (J/g-K)**
$N_2(g)$	1.04	$H_2O(l)$	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 (or 1 °C).



1.000 g $H_2O(l)$
$T = 15.5\ °C$

+ 4.184 J (1 cal) of heat

1.000 g $H_2O(l)$
$T = 14.5\ °C$

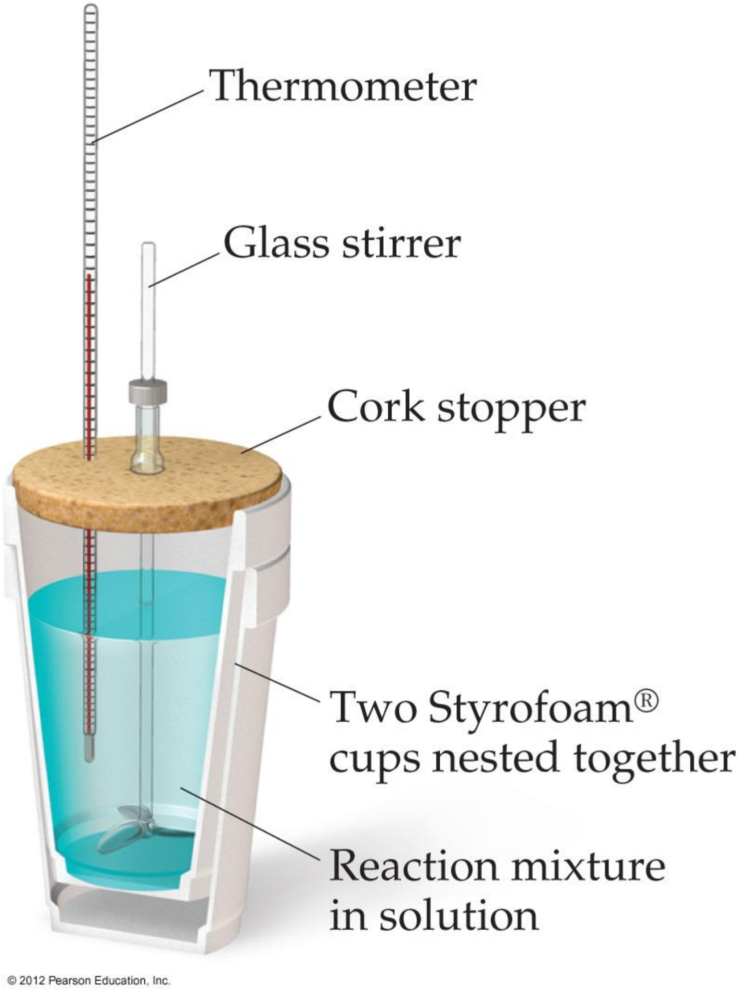
Heat Capacity and Specific Heat

Specific heat, then, is

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

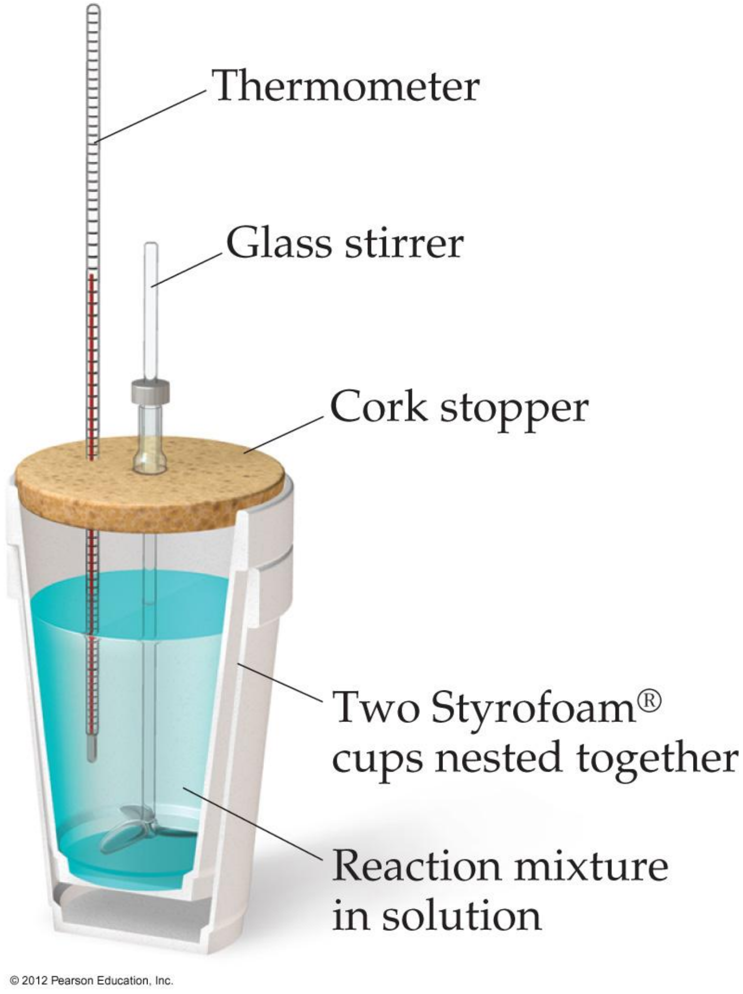
$$s = \frac{q}{m \times \Delta T}$$

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

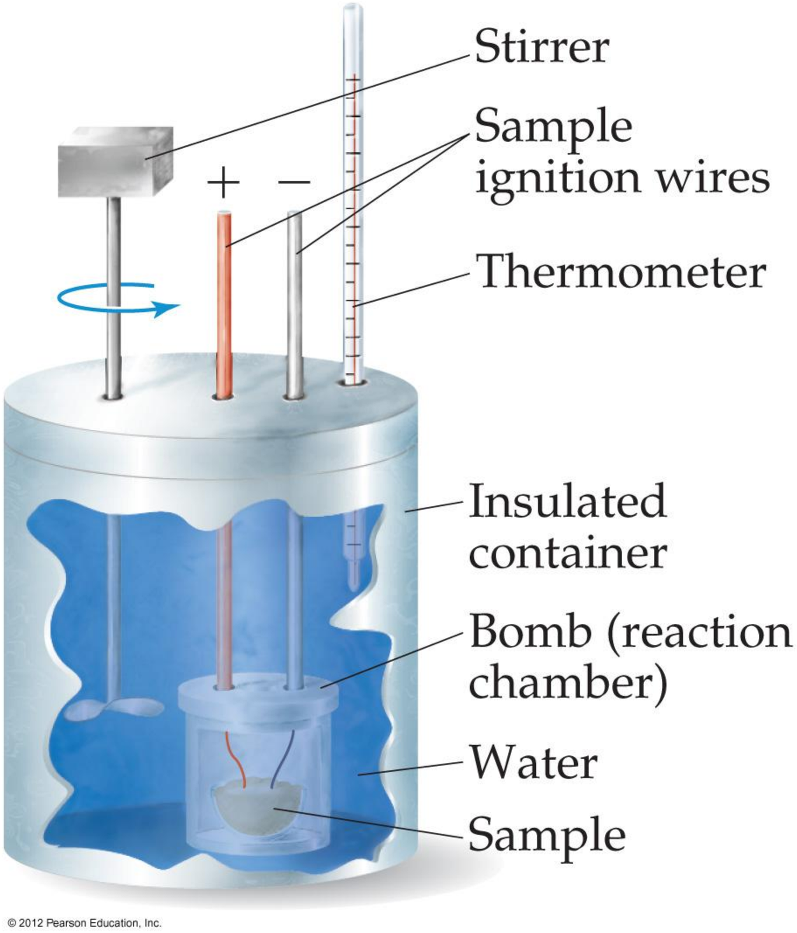


Because the specific heat for water is well known (4.184 J/g-K), we can measure ΔH for the reaction with this equation:

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

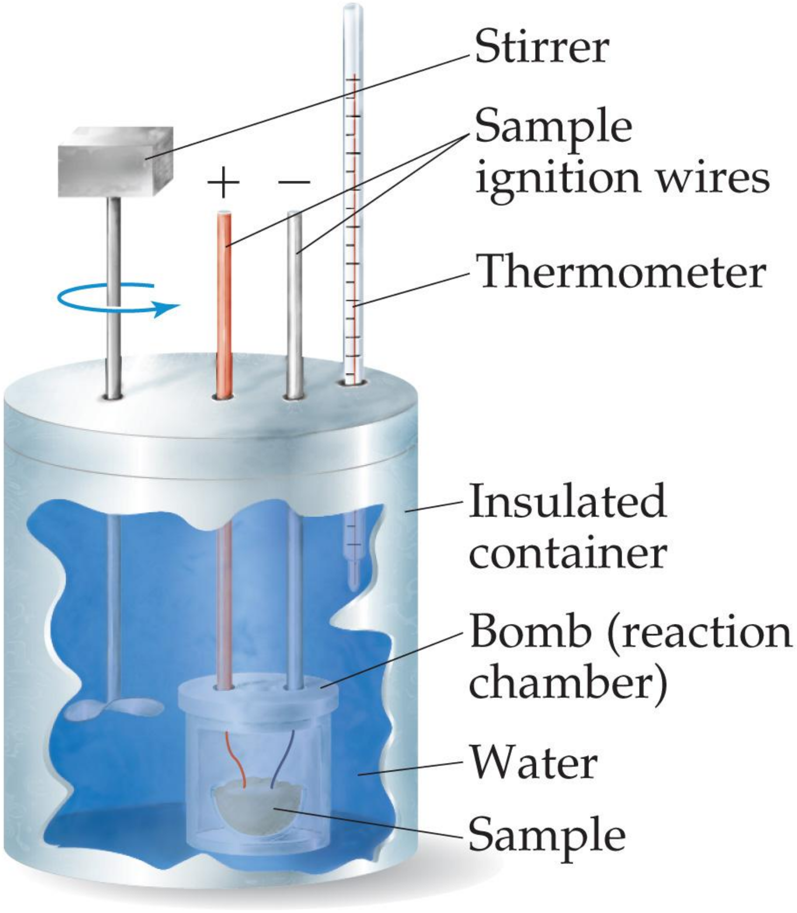
Bomb Calorimetry

- Reactions can be carried out in a sealed “bomb” such as this one.
- The heat absorbed (or released) by the water is a very good approximation of the enthalpy change for the reaction.



Bomb Calorimetry

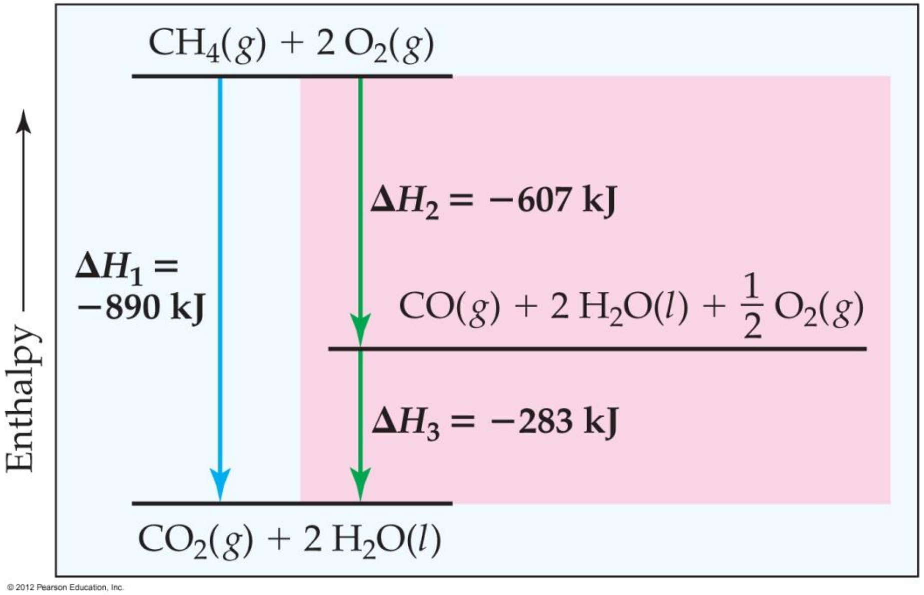
- Because the volume in the bomb calorimeter is constant, what is measured is really the change in internal energy, ΔE, not ΔH.
- For most reactions, the difference is very small.



Hess’s Law

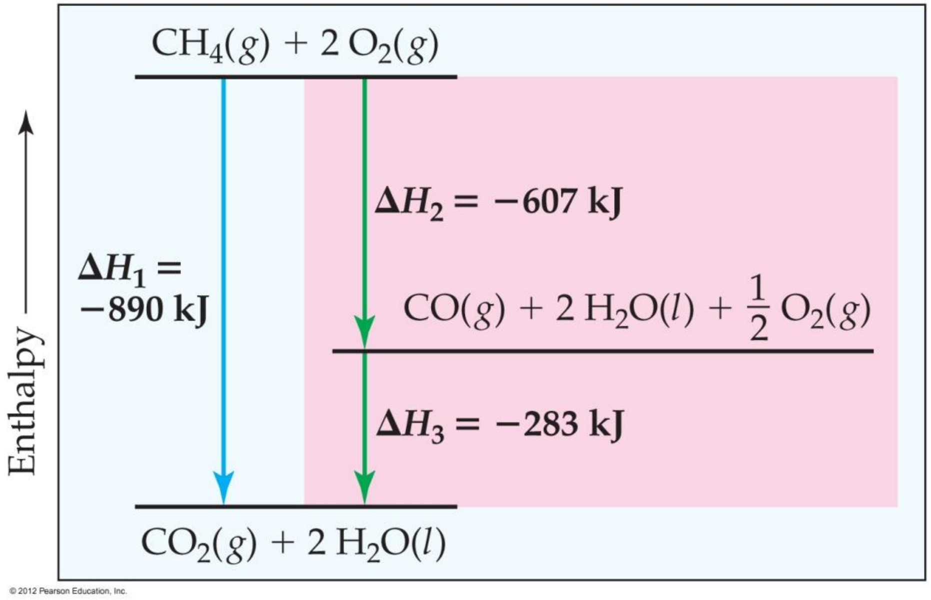
- ΔH is well known for many reactions, and it is inconvenient to measure ΔH for every reaction in which we are interested.
- However, we can estimate ΔH using published ΔH values and the properties of enthalpy.

Hess's Law



Hess's law states that "[i]f 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).

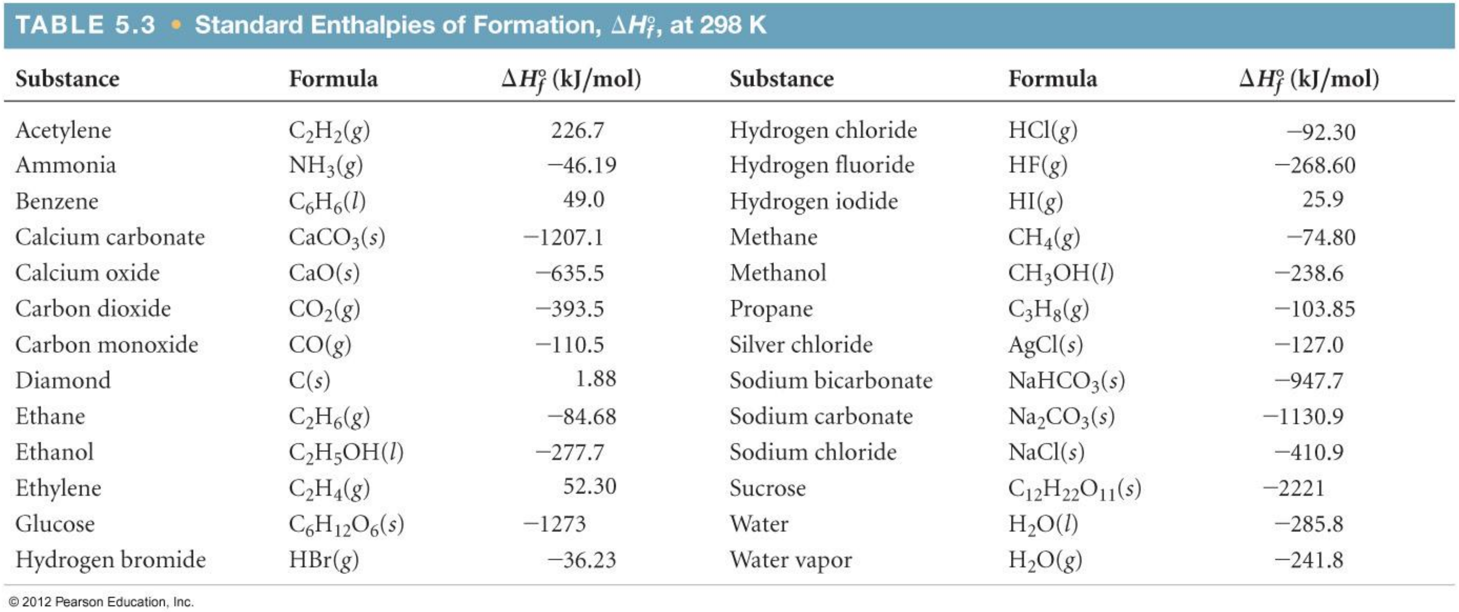


TABLE 5.3 • Standard Enthalpies of Formation, ΔH_f°, at 298 K

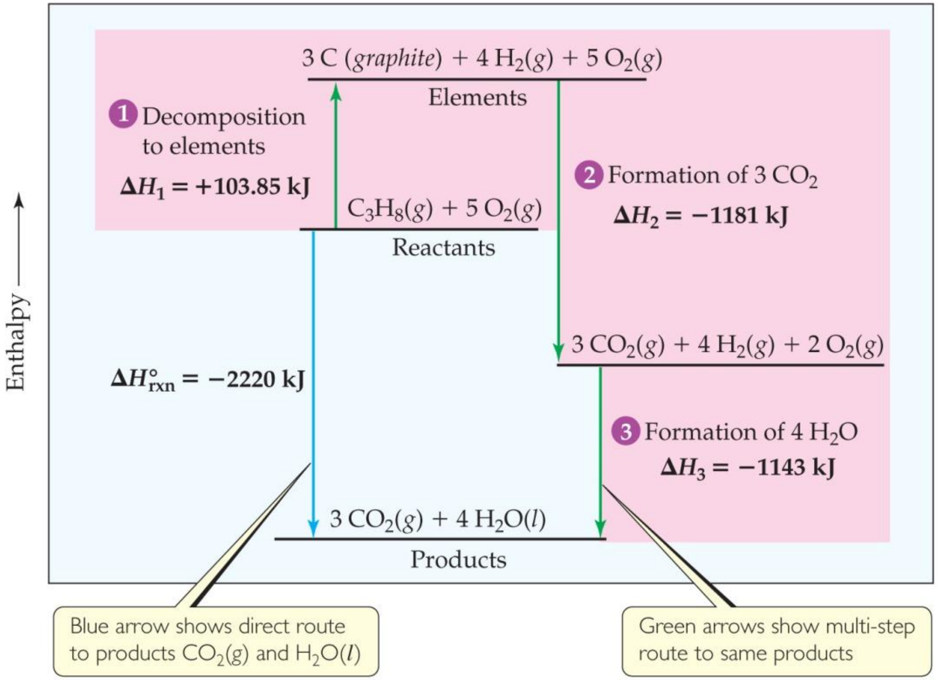
Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80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

Calculation of ΔH

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

- Imagine this as occurring in three steps:

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



Blue arrow shows direct route to products $CO_2(g)$ and $H_2O(l)$

Green arrows show multi-step route to same products

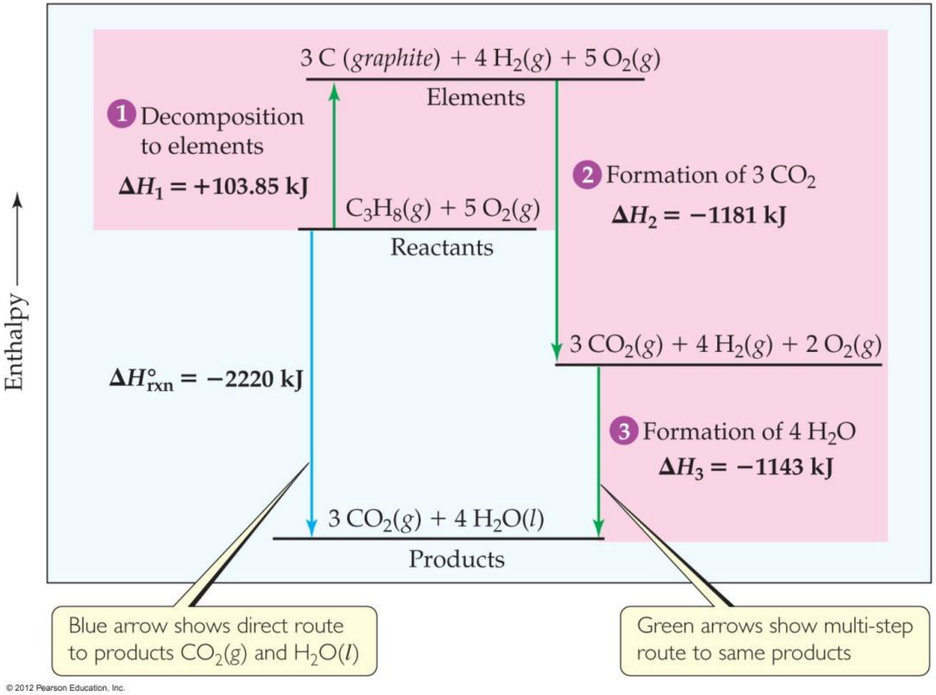
Calculation of Δ*H*

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

- Imagine this as occurring in three steps:

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

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



Calculation of ΔH

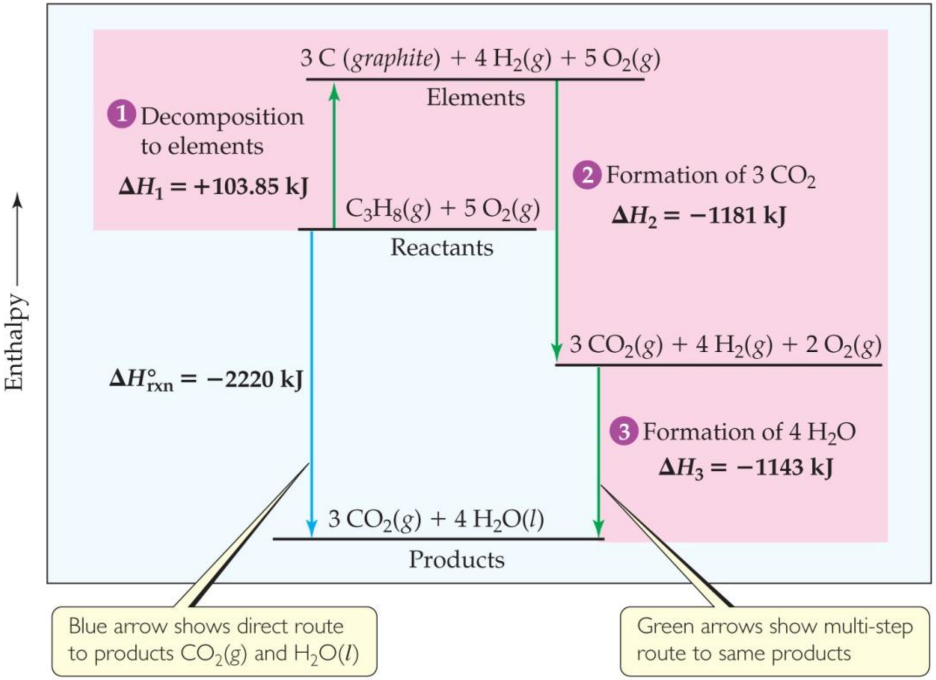
$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

- Imagine this as occurring in three steps:

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

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

$$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l)$$



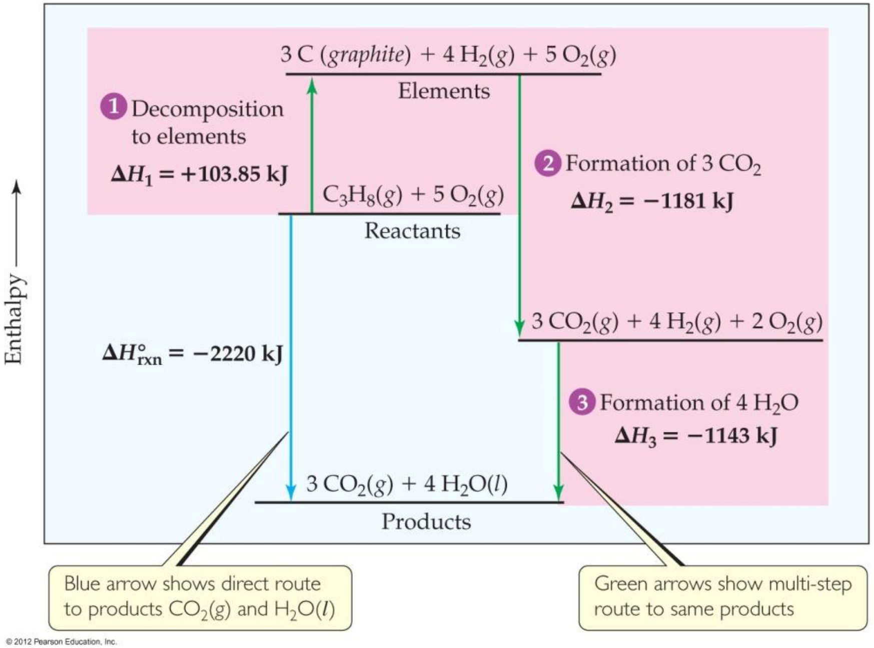
Calculation of Δ*H*

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

- The sum of these equations is

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

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



Blue arrow shows direct route to products $CO_2(g)$ and $H_2O(l)$

Green arrows show multi-step route to same products

Calculation of ΔH

We can use Hess's law in this way:

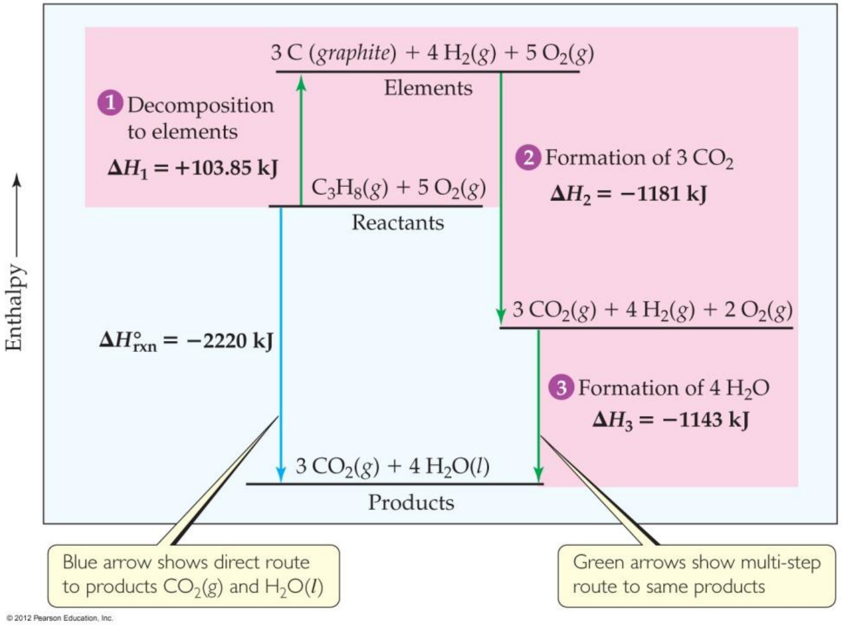
$$\Delta H = \Sigma n\Delta H_{f,\text{products}} - \Sigma m\Delta H_{f}^{\circ}{}_{,\text{reactants}}$$

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

Calculation of Δ*H*

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

$$\begin{aligned}\Delta H &= [3(-393.5\text{ kJ}) + 4(-285.8\text{ kJ})] - [1(-103.85\text{ kJ}) + 5(0\text{ kJ})]\\ &= [(-1180.5\text{ kJ}) + (-1143.2\text{ kJ})] - [(-103.85\text{ kJ}) + (0\text{ kJ})]\\ &= (-2323.7\text{ kJ}) - (-103.85\text{ kJ}) \quad = \quad -2219.9\text{ kJ}\end{aligned}$$



Blue arrow shows direct route to products $CO_2(g)$ and $H_2O(l)$

Green arrows show multi-step route to same products

Energy in Foods

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

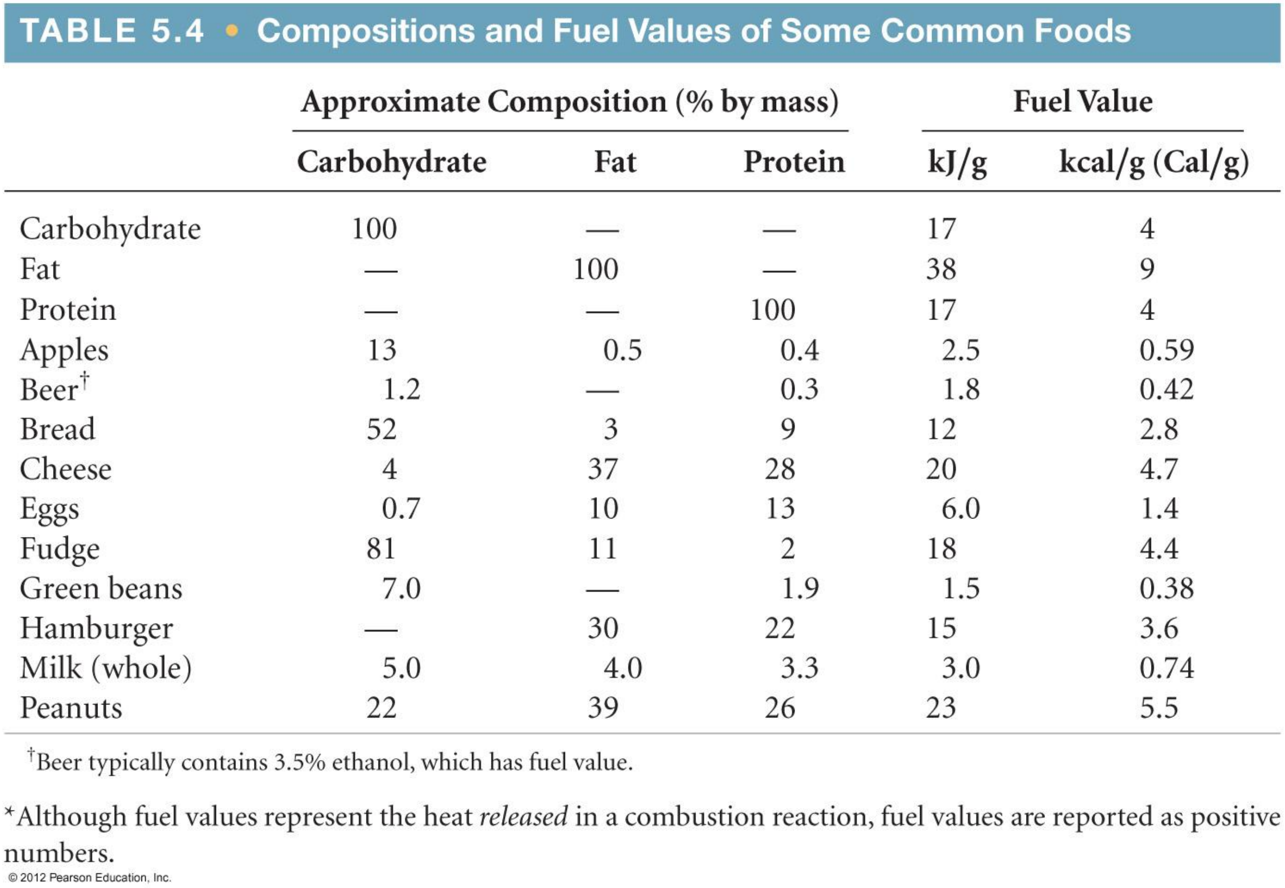


TABLE 5.4 • Compositions and Fuel Values of Some Common Foods

	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

[†] Beer typically contains 3.5% ethanol, which has fuel value.

*Although fuel values represent the heat *released* in a combustion reaction, fuel values are reported as positive numbers.

Energy in Fuels

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

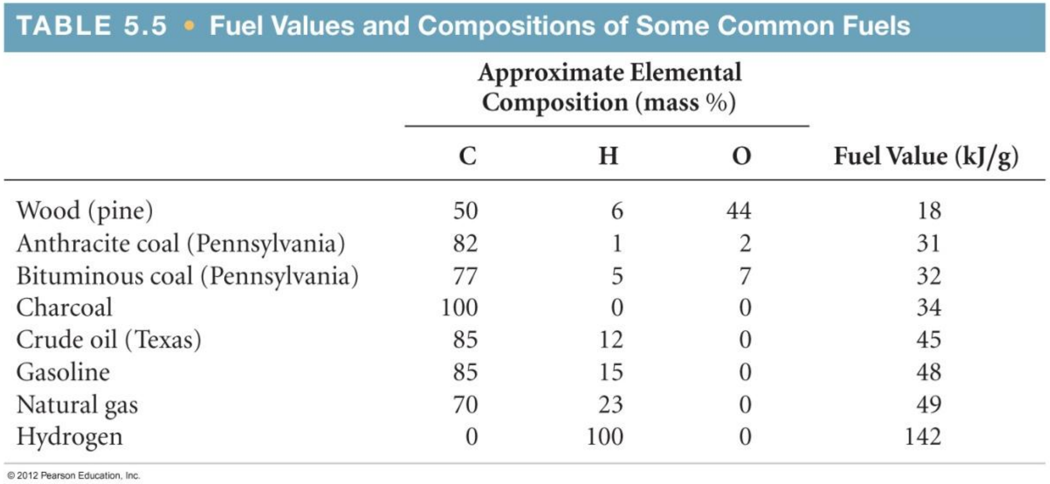


TABLE 5.5 • Fuel Values and Compositions of Some Common Fuels

	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