

Lecture Presentation

Chapter 5

Thermochimistry

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**.
- This chapter is about **thermodynamics**, which is the study of energy transformations, and **thermochemistry**, which applies the field to chemical reactions, specifically.

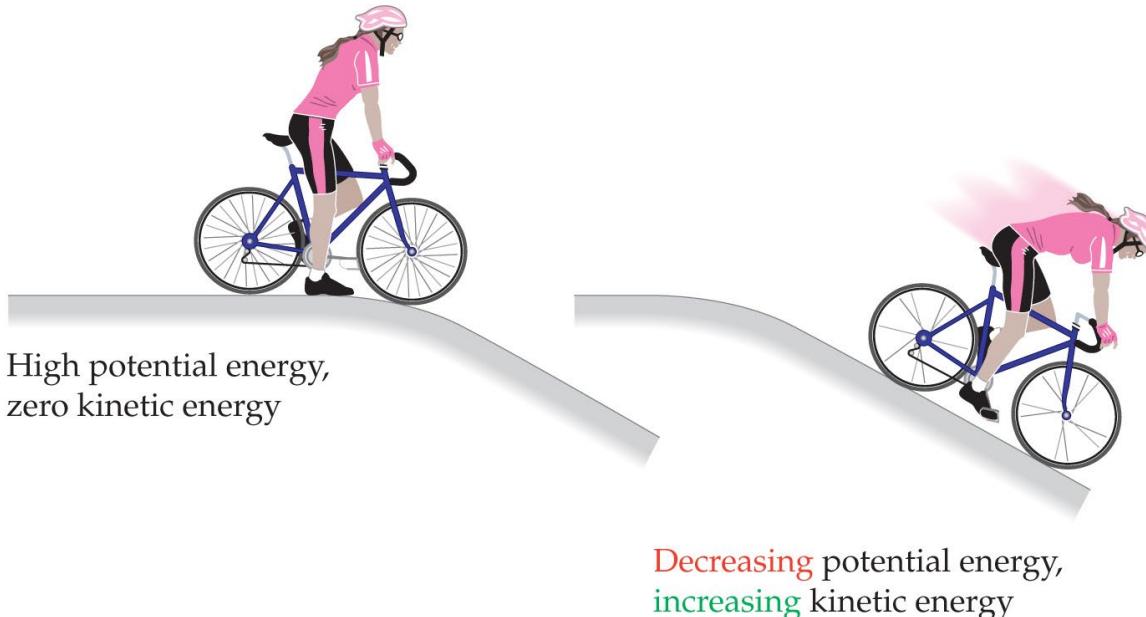
Thermochemistry



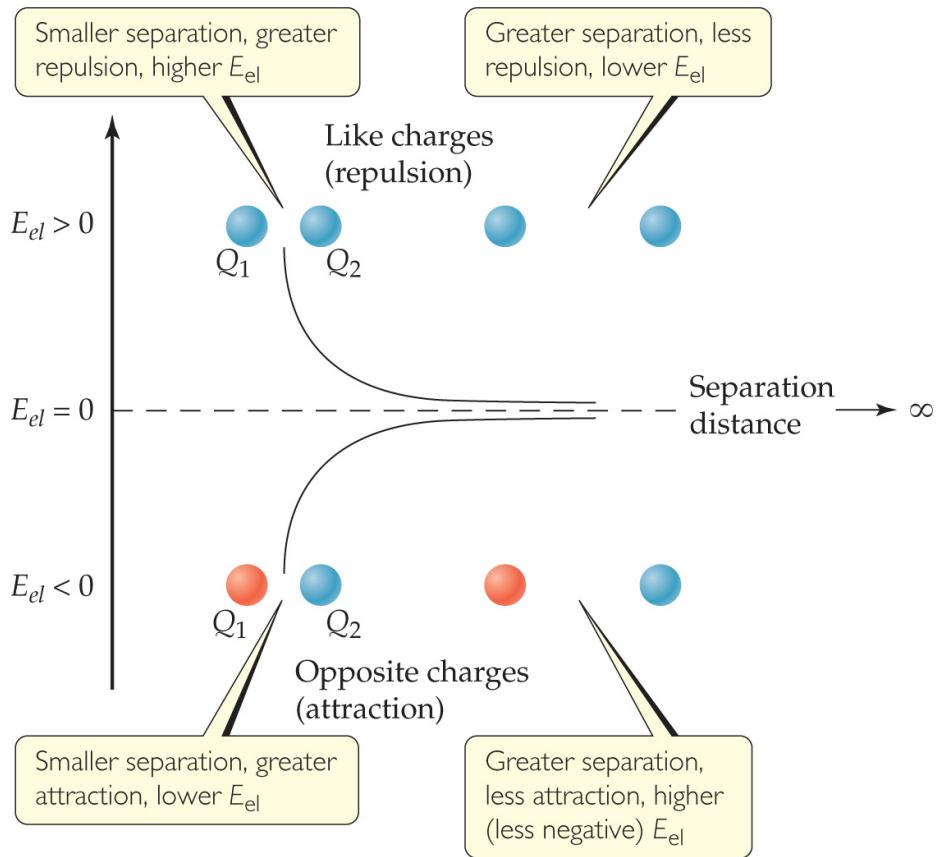
Kinetic Energy

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} :

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

Units of Energy

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

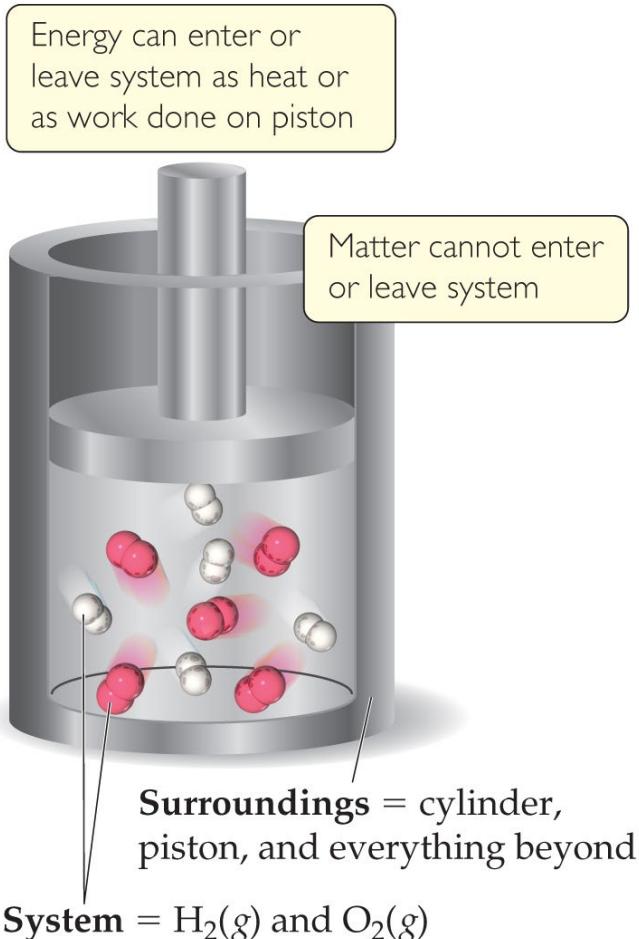
$$1 \text{ J} = 1 \frac{\text{kg m}^2}{\text{s}^2}$$

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

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

(Note: this is *not* the same as the calorie of foods; the food calorie is 1 kcal!)

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).

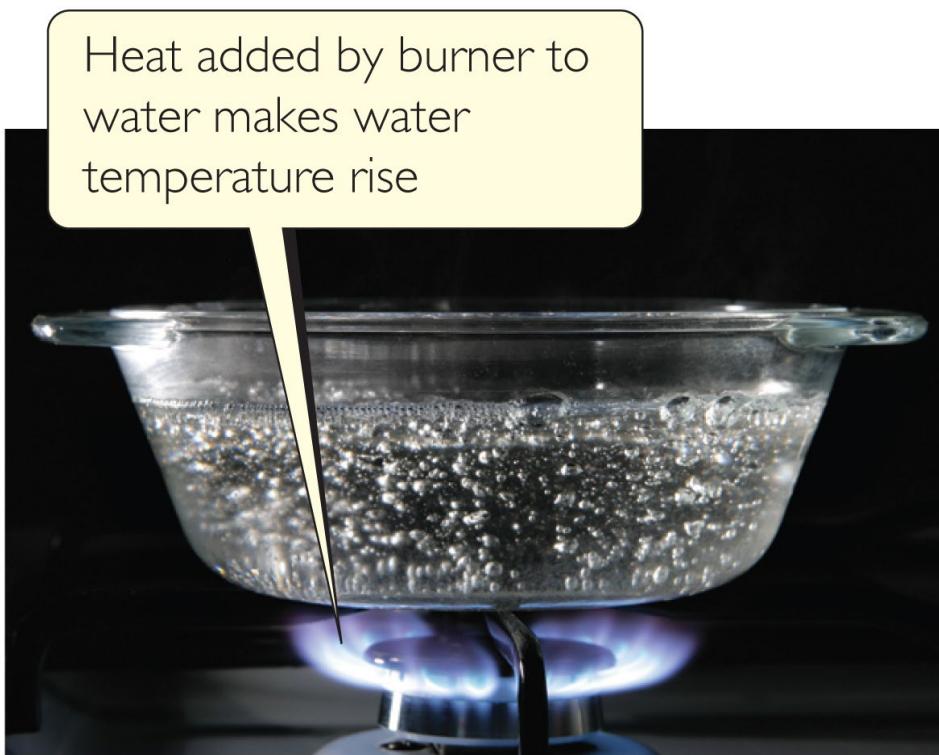
Definitions: Work

- 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

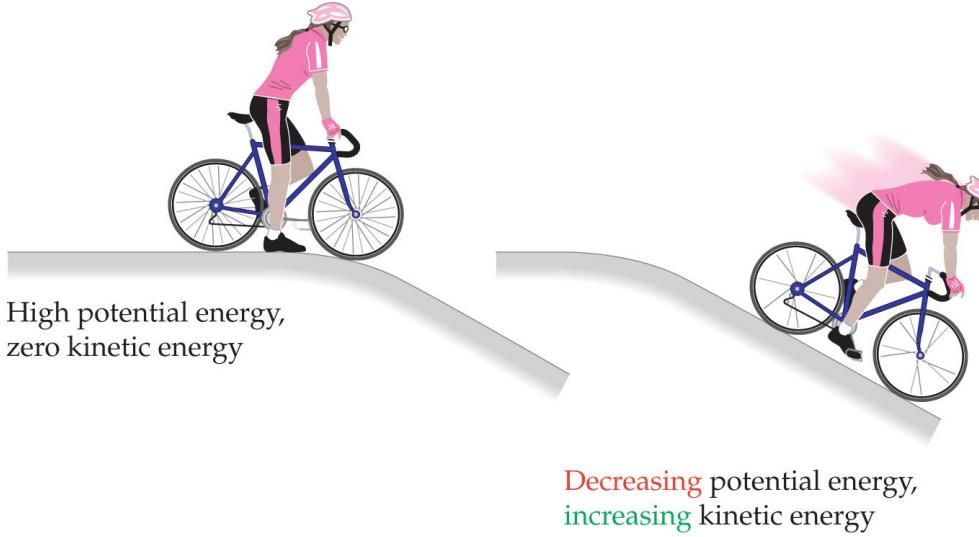


- Energy can also be transferred as heat.
- Heat flows from warmer objects to cooler objects.



Conversion of Energy

- Energy can be converted from one type to another.
- The cyclist has potential energy as she sits on top of the hill.
- As she coasts down the hill, her potential energy is converted to kinetic energy until the bottom, where the energy is converted to kinetic energy.



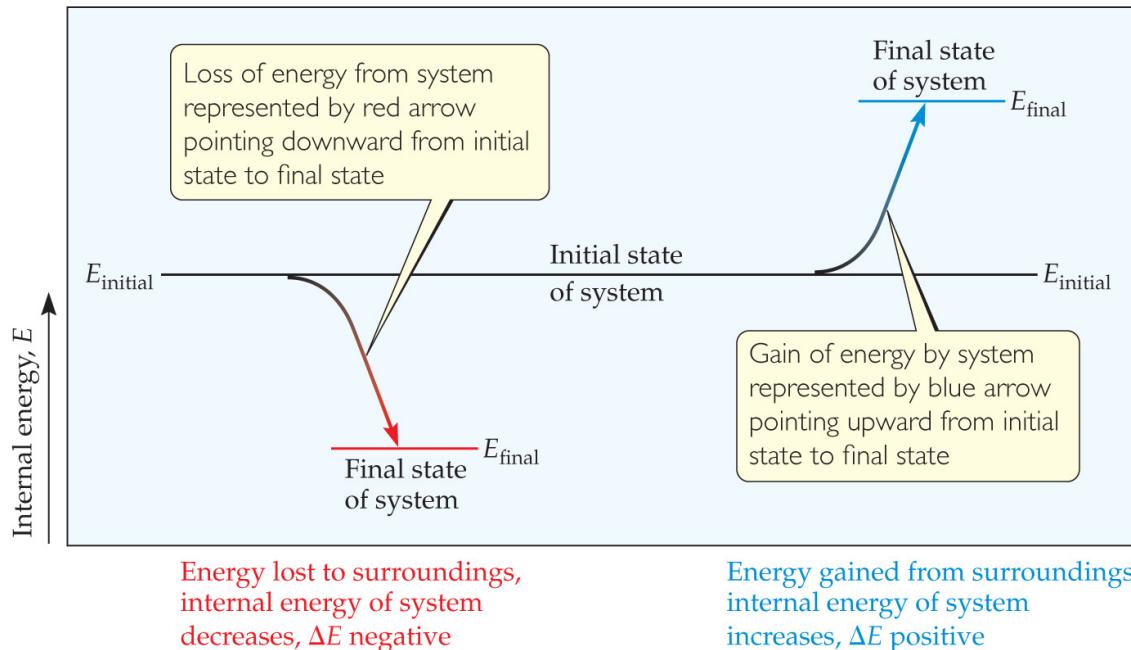
First Law of Thermodynamics

- 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

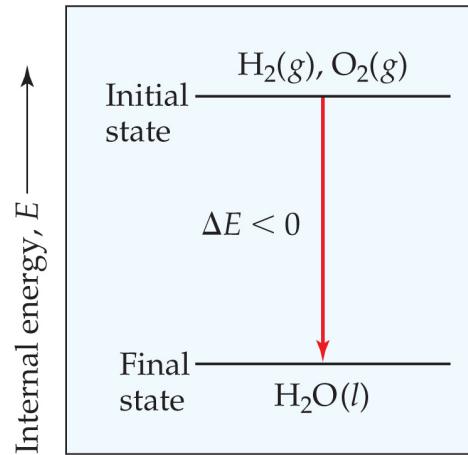
The **internal energy** of a system is the sum of all kinetic and potential energies of all components of the system; we call it E .



Internal Energy

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

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

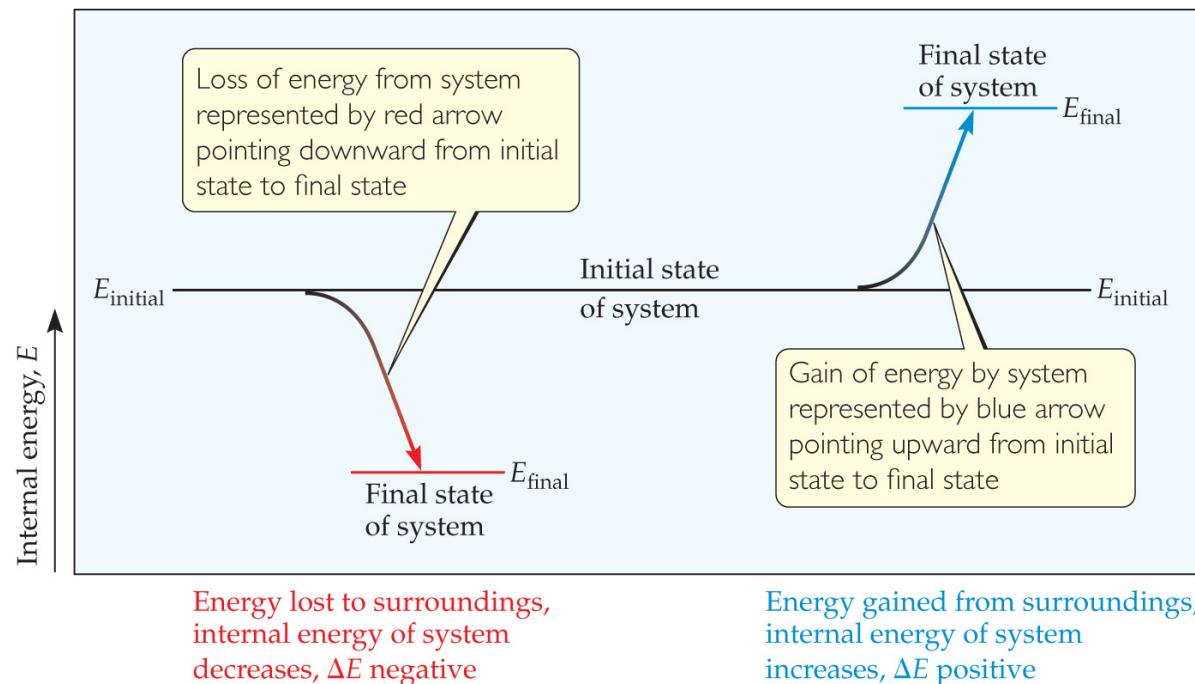


E_{initial} greater than E_{final} ;
therefore, energy is released
from system to surroundings
during reaction and $\Delta E < 0$



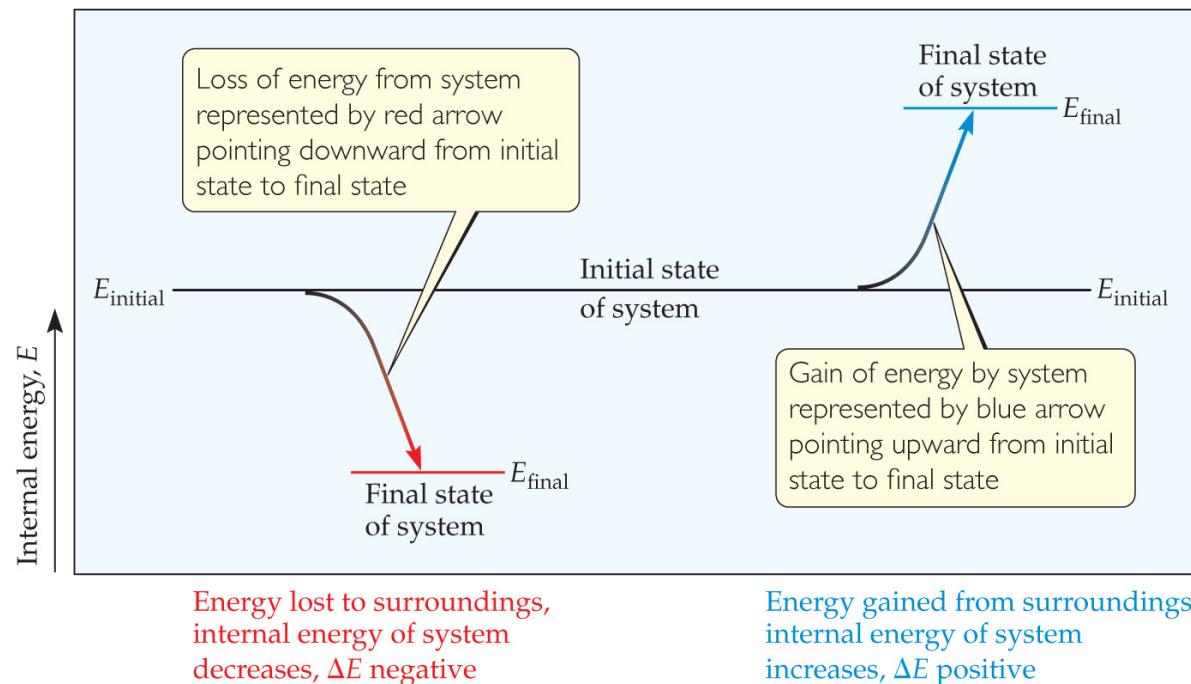
Changes in Internal Energy

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

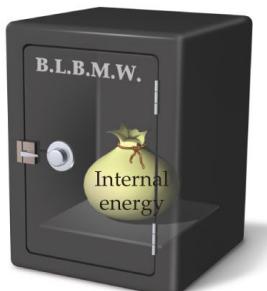


Changes in Internal Energy

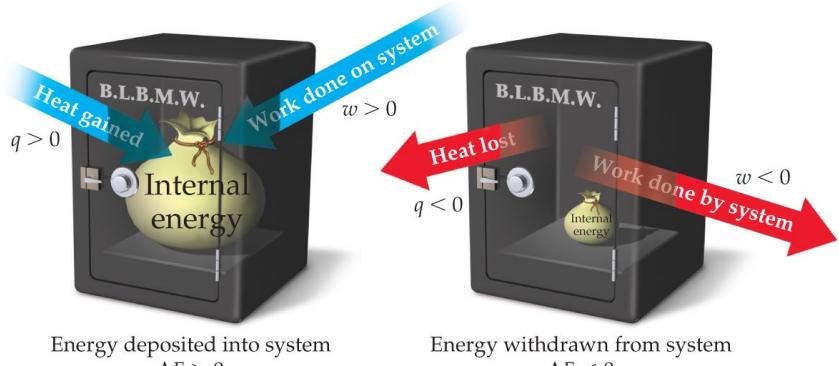
- If $\Delta E < 0$, $E_{\text{final}} < E_{\text{initial}}$
 - Therefore, the system *released* energy to the surroundings.
 - This energy change is called **exergonic**.



Changes in Internal Energy



System is interior of vault



- 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

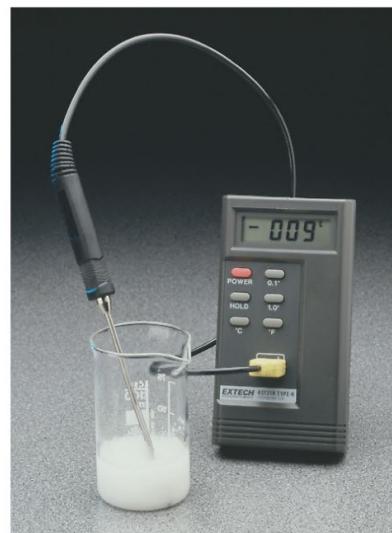
For q	+ means system <i>gains</i> heat	- means system <i>loses</i> heat
For w	+ means work done <i>on</i> system	- means work done <i>by</i> system
For ΔE	+ means <i>net gain</i> of energy by system	- means <i>net loss</i> of energy by system

Exchange of Heat between System and Surroundings

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

System: reactants + products

Surroundings: solvent,
initially at room temperature



(a) An endothermic reaction

Heat flows from surroundings into system, temperature of surroundings drops, thermometer reads temperature well below room temperature

Thermochemistry



Exchange of Heat between System and Surroundings

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

System: reactants + products

Surroundings:
air around reactants



(b) An exothermic reaction

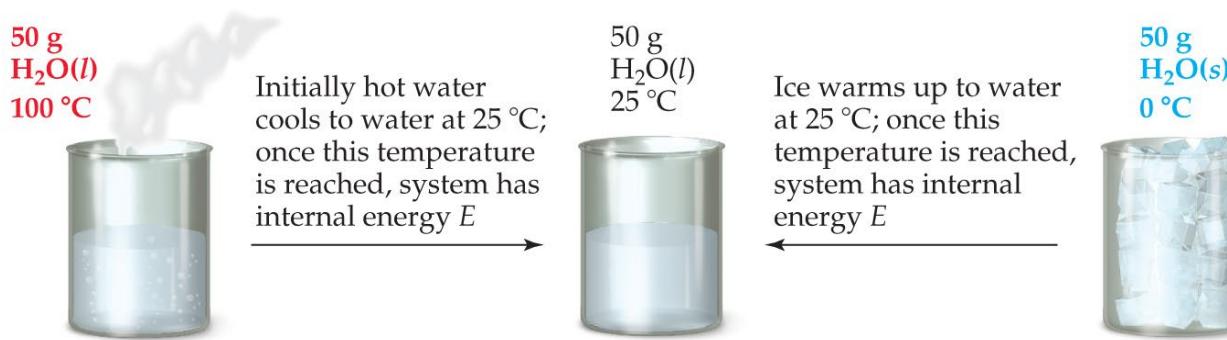
Heat flows (violently) from system into surroundings, temperature of surroundings increases

Thermochemistry



State Functions

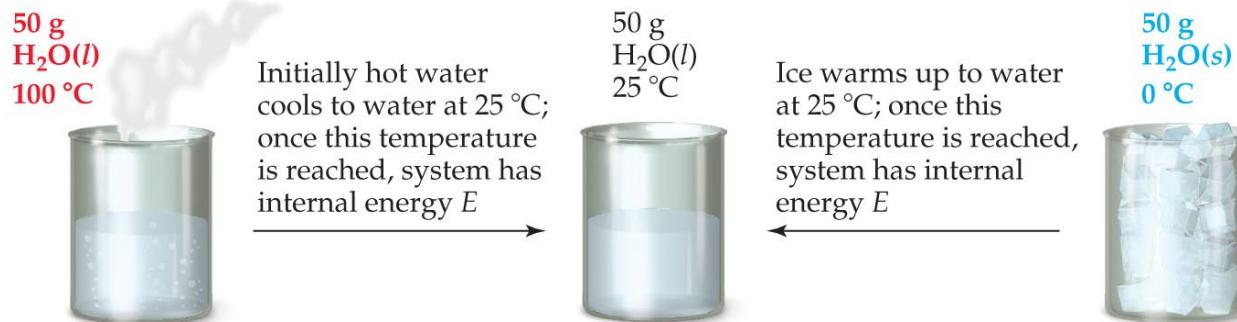
- Usually we have no way of knowing the internal energy of a system; finding that value is simply too complex a problem.
- However, we do know that the internal energy of a system is independent of the path by which the system achieved that state.
 - In the system below, the water could have reached room temperature from either direction.



Thermochemistry

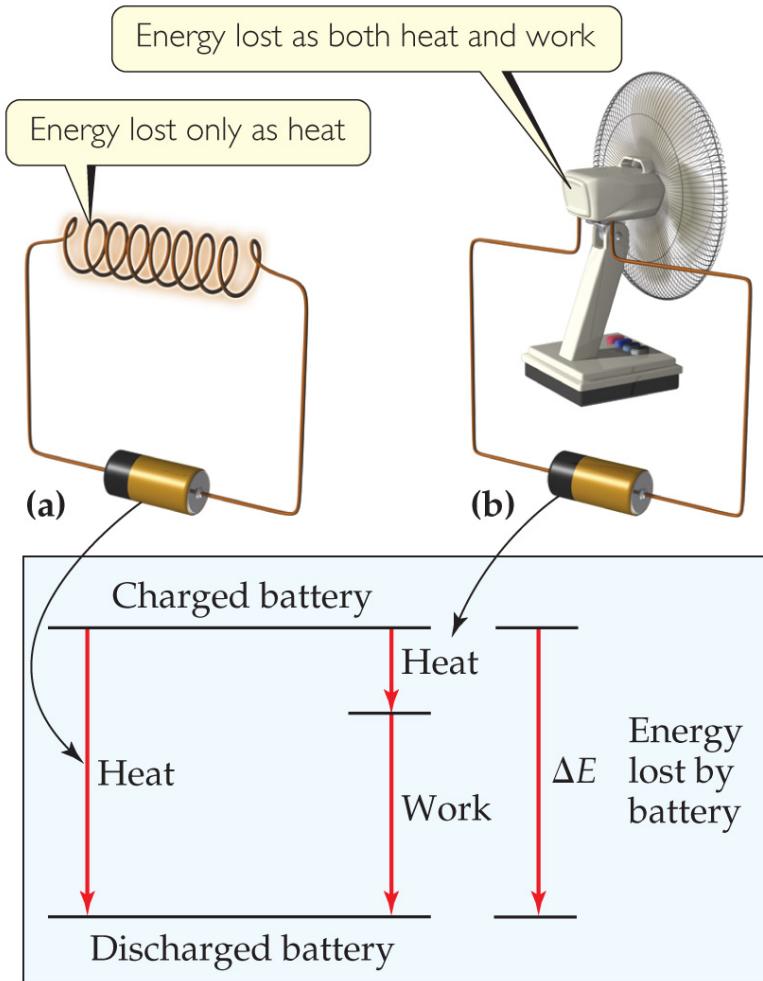
State Functions

- 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} .



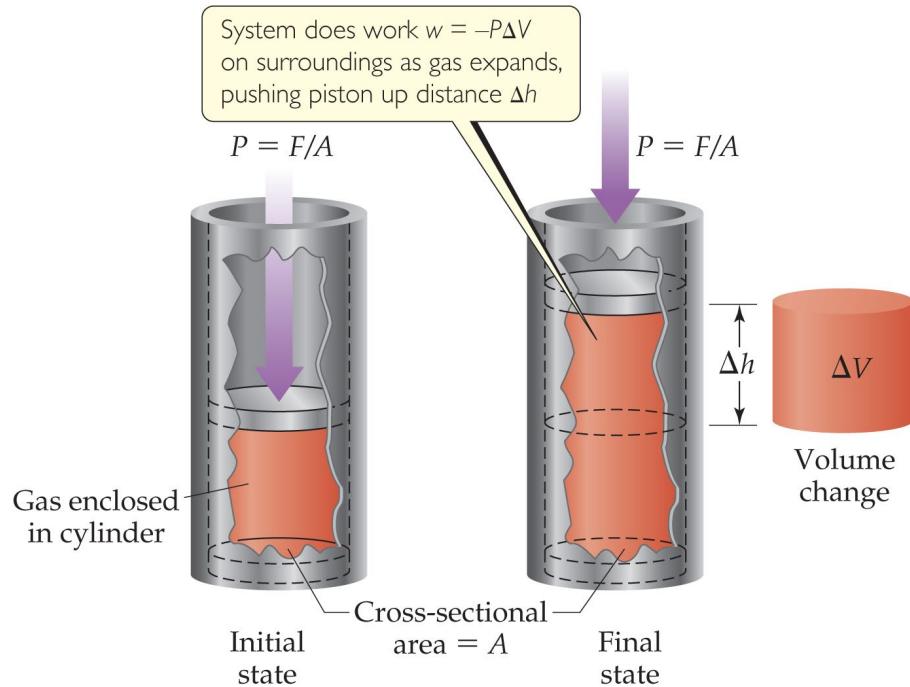
Thermochemistry

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

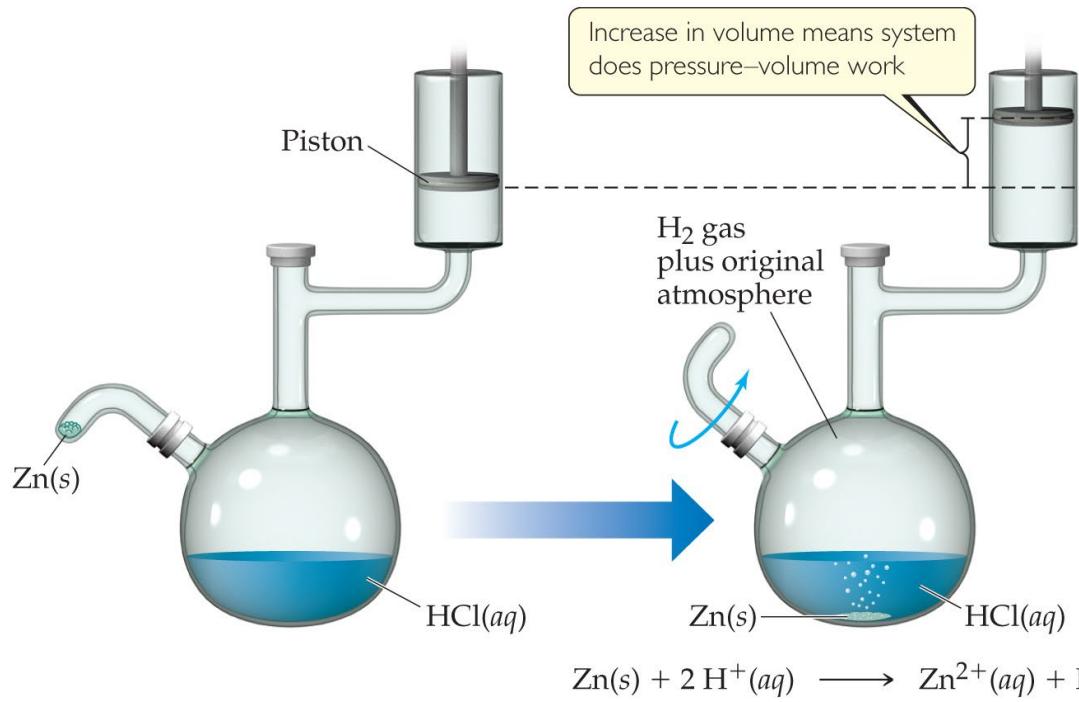


Usually in an open container the only work done is by a gas pushing on the surroundings (or by the surroundings pushing on the gas).

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:

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

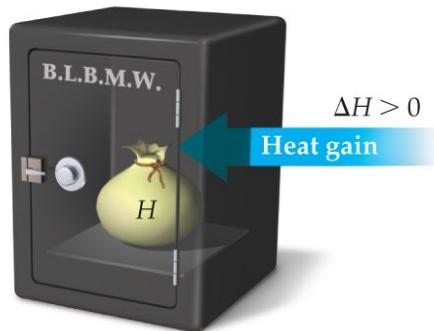
$$\Delta H = (q + w) - w$$

$$\Delta H = q$$

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

Endothermic and Exothermic

Constant pressure
maintained in system



(a) An endothermic reaction



(b) An exothermic reaction

ΔH is amount of heat that
flows into or out of system
under constant pressure

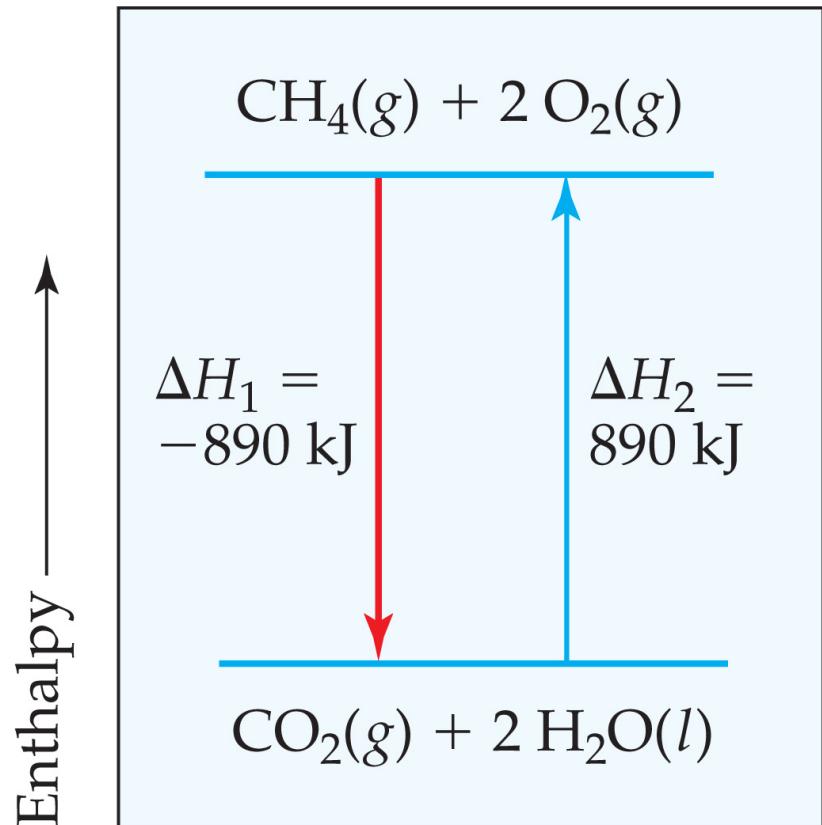
- A process is endothermic when ΔH is positive.
- A process is exothermic when ΔH is negative.



Enthalpy of Reaction

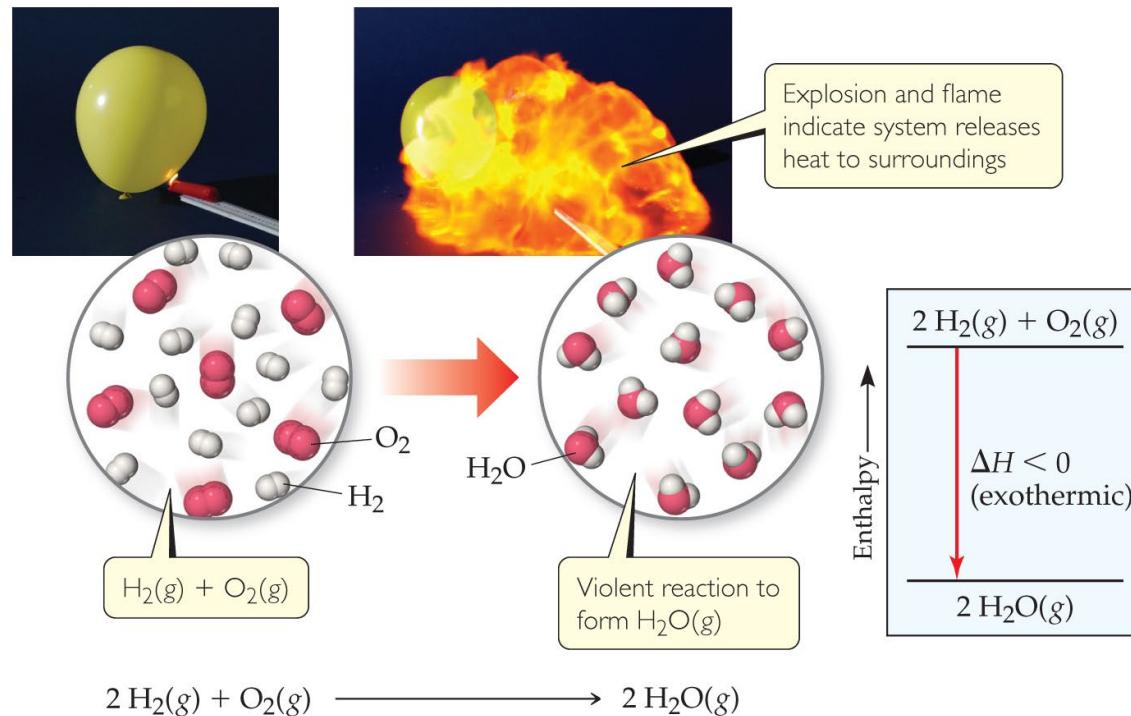
The *change* in enthalpy, ΔH , is the enthalpy of the products minus the enthalpy of the reactants:

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



Enthalpy of Reaction

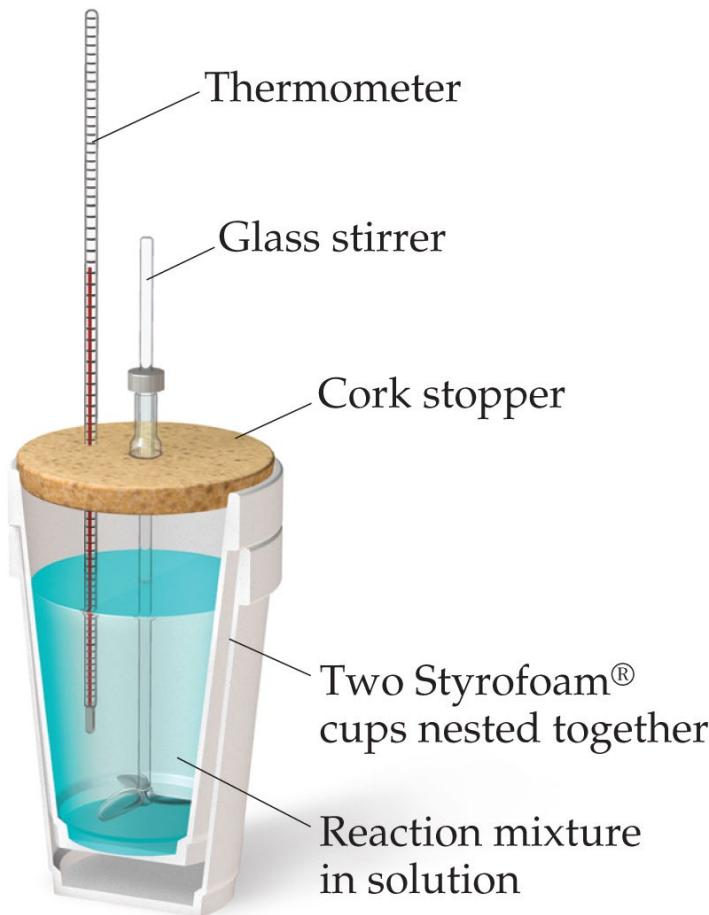
This quantity, ΔH , is called the **enthalpy of reaction**, or the **heat of reaction**.



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.

Calorimetry



- Since we cannot know the exact enthalpy of the reactants and products, we measure ΔH through **calorimetry**, the measurement of heat flow.
- The instrument used to measure heat flow is called a **calorimeter**.

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**, usually given for one mole of the substance.

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 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 (or 1 °C)**.

1.000 g H₂O(*l*)
T = 15.5 °C

+ 4.184 J (1 cal)
of heat

1.000 g H₂O(*l*)
T = 14.5 °C

Heat Capacity and Specific Heat

Specific heat, then, is

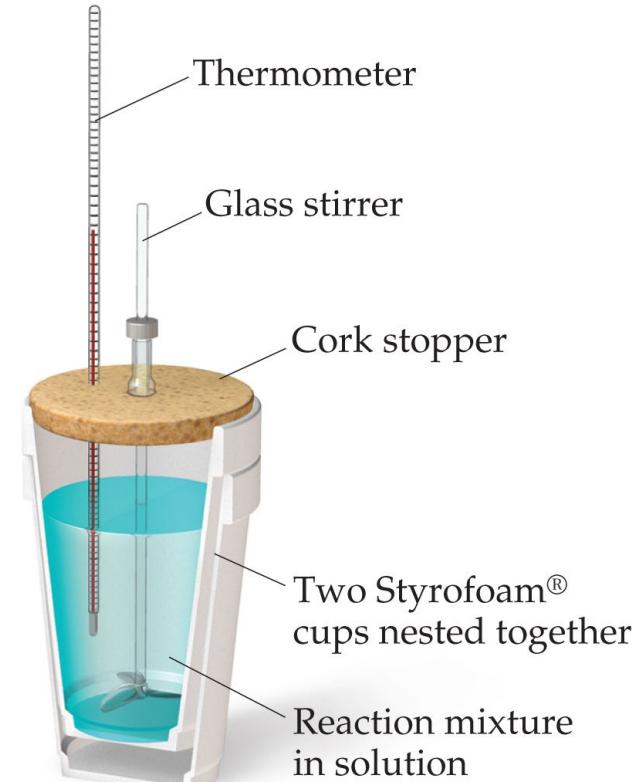
$$\text{Specific heat} = \frac{\text{heat transferred}}{\text{mass} \times \text{temperature change}}$$

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

Constant Pressure Calorimetry

- By carrying out a reaction in aqueous solution in a simple calorimeter, the heat change for the system can be found by measuring the heat change for the water in the calorimeter.
- The specific heat for water is well known (4.184 J/g·K).
- We can calculate ΔH for the reaction with this equation:

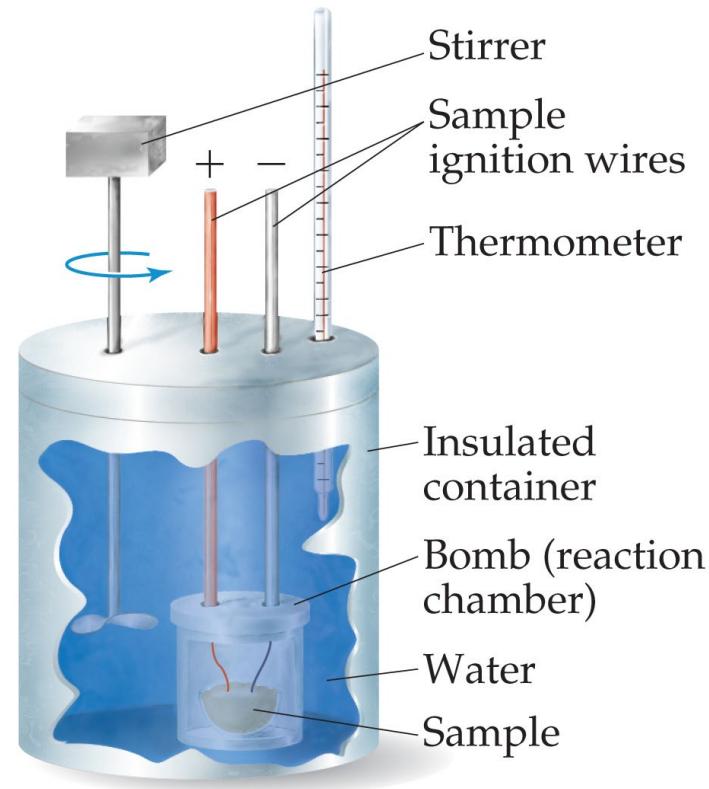
$$q = m \times C_s \times \Delta T$$



Thermochemistry

Bomb Calorimetry

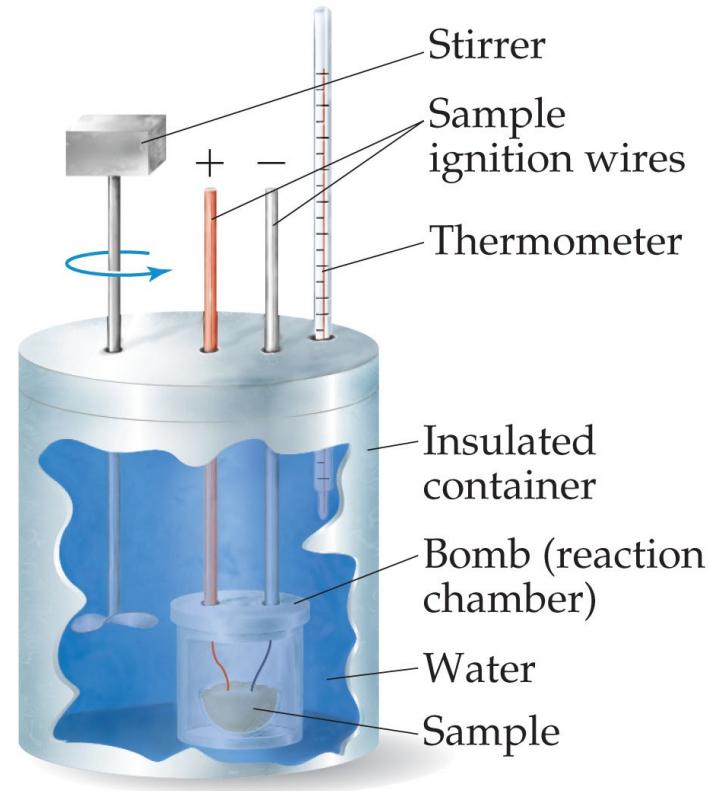
- Reactions can be carried out in a sealed “bomb” such as this one.
- The heat absorbed (or released) by the water is a very good approximation of the enthalpy change for the reaction.
- $q_{rxn} = - C_{cal} \times \Delta T$



Thermochemistry

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.



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

Thermochemistry

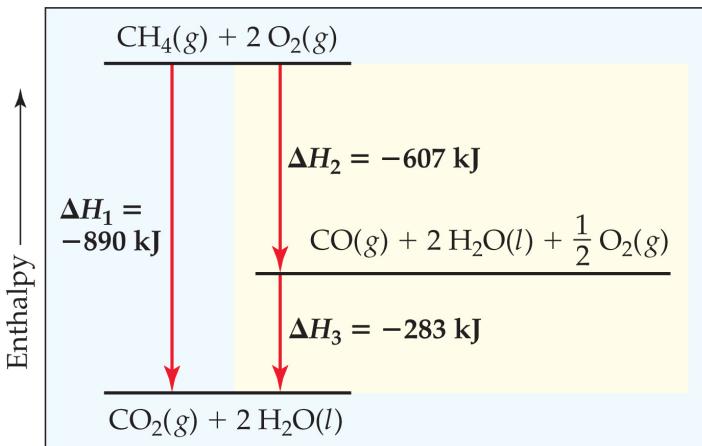
Hess's Law

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



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.**



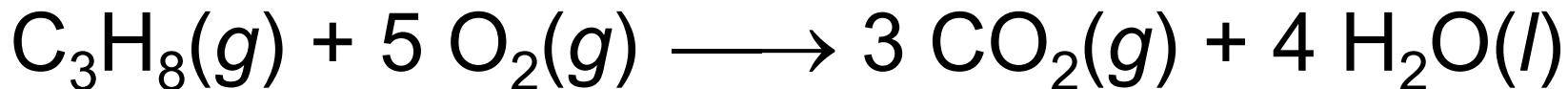
Standard Enthalpies of Formation

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

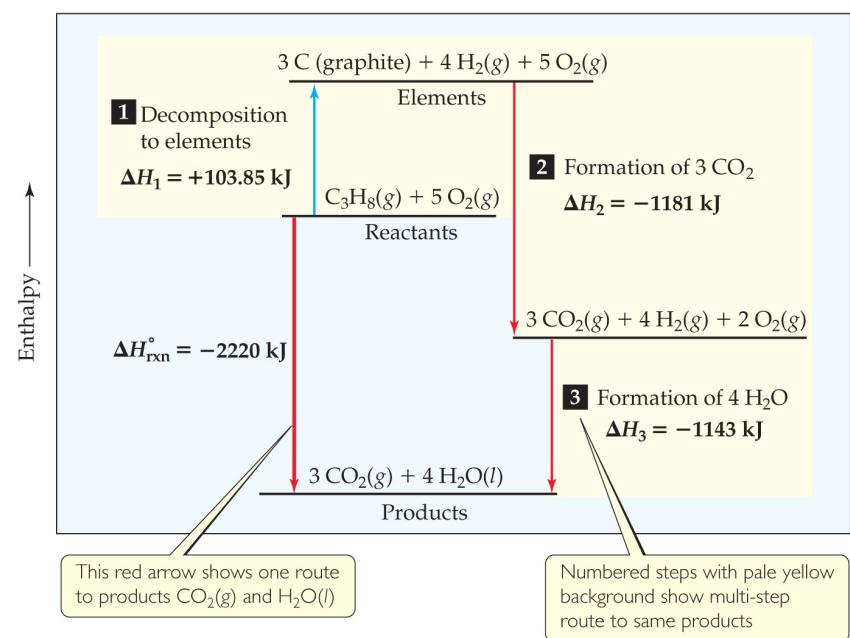
Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	-92.30
Ammonia	$NH_3(g)$	-46.19	Hydrogen fluoride	$HF(g)$	-268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	-1207.1	Methane	$CH_4(g)$	-74.80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

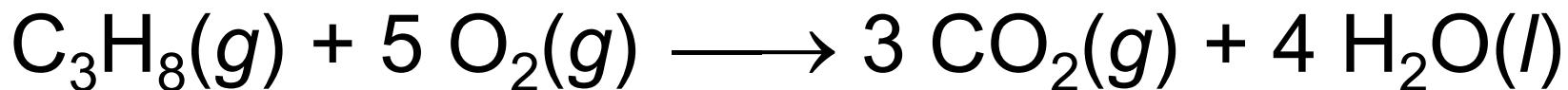


- Imagine this as occurring in three steps:

1) Decomposition of propane to the elements:

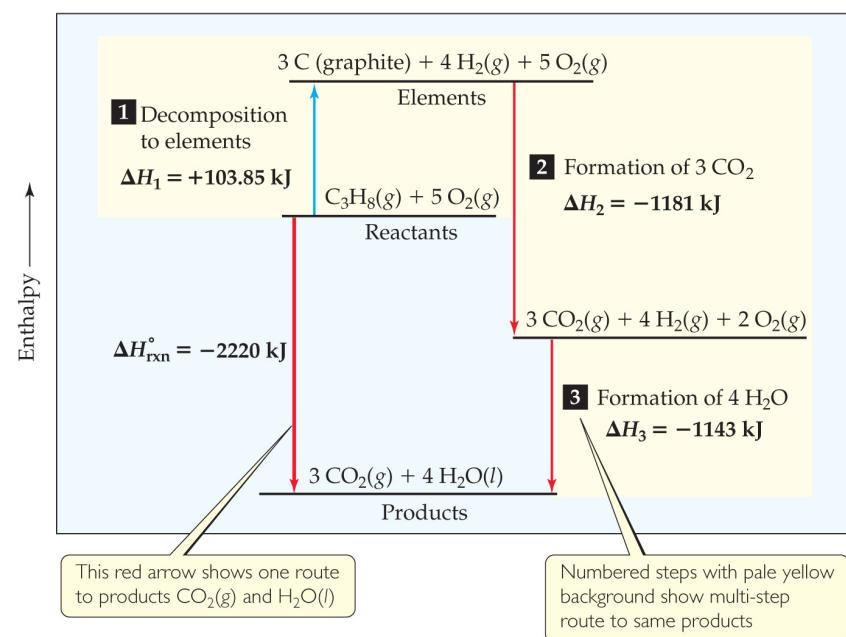
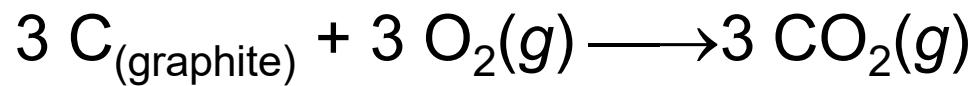


Calculation of ΔH

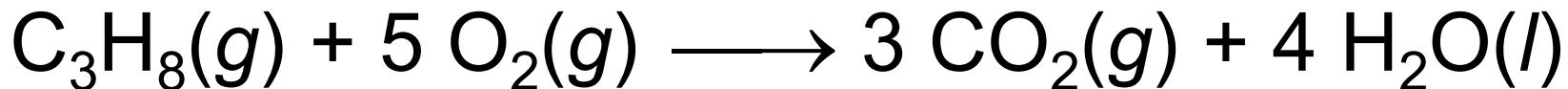


- Imagine this as occurring in three steps:

2) Formation of CO_2 :

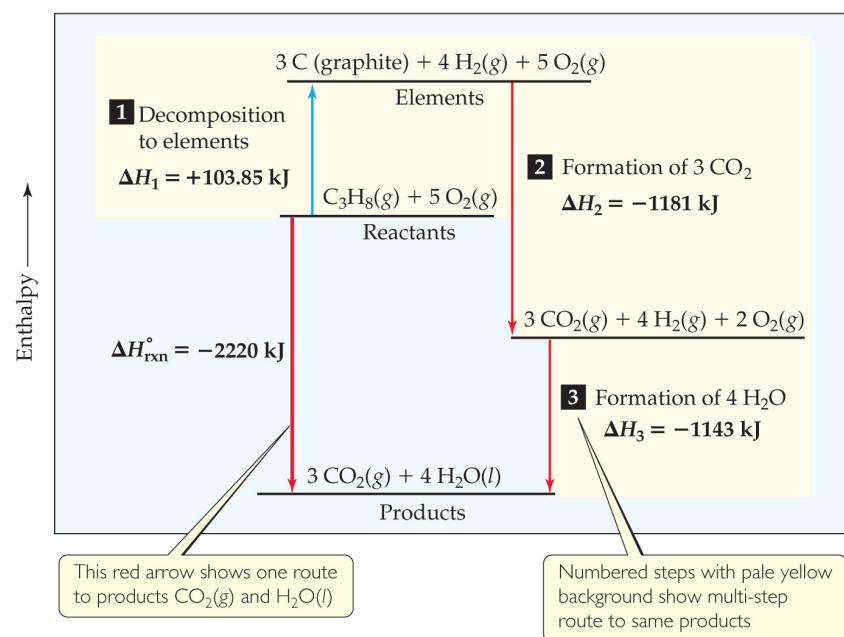
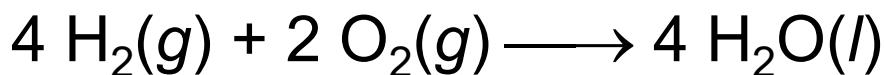


Calculation of ΔH

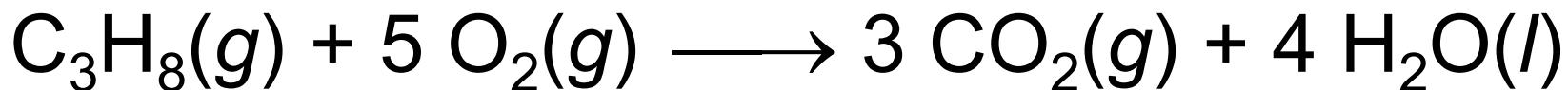


- Imagine this as occurring in three steps:

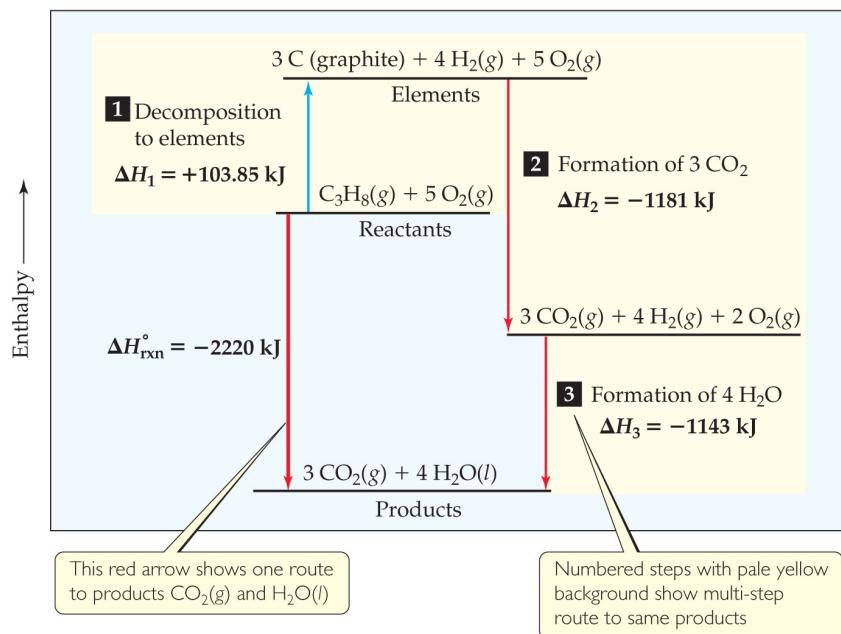
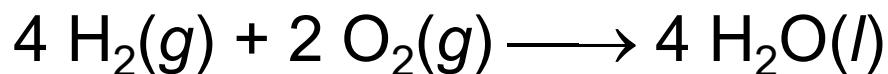
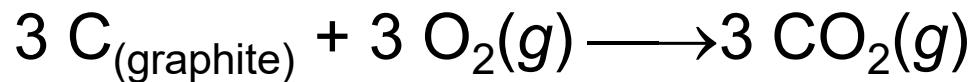
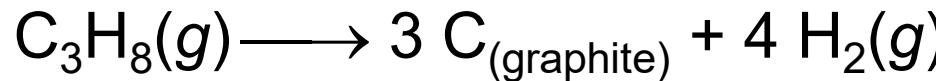
3) Formation of H_2O :



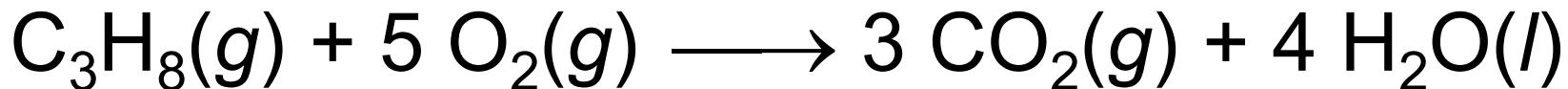
Calculation of ΔH



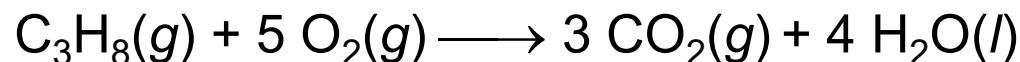
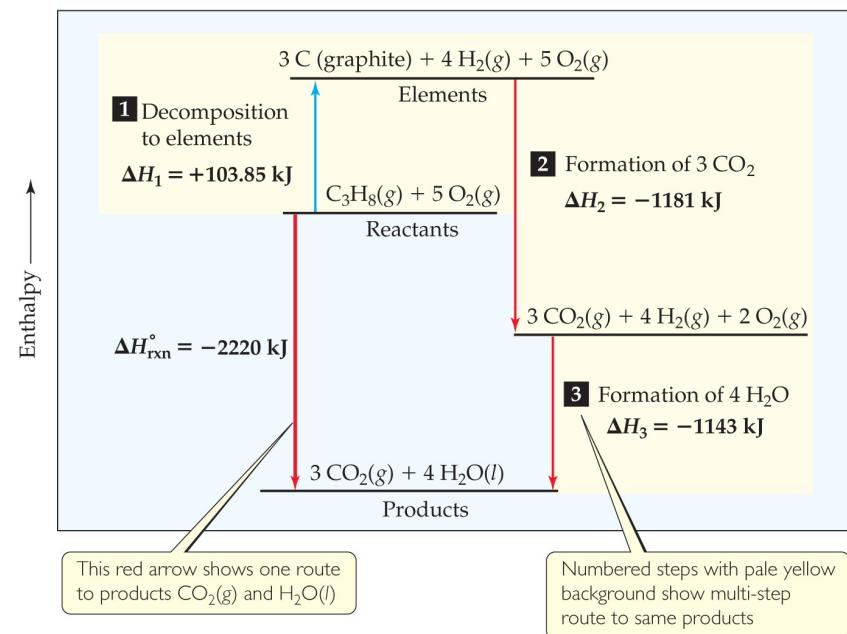
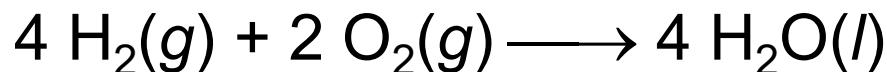
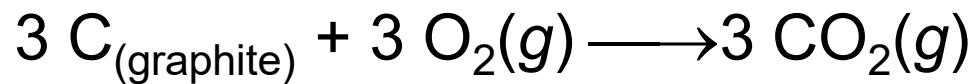
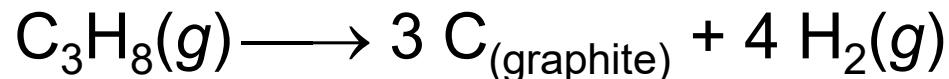
- So, all steps look like this:



Calculation of ΔH



- The sum of these equations is the overall equation!



Thermochemistry

Calculation of ΔH

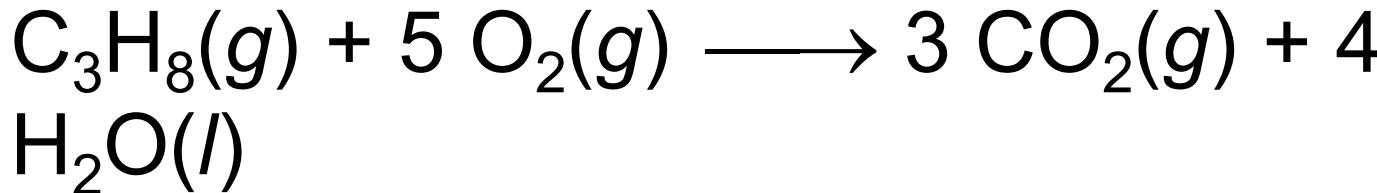
We can use Hess's law in this way:

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

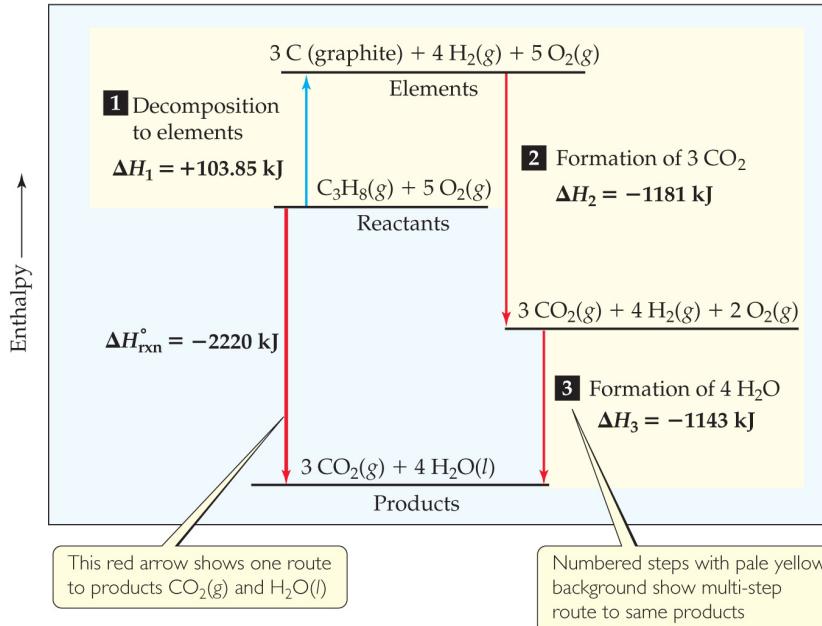
where n and m are the stoichiometric coefficients.



Calculation of ΔH using Values from the Standard Enthalpy Table



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



Thermochemistry

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 ^a	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

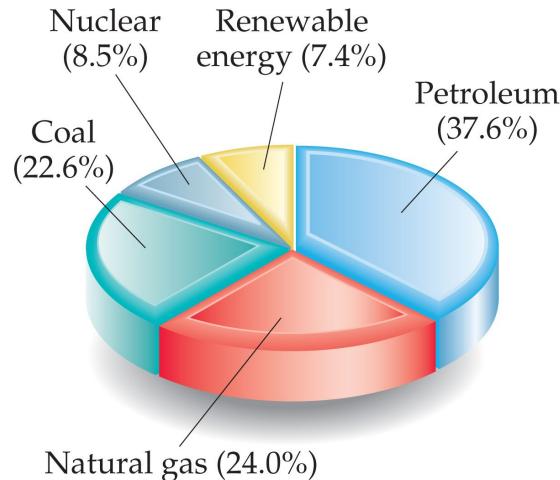
^aBeer typically contains 3.5% ethanol, which has fuel value.



Energy in Fuels

Table 5.5 Fuel Values and Compositions of Some Common Fuels

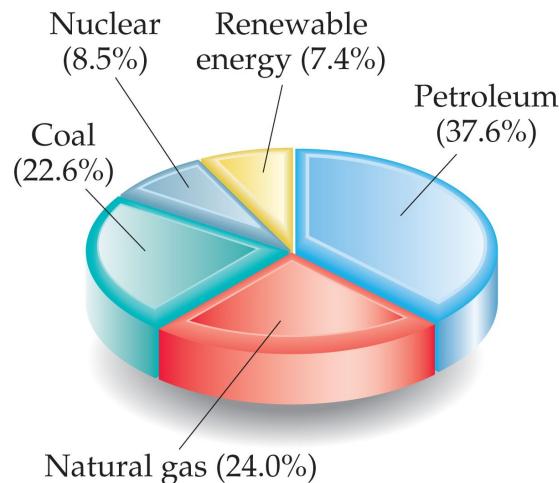
	Approximate Elemental Composition (Mass %)			Fuel Value (kJ/g)
	C	H	O	
Wood (pine)	50	6	44	18
Anthracite coal (Pennsylvania)	82	1	2	31
Bituminous coal (Pennsylvania)	77	5	7	32
Charcoal	100	0	0	34
Crude oil (Texas)	85	12	0	45
Gasoline	85	15	0	48
Natural gas	70	23	0	49
Hydrogen	0	100	0	142



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

Other Energy Sources

- Nuclear fission produces 8.5% of the U.S. energy needs.
- **Renewable energy sources**, like solar, wind, geothermal, hydroelectric, and biomass sources produce 7.4% of the U.S. energy needs.



Thermochemistry