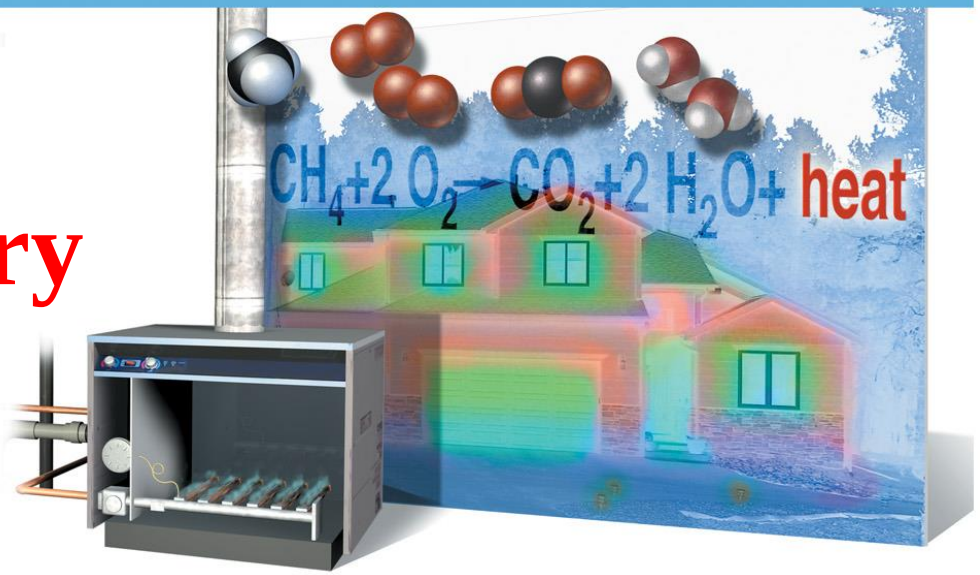
Chemistry – A Molecular Approach, 1st Edition
Nivaldo Tro

Chapter 6
Thermochemistry



Roy Kennedy
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2008, Prentice Hall

Heating Your Home

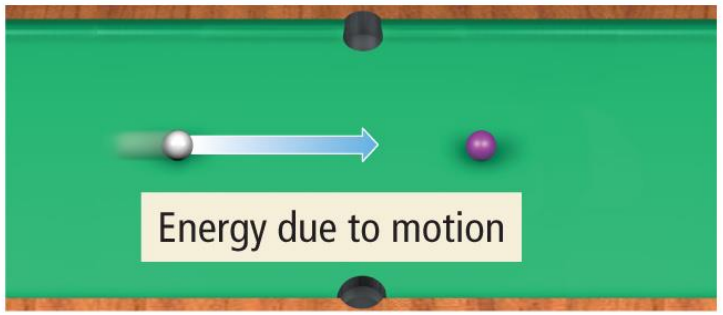
- most homes burn fossil fuels to generate heat
- the amount the temperature of your home increases depends on several factors
  - ✓how much fuel is burned
  - ✓the volume of the house
  - ✓the amount of heat loss
  - ✓the efficiency of the burning process
  - ✓can you think of any others?

Nature of Energy

- even though Chemistry is the study of matter, energy effects matter
- **energy** is anything that has the capacity to do work
- **work** is a force acting over a distance
  - ✓Energy = Work = Force x Distance
- energy can be exchanged between objects through contact
  - ✓collisions

Classification of Energy

- **Kinetic energy** is energy of motion or energy that is being transferred
  - ✓thermal energy is kinetic



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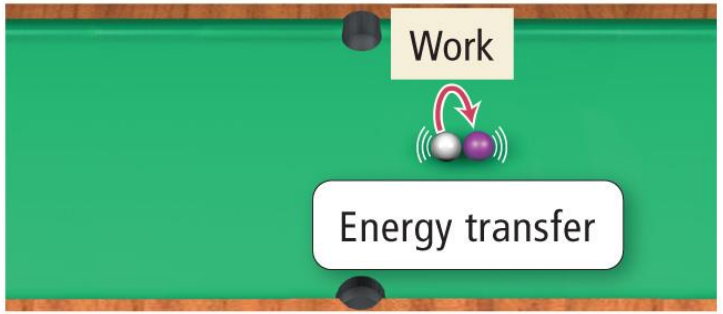

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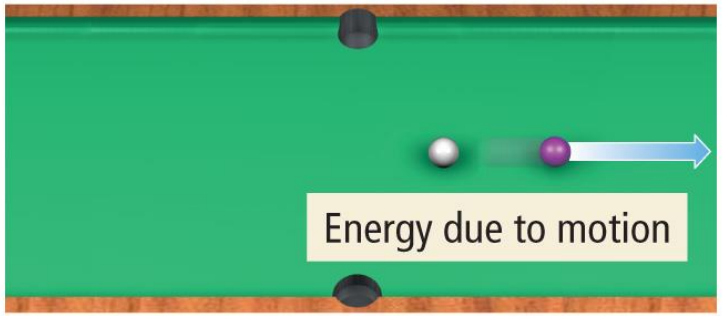

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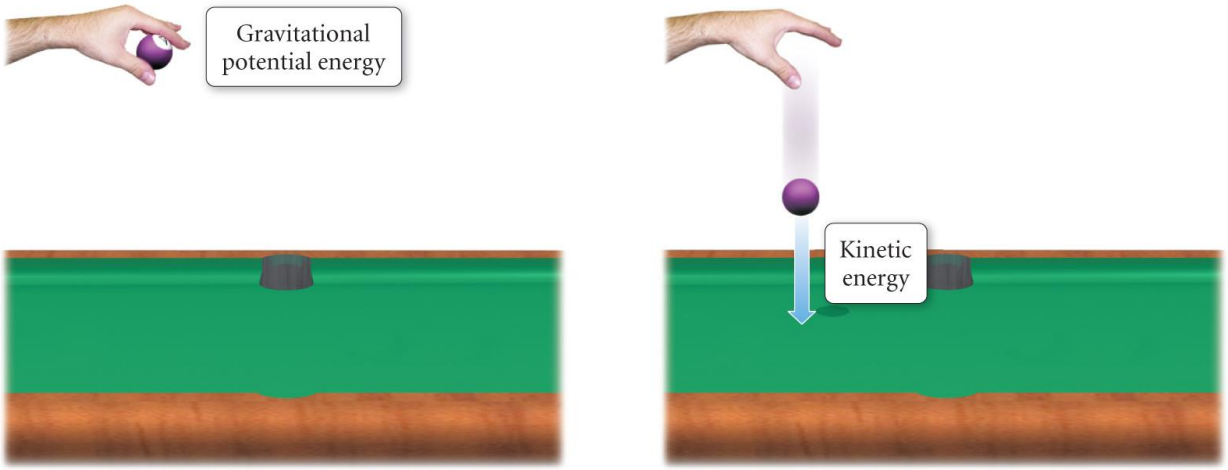
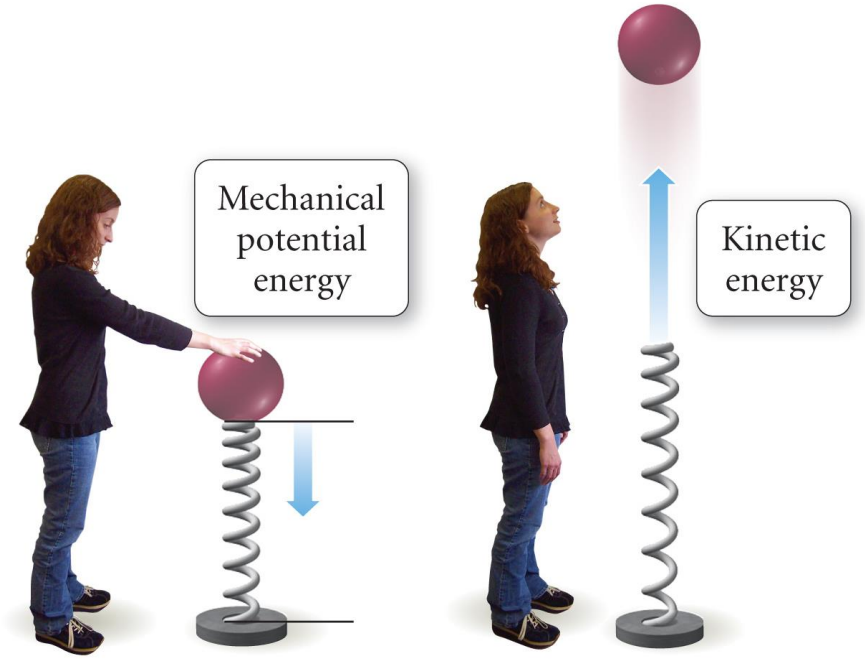
Classification of Energy

- **Potential energy** is energy that is stored in an object, or energy associated with the composition and position of the object
  - ✓energy stored in the structure of a compound is potential



Law of Conservation of Energy

- energy cannot be created or destroyed
  - ✓ First Law of Thermodynamics
- energy can be transferred between objects
- energy can be transformed from one form to another
  - ✓ heat → light → sound



Some Forms of Energy

- Electrical
  - ✓ kinetic energy associated with the flow of electrical charge
- Heat or Thermal Energy
  - ✓ kinetic energy associated with molecular motion
- Light or Radiant Energy
  - ✓ kinetic energy associated with energy transitions in an atom
- Nuclear
  - ✓ potential energy in the nucleus of atoms
- Chemical
  - ✓ potential energy in the attachment of atoms or because of their position

Units of Energy

- the amount of kinetic energy an object has is directly proportional to its mass and velocity
  - ✓ $KE = \frac{1}{2}mv^2$
- when the mass is in kg and speed in m/s, the unit for kinetic energy is $\frac{kg \bullet m^2}{s^2}$
- 1 joule of energy is the amount of energy needed to move a 1 kg mass at a speed of 1 m/s
  - ✓ $1\ J = 1\ \frac{kg \bullet m^2}{s^2}$

3.6×10^5 J or 0.10 kWh used in 1 hour

Units of Energy

- **joule** (J) is the amount of energy needed to move a 1 kg mass a distance of 1 meter
  - ✓**1 J = 1 N·m = 1 kg·m^2/s^2**
- **calorie (cal)** is the amount of energy needed to raise one gram of water by 1°C
  - ✓kcal = energy needed to raise 1000 g of water 1°C
  - ✓food Calories = kcals

Energy Conversion Factors

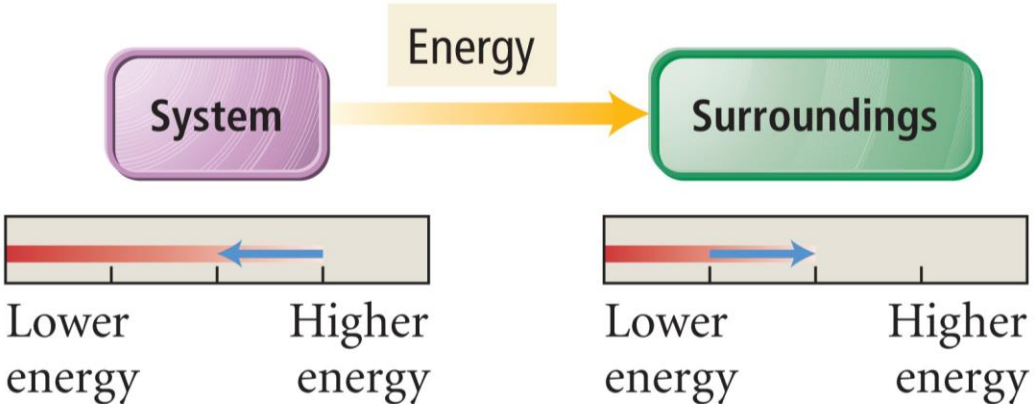
1 calorie (cal)	=	4.184 joules (J) (exact)
1 Calorie (Cal)	=	1000 calories (cal)
1 kilowatt-hour (kWh)	=	3.60 x 10^6 joules (J)

Energy Use

Unit	Energy Required to Raise Temperature of 1 g of Water by 1°C	Energy Required to Light 100-W Bulb for 1 hr	Energy used to Run 1 Mile (approx)	Energy Used by Average U.S. Citizen in 1 Day
joule (J)	4.18	3.60×10^{5}	4.2×10^{5}	9.0×10^{8}
calorie (cal)	1.00	8.60×10^{4}	1.0×10^{5}	2.2×10^{8}
Calorie (Cal)	0.00100	86.0	100.	2.2×10^{5}
kWh	1.16×10^{-6}	0.100	0.12	2.5×10^{2}

Energy Flow and Conservation of Energy

- we define the **system** as the material or process we are studying the energy changes within
- we define the **surroundings** as everything else in the universe
- Conservation of Energy requires that the total energy change in the system and the surrounding must be zero
  - ✓ $\Delta Energy_{universe} = 0 = \Delta Energy_{system} + \Delta Energy_{surroundings}$
  - ✓ Δ is the symbol that is used to mean change
    - ➢ final amount – initial amount

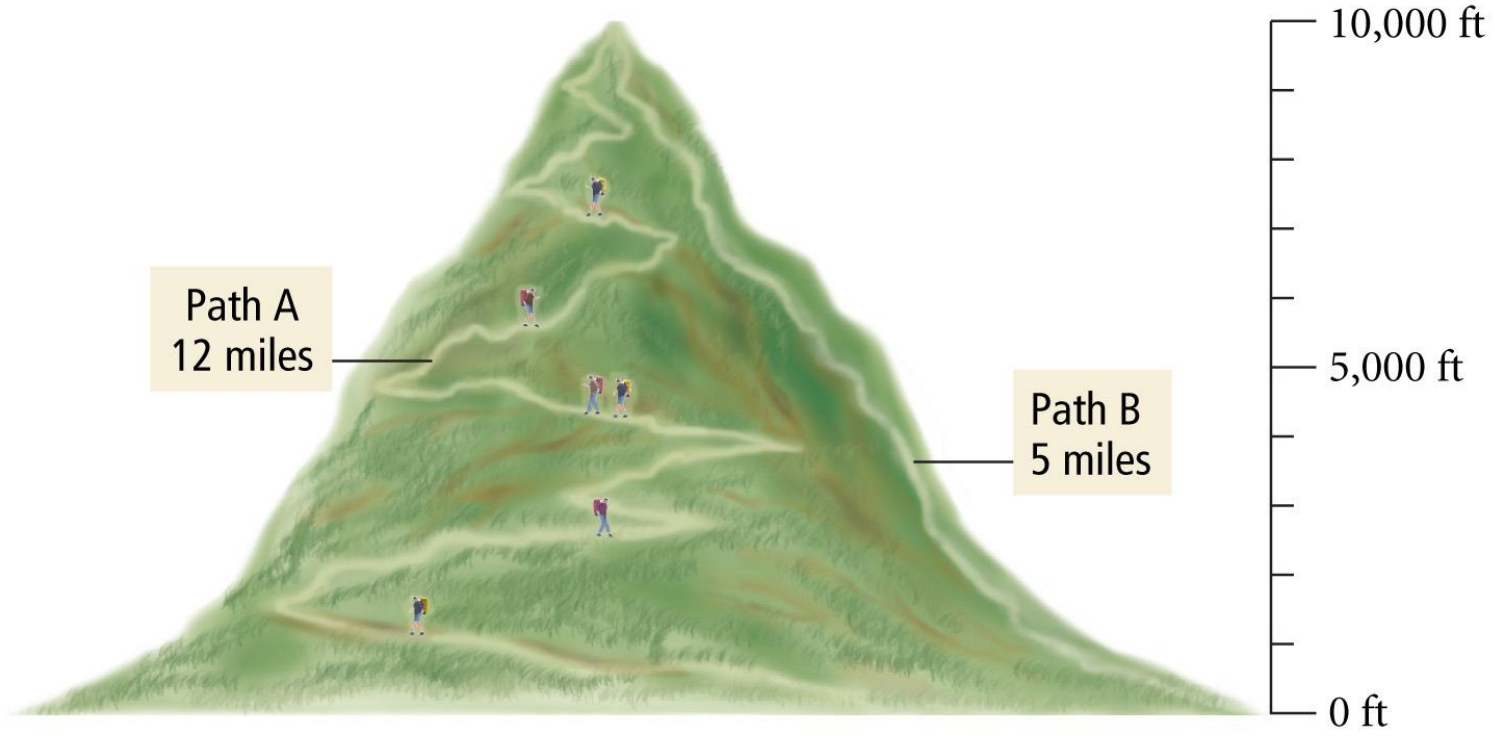


Internal Energy

- the **internal energy** is the total amount of kinetic and potential energy a system possesses
- the change in the internal energy of a system only depends on the amount of energy in the system at the beginning and end
  - ✓ a **state function** is a mathematical function whose result only depends on the initial and final conditions, not on the process used
  - ✓ $\Delta E = E_{final} - E_{initial}$
  - ✓ $\Delta E_{reaction} = E_{products} - E_{reactants}$

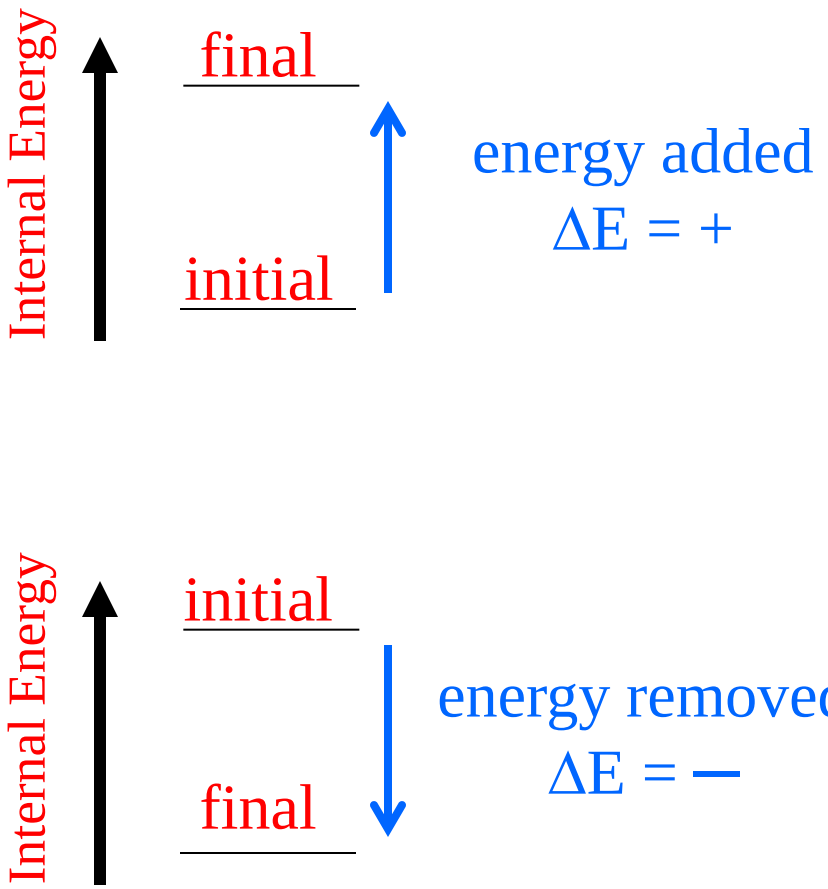
State Function

A State Function
Change in altitude depends only on the difference between the initial and final values, not on the path taken.



Energy Diagrams

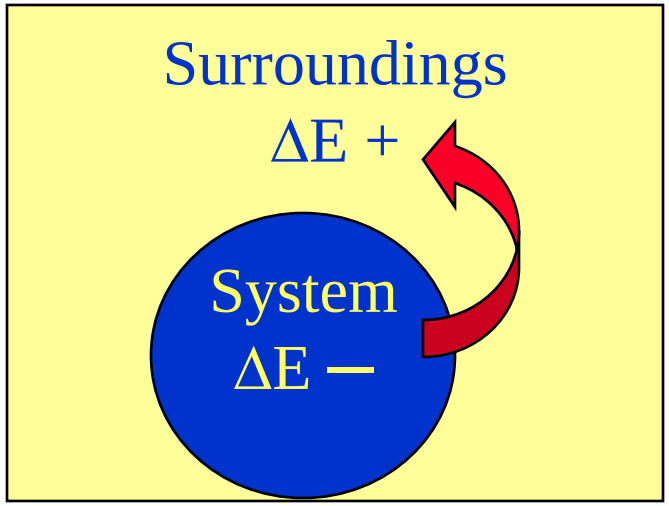
- energy diagrams are a "graphical" way of showing the direction of energy flow during a process
- if the final condition has a larger amount of internal energy than the initial condition, the change in the internal energy will be +
- if the final condition has a smaller amount of internal energy than the initial condition, the change in the internal energy will be −

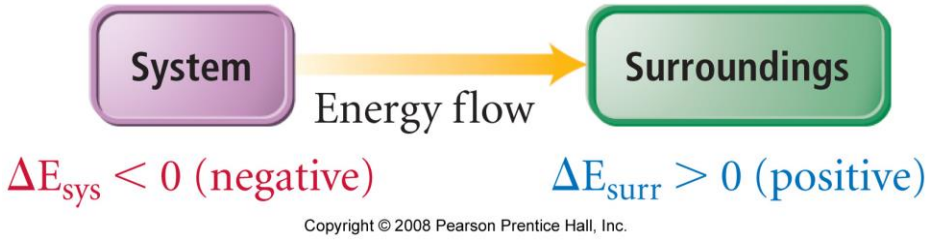


Energy Flow

- when energy flows out of a system, it must all flow into the surroundings
- when energy flows out of a system, ΔE_{system} is –
- when energy flows into the surroundings, $\Delta E_{surroundings}$ is +
- therefore:

$$-\Delta E_{system} = \Delta E_{surroundings}$$

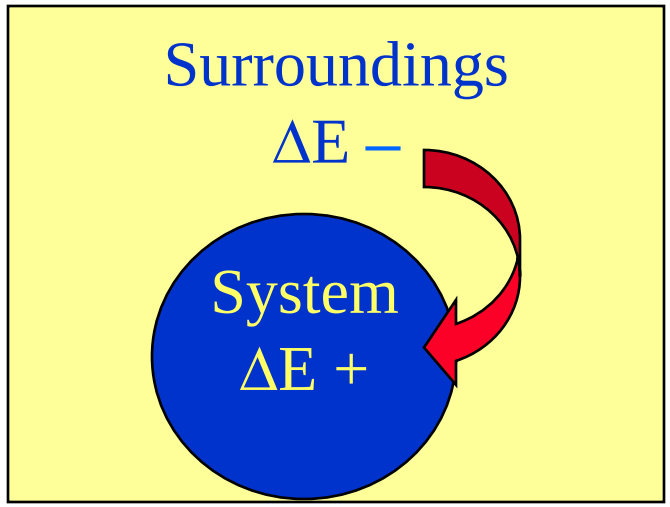


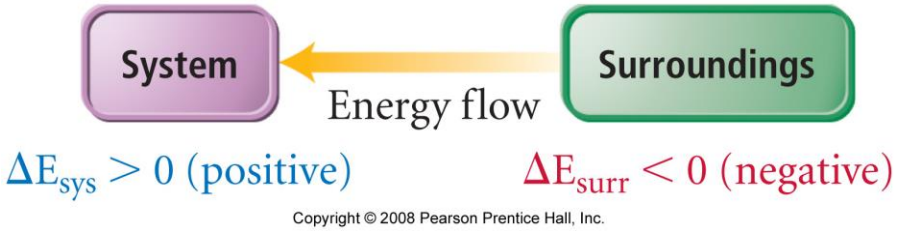


Energy Flow

- when energy flows into a system, it must all come from the surroundings
- when energy flows into a system, ΔE_{system} is +
- when energy flows out of the surroundings, $\Delta E_{surroundings}$ is –
- therefore:

$$\Delta E_{system} = -\Delta E_{surroundings}$$





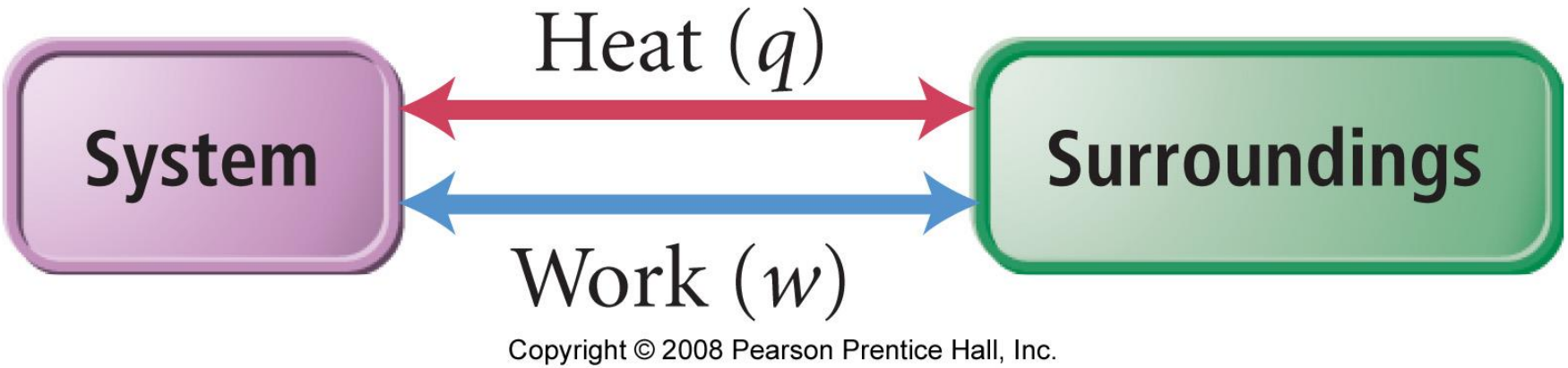
How Is Energy Exchanged?

- energy is exchanged between the system and surroundings through heat and work
  - ✓ q = heat (thermal) energy
  - ✓ w = work energy
  - ✓ q and w are NOT state functions, their value depends on the process

$$\Delta E = q + w$$

q (heat)	system gains heat energy +	system releases heat energy –
w (work)	system gains energy from work +	system releases energy by doing work –
ΔE	system gains energy +	system releases energy –

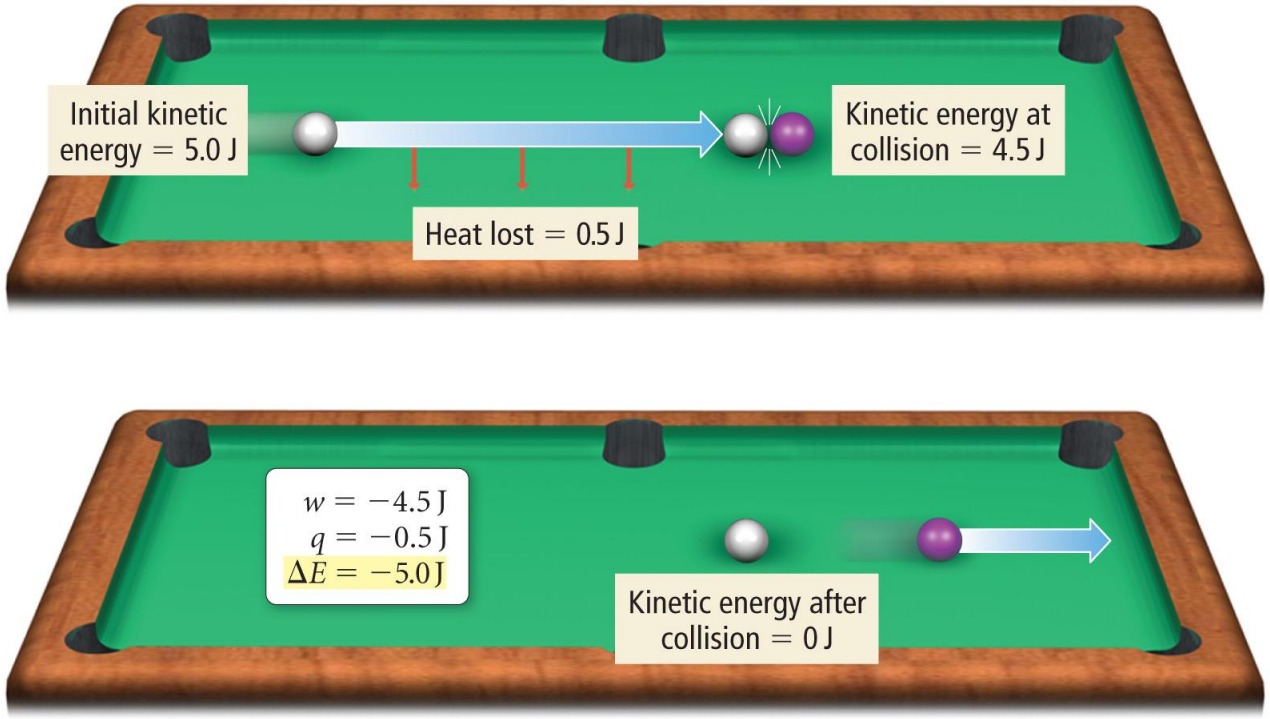
Energy Exchange



- energy is exchanged between the system and surroundings through either heat exchange or work being done

Heat & Work

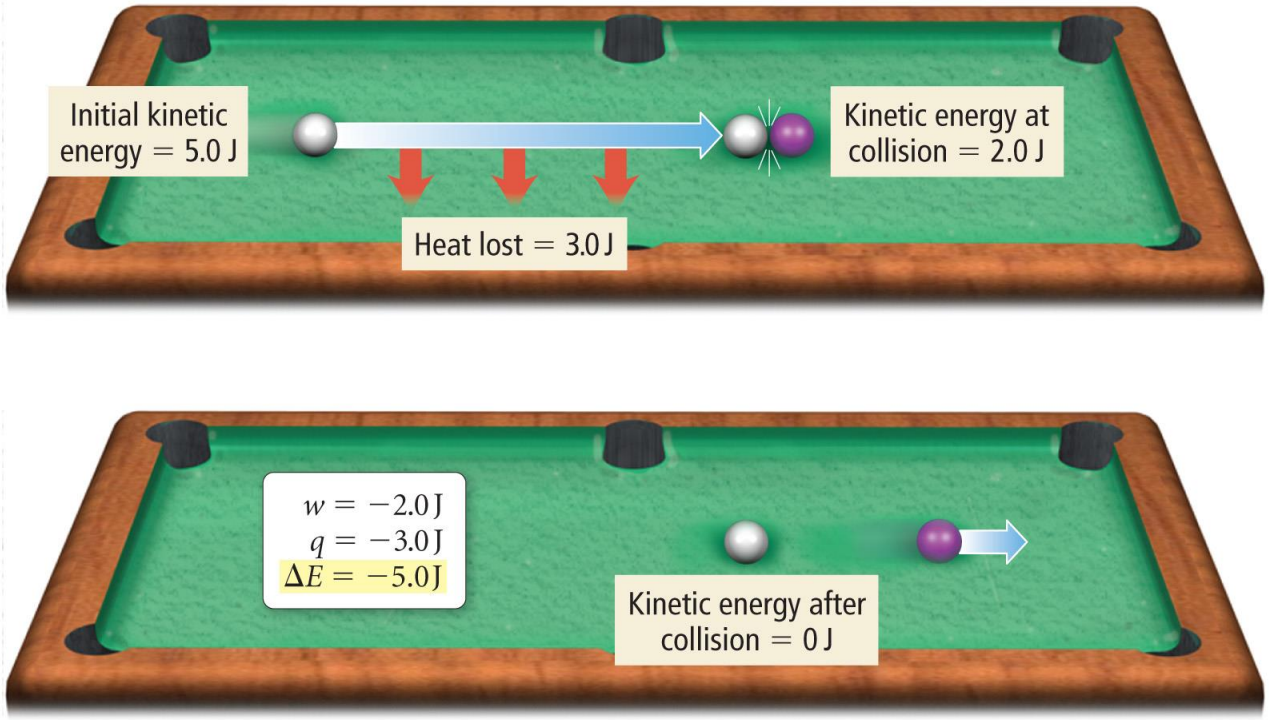
- on a smooth table, most of the kinetic energy is transferred from the first ball to the second – with a small amount lost through friction



(a) Smooth table

Heat & Work

- on a rough table, most of the kinetic energy of the first ball is lost through friction – less than half is transferred to the second



(b) Rough table

Heat Exchange

- heat is the exchange of thermal energy between the system and surroundings
- occurs when system and surroundings have a difference in temperature
- heat flows from matter with high temperature to matter with low temperature until both objects reach the same temperature
  - ✓thermal equilibrium

Quantity of Heat Energy Absorbed
Heat Capacity

- when a system absorbs heat, its temperature increases
- the increase in temperature is directly proportional to the amount of heat absorbed
- the proportionality constant is called the **heat capacity, C**
  - ✓ units of C are J/°C or J/K

$$q = C \times \Delta T$$

- the heat capacity of an object depends on its mass
  - ✓ 200 g of water requires twice as much heat to raise its temperature by 1°C than 100 g of water
- the heat capacity of an object depends on the type of material
  - ✓ 1000 J of heat energy will raise the temperature of 100 g of sand 12°C, but only raise the temperature of 100 g of water by 2.4°C

Specific Heat Capacity

- measure of a substance's ***intrinsic*** ability to absorb heat
- the **specific heat capacity** is the amount of heat energy required to raise the temperature of one gram of a substance 1°C
  - ✓ $\mathbf{C_s}$
  - ✓ units are J/(g·°C)
- the **molar heat capacity** is the amount of heat energy required to raise the temperature of one mole of a substance 1°C
- the rather high specific heat of water allows it to absorb a lot of heat energy without large increases in temperature
  - ✓ keeping ocean shore communities and beaches cool in the summer
  - ✓ allows it to be used as an effective coolant to absorb heat

TABLE 6.4 Specific Heat Capacities of Some Common Substances

Substance	Specific Heat Capacity, C_s (J/g · °C)*
Elements	
Lead	0.128
Gold	0.128
Silver	0.235
Copper	0.385
Iron	0.449
Aluminum	0.903
Compounds	
Ethanol	2.42
Water	4.18
Materials	
Glass (Pyrex)	0.75
Granite	0.79
Sand	0.84

*At 298 K.

Quantifying Heat Energy

- the heat capacity of an object is proportional to its mass and the specific heat of the material
- so we can calculate the quantity of heat absorbed by an object if we know the mass, the specific heat, and the temperature change of the object

Heat **= (mass) x (specific heat capacity) x (temp. change)**

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

Example 6.2 – How much heat is absorbed by a copper penny with mass 3.10 g whose temperature rises from -8.0°C to 37.0°C?

• Sort Information	**Given:**	T_1= -8.0°C, T_2= 37.0°C, m=3.10 g
	Find:	q, J
• Strategize	**Concept Plan:**	C_s m, ΔT ⇒ q
		$q = m \bullet C_s \bullet \Delta T$
	Relationships:	$q = m \cdot C_s \cdot \Delta T$ C_s = 0.385 J/g (Table 6.4)
• Follow the Concept Plan to **Solve** the problem	**Solution:**	$\Delta T = T_2 - T_1$ $\Delta T = 37.0\,°C - (-8.0°C)$ $= 45.0\,°C$
		$q = m \bullet C_s \bullet \Delta T$ $= (3.10\,\cancel{g}) \bullet \left(0.385\ \frac{J}{\cancel{g}\cdot\cancel{°C}}\right) \bullet (45.0\,\cancel{°C})$ $= 53.7$ J
• Check	**Check:**	the unit and sign are correct

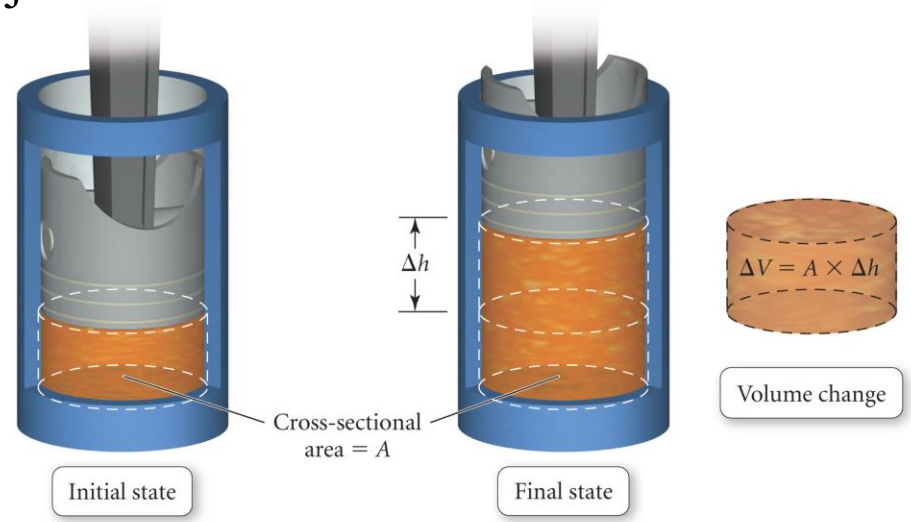
Pressure -Volume Work

- PV work is work that is the result of a volume change against an external pressure
- when gases expand, ΔV is +, but the system is doing work on the surroundings so *w* is −
- as long as the external pressure is kept constant

−*Work* = External Pressure x Change in Volume

$$w = -P\Delta V$$

✓ to convert the units to joules use 101.3 J = 1 atm·L



Example 6.3 – If a balloon is inflated from 0.100 L to 1.85 L against an external pressure of 1.00 atm, how much work is done?

Given: V_1=0.100 L, V_2=1.85 L, P=1.00 atm

Find: *w*, J

Concept Plan:

P, ΔV ⇨ *w*

$$w = -P \bullet \Delta V$$

Relationships: 101.3 J = 1 atm L

Solution:

$$\Delta V = V_2 - V_1$$

$$\Delta V = 1.85\,\text{L} - 0.100\,\text{L}$$

$$= 1.75\,\text{L}$$

$$w = -P \bullet \Delta V$$

$$= -(1.00\,\text{atm}) \bullet (1.75\,\text{L})$$

$$= -1.75\,\text{atm} \bullet \text{L}$$

$$-1.75\,\text{atm} \bullet \text{L} \times \frac{101.3\,\text{J}}{1\,\text{atm} \bullet \text{L}}$$

$$= -177\,\text{J}$$

Check: the unit and sign are correct

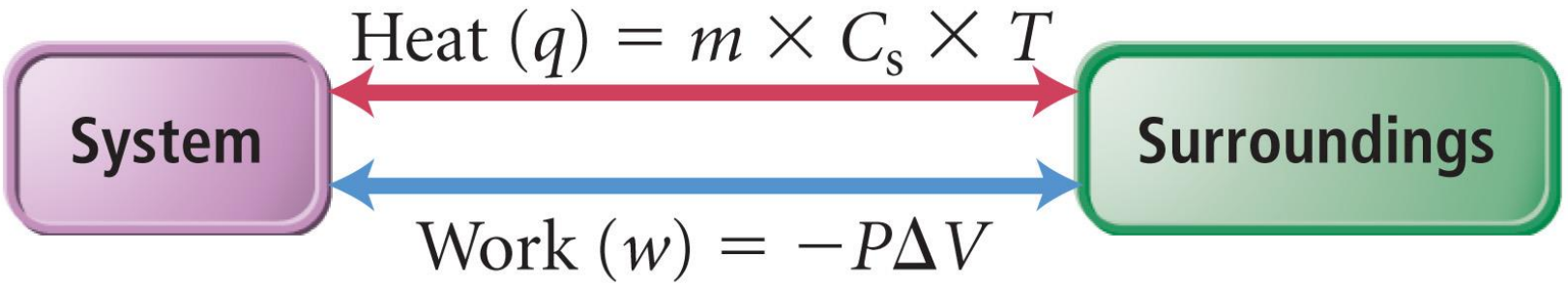
Exchanging Energy Between System and Surroundings

- exchange of heat energy

  q = mass x specific heat x ΔTemperature

- exchange of work

  w = −Pressure x ΔVolume



Measuring ΔE, Calorimetry at Constant Volume

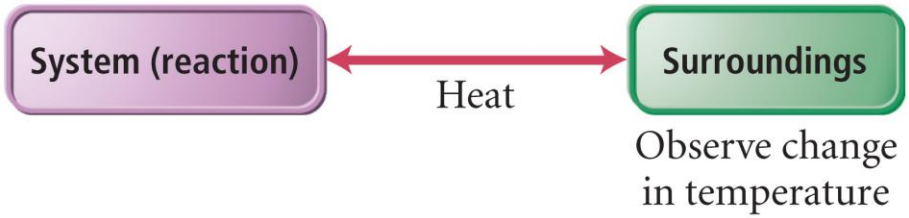
- since $\Delta E = q + w$, we can determine ΔE by measuring q and w
- in practice, it is easiest to do a process in such a way that there is no change in volume, $w = 0$
  - ✓ at constant volume, $\Delta E_{system} = q_{system}$
- in practice, it is not possible to observe the temperature changes of the individual chemicals involved in a reaction – so instead, we use an insulated, controlled surroundings and measure the temperature change in it
- the surroundings is called a **bomb calorimeter** and is usually made of a sealed, insulated container filled with water

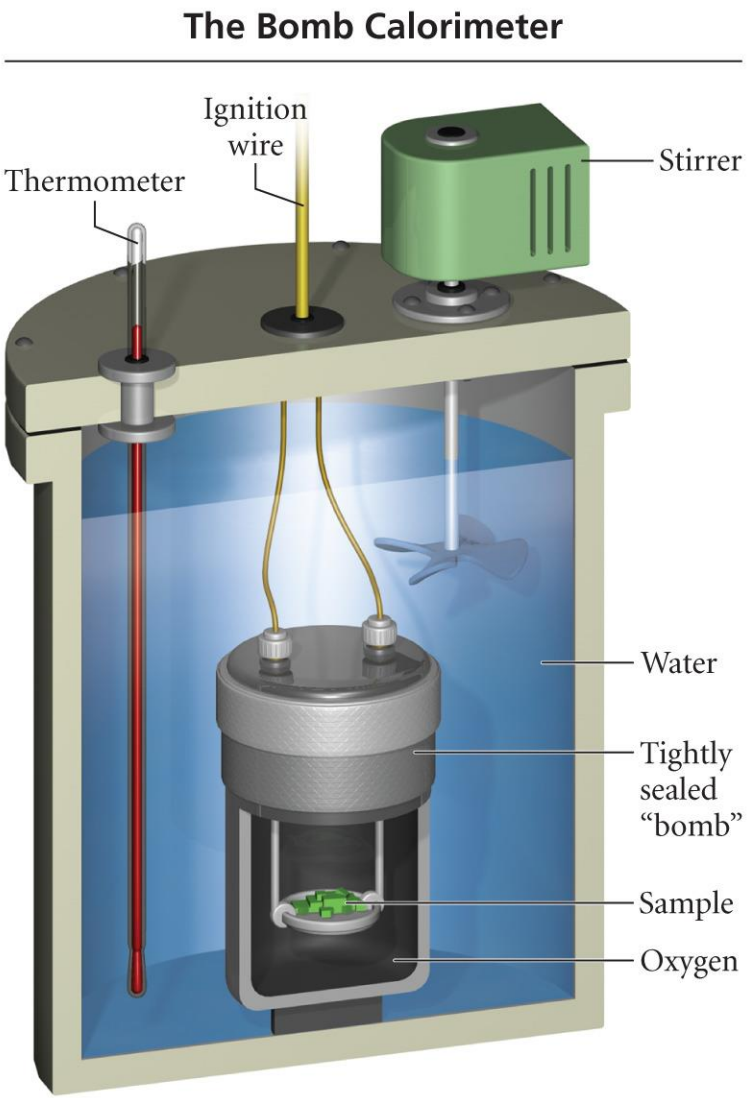
$$\boldsymbol{q_{surroundings} = q_{calorimeter} = -q_{system}}$$

$$\boldsymbol{-\Delta E_{reaction} = q_{cal} = C_{cal} \times \Delta T}$$

Bomb Calorimeter

- used to measure ΔE because it is a constant volume system





Example 6.4 – When 1.010 g of sugar is burned in a bomb calorimeter, the temperature rises from 24.92°C to 28.33°C. If C_{cal} = 4.90 kJ/°C, find ΔE for burning 1 mole

Given: 1.010 g $C_{12}H_{22}O_{11}$, T_1 = 24.92°C, T_2 = 28.33°C, C_{cal} = 4.90 kJ/°C

Find: ΔE_{rxn}, kJ/mol

Concept Plan:

C_{cal}, ΔT → q_{cal} → q_{rxn}

$q_{cal} = C_{cal} \times \Delta T$ $\qquad$ $q_{rxn} = -q_{cal}$

Relationships:

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

MM $C_{12}H_{22}O_{11}$ = 342.3 g/mol

$$\Delta E = \frac{q_{rxn}}{\text{mol } C_{12}H_{22}O_{11}}$$

Solution:

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

$$1.010\text{ g } C_{12}H_{22}O_{11} \times \frac{1\text{ mol } C_{12}H_{22}O_{11}}{342.3\text{ g}} = 2.9506 \times 10^{-3}\text{ mol}$$

$$= 4.90\ \frac{\text{kJ}}{^\circ\text{C}} \times 3.41^\circ\text{C} = 16.7\text{ kJ}$$

$$\Delta T = 28.33^\circ\text{C} - 24.92^\circ\text{C}$$

$$\Delta T = 3.41^\circ\text{C}$$

$$q_{rxn} = -q_{cal} = -16.7\text{ kJ}$$

$$\Delta E = \frac{q_{rxn}}{\text{mol } C_{12}H_{22}O_{11}} = \frac{-16.7\text{ kJ}}{2.9506 \times 10^{-3}\text{ mol}}$$

$$= -5.66 \times 10^3\text{ kJ/mol}$$

Check: the units and sign are correct

Enthalpy

- the **enthalpy, H,** of a system is the sum of the internal energy of the system and the product of pressure and volume
  - ✓ H is a state function

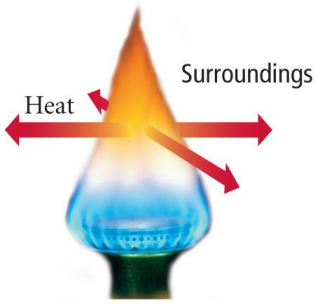
$$H = E + PV$$

- the **enthalpy change, ΔH,** of a reaction is the heat evolved in a reaction at constant pressure

$$\Delta H_{reaction} = q_{reaction\ at\ constant\ pressure}$$

- usually ΔH and ΔE are similar in value, the difference is largest for reactions that produce or use large quantities of gas

Endothermic



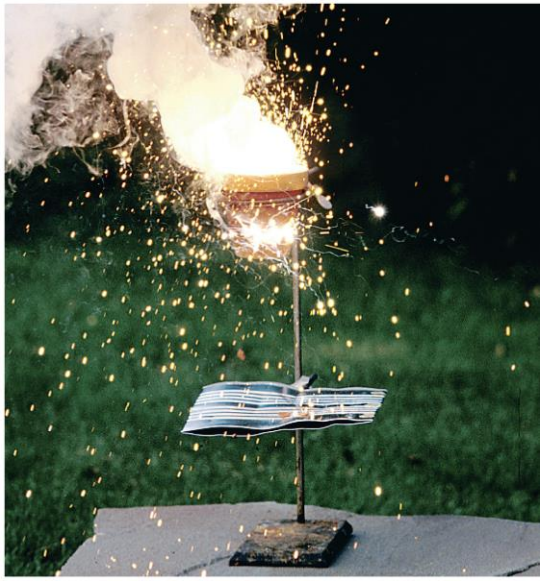
Exothermic

Endothermic and Exothermic Reactions

- when ΔH is ─, heat is being released by the system
- reactions that release heat are called **exothermic reactions**
- when ΔH is +, heat is being absorbed by the system
- reactions that release heat are called **endothermic reactions**
- chemical heat packs contain iron filings that are oxidized in an exothermic reaction ─ your hands get warm because the released heat of the reaction is absorbed by your hands
- chemical cold packs contain NH_4NO_3 that dissolves in water in an endothermic process ─ your hands get cold because they are giving away your heat to the reaction

Molecular View of Exothermic Reactions

- in an exothermic reaction, the temperature rises due to release of thermal energy
- this extra thermal energy comes from the conversion of some of the chemical potential energy in the reactants into kinetic energy in the form of heat
- during the course of a reaction, old bonds are broken and new bonds made
- the products of the reaction have less chemical potential energy than the reactants
- the difference in energy is released as heat



Molecular View of Endothermic Reactions

- in an endothermic reaction, the temperature drops due to absorption of thermal energy
- the required thermal energy comes from the surroundings
- during the course of a reaction, old bonds are broken and new bonds made
- the products of the reaction have more chemical potential energy than the reactants
- to acquire this extra energy, some of the thermal energy of the surroundings is converted into chemical potential energy stored in the products

Enthalpy of Reaction

- the enthalpy change in a chemical reaction is an extensive property
  - ✓ the more reactants you use, the larger the enthalpy change
- by convention, we calculate the enthalpy change for the number of moles of reactants in the reaction as written

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g) \qquad \Delta H = -2044\ kJ$$

$\Delta H_{reaction}$ for 1 mol C_3H_8 = -2044 kJ

$$\frac{-2044\ kJ}{1\ mol\ C_3H_8} \text{ or } \frac{1\ mol\ C_3H_8}{-2044\ kJ}$$

$\Delta H_{reaction}$ for 5 mol O_2 = -2044 kJ

$$\frac{-2044\ kJ}{5\ mol\ O_2} \text{ or } \frac{5\ mol\ O_2}{-2044\ kJ}$$

Example 6.6 – How much heat is evolved in the complete combustion of 13.2 kg of $C_3H_8(g)$?

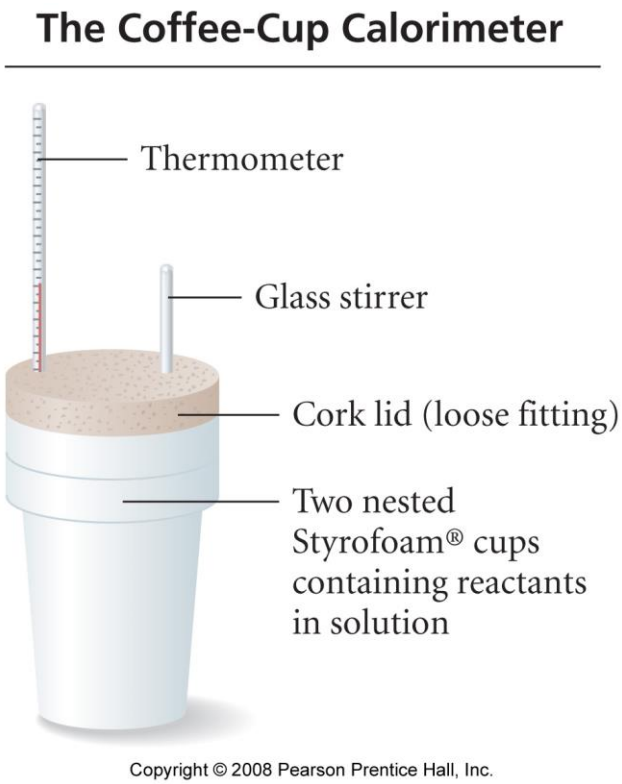
Given:	13.2 kg C_3H_8,
Find:	q, kJ/mol
Concept Plan:	kg → g → mol → kJ $\frac{1000\text{ g}}{1\text{ kg}}$ $\frac{1\text{ mol } C_3H_8}{44.09\text{ g}}$ $\frac{-2044\text{ kJ}}{1\text{ mol } C_3H_8}$
Relationships:	1 kg = 1000 g, 1 mol C_3H_8 = -2044 kJ, Molar Mass = 44.09 g/mol
Solution:	$13.2\,\text{kg} \times \frac{1000\text{ g}}{1\text{ kg}} \times \frac{1\text{ mol}}{44.09\text{ g}} \times \frac{-2044\text{ kJ}}{1\text{ mol}} = -6.12 \times 10^5\text{ kJ}$
Check:	the sign is correct and the value is reasonable

Measuring ΔH
Calorimetry at Constant Pressure

- reactions done in aqueous solution are at constant pressure
  - ✓ open to the atmosphere
- the calorimeter is often nested foam cups containing the solution

$$q_{reaction} = -q_{solution} = -(mass_{solution} \times C_{s,\,solution} \times \Delta T)$$

- $\Delta H_{reaction} = q_{constant\ pressure} = q_{reaction}$
  - ✓ to get $\Delta H_{reaction}$ per mol, divide by the number of moles



Example 6.7 – What is $\Delta H_{rxn/mol\ Mg}$ for the reaction $Mg(s) + 2\ HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ if 0.158 g Mg reacts in 100.0 mL of solution changes the temperature from 25.6°C to 32.8°C?

Given:	0.158 g Mg, 100.0 mL,
Find:	q, kJ/mol
Concept Plan:	kg → g → mol → kJ $\frac{1000\ g}{1\ kg}$ $\quad \frac{1\ mol\ C_3H_8}{44.09\ g}$ $\quad \frac{-2044\ kJ}{1\ mol\ C_3H_8}$
Relationships:	1 kg = 1000 g, 1 mol C_3H_8 = -2044 kJ, Molar Mass = 44.09 g/mol
Solution:	$13.2\ \cancel{kg} \times \frac{1000\ \cancel{g}}{1\ \cancel{kg}} \times \frac{1\ \cancel{mol}}{44.09\ \cancel{g}} \times \frac{-2044\ kJ}{1\ \cancel{mol}} = -6.12 \times 10^5\ kJ$
Check:	the sign is correct and the value is reasonable

Example 6.7 – What is $\Delta H_{rxn/mol\ Mg}$ for the reaction $Mg(s) + 2\ HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ if 0.158 g Mg reacts in 100.0 mL of solution to change the temperature from 25.6°C to 32.8°C?

Given: 0.158 g Mg, 100.0 mL sol'n, $T_1 = 25.6°C$, $T_2 = 32.8°C$, $C_s = 4.18$ J/°C, $d_{soln} = 1.00$ g/mL

Find: ΔH_{rxn}, J/mol Mg

Concept Plan:

$m, C_s, \Delta T \rightarrow q_{soln}$ $\qquad$ $q_{soln} \rightarrow q_{rxn}$

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

Relationships: $q_{soln} = m \times C_s \times \Delta T = -q_{rxn}$ $\qquad$ $\Delta H = \dfrac{q_{rxn}}{\text{mol Mg}}$

Solution:

$$100.0\ \text{mL} \times \frac{1.00\ \text{g}}{1\ \text{mL}} = 1.00 \times 10^2\ \text{g}$$

$$q_{soln} = m \times C_s \times \Delta T$$

$$0.158\ \text{g Mg} \times \frac{1\ \text{mol}}{24.31\ \text{g}} = 6.4994 \times 10^{-3}\ \text{mol}$$

$$= 1.00 \times 10^2\ \text{g} \times 4.18\ \frac{\text{J}}{\text{g}\cdot°\text{C}} \times 7.2°\text{C} = 3.0 \times 10^3\ \text{J}$$

$$\Delta T = 32.8°\text{C} - 25.6°\text{C} = 7.2°\text{C}$$

$$q_{rxn} = -q_{soln} = -3.0 \times 10^3\ \text{J}$$

$$\Delta H = \frac{q_{rxn}}{\text{mol Mg}} = \frac{-3.0 \times 10^3\ \text{J}}{6.4994 \times 10^{-3}\ \text{mol}}$$

$$= -4.6 \times 10^5\ \text{J/mol}$$

Check: the units and sign are correct

Relationships Involving ΔH_{rxn}

- when reaction is multiplied by a factor, ΔH_{rxn} is multiplied by that factor
  - ✓because ΔH_{rxn} is extensive

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

$2\ C(s) + 2\ O_2(g) \rightarrow 2\ CO_2(g)$ $\Delta H = 2(-393.5\ kJ) = 787.0$ kJ

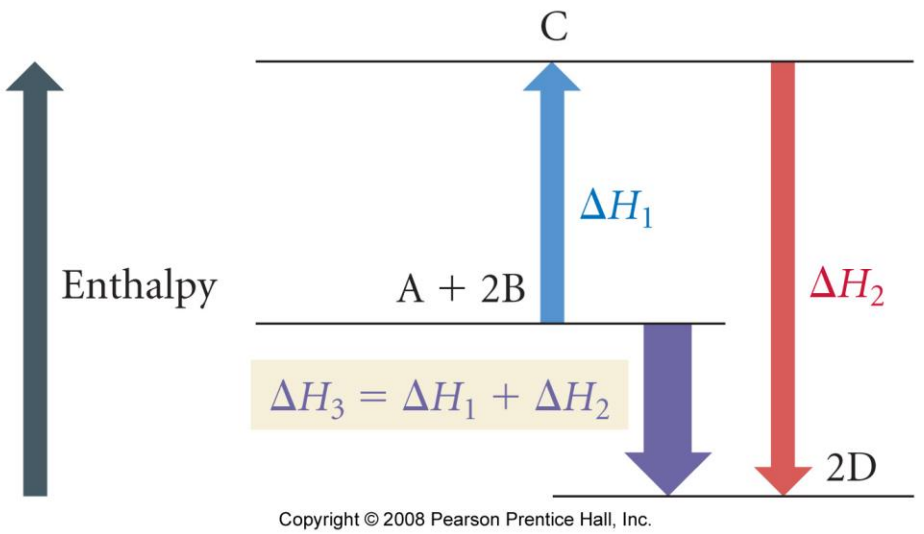
- if a reaction is reversed, then the sign of ΔH is reversed

$CO_2(g) \rightarrow C(s) + O_2(g)$ $\Delta H = +393.5$ kJ

Relationships Involving ΔH_{rxn} Hess's Law

- if a reaction can be expressed as a series of steps, then the ΔH_{rxn} for the overall reaction is the sum of the heats of reaction for each step

Hess's Law
The change in enthalpy for a stepwise process is the sum of the enthalpy changes of the steps.



Sample – Hess's Law

Given the following information:

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$ $\Delta H° = -173$ kJ

$2\ N_2(g) + 5\ O_2(g) + 2\ H_2O(l) \rightarrow 4\ HNO_3(aq)$ $\Delta H° = -255$ kJ

$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$ $\Delta H° = +181$ kJ

Calculate the $\Delta H°$ for the reaction below:

$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$ $\Delta H° = ?$

$[3\ NO_2(g) \rightarrow 3\ NO(g) + 1.5\ O_2(g)] \times 1$ $\Delta H° = (+259.5\ kJ)$

$[2\ N_2(g) + 5\ O_2(g) + 2\ H_2O(l) \rightarrow 4\ HNO_3(aq)] \times 0.5$ $\Delta H° = (-127.5\ kJ)$

$[2\ NO(g) \rightarrow N_2(g) + O_2(g)]$ $\Delta H° = -181$ kJ

$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$ $\Delta H° = -49$ kJ

Standard Conditions

- the **standard state** is the state of a material at a defined set of conditions
  - ✓ pure gas at exactly 1 atm pressure
  - ✓ pure solid or liquid in its most stable form at exactly 1 atm pressure and temperature of interest
    - ➢ usually 25°C
  - ✓ substance in a solution with concentration 1 M
- the **standard enthalpy change, $\Delta H°$,** is the enthalpy change when all reactants and products are in their standard states
- the **standard enthalpy of formation, $\Delta H_f°$,** is the enthalpy change for the reaction forming 1 mole of a pure compound from its constituent elements
  - ✓ the elements must be in their standard states
  - ✓ the $\Delta H_f°$ for a pure element in its standard state = 0 kJ/mol
    - ➢ by definition

Formation Reactions

- reactions of elements in their standard state to form 1 mole of a pure compound
  - ✓if you are not sure what the standard state of an element is, find the form in Appendix IIB that has a $\Delta H_f° = 0$
  - ✓since the definition requires 1 mole of compound be made, the coefficients of the reactants may be fractions

Writing Formation Reactions

Write the formation reaction for CO(*g*)

- the formation reaction is the reaction between the elements in the compound, which are C and O

$$C + O \rightarrow CO(g)$$

- the elements must be in their standard state
  - ✓ there are several forms of solid C, but the one with $\Delta H_f° = 0$ is graphite
  - ✓ oxygen's standard state is the diatomic gas

$$C(s, \textit{graphite}) + O_2(g) \rightarrow CO(g)$$

- the equation must be balanced, but the coefficient of the product compound must be 1
  - ✓ use whatever coefficient in front of the reactants is necessary to make the atoms on both sides equal without changing the product coefficient

$$C(s, \textit{graphite}) + \tfrac{1}{2}\, O_2(g) \rightarrow CO(g)$$

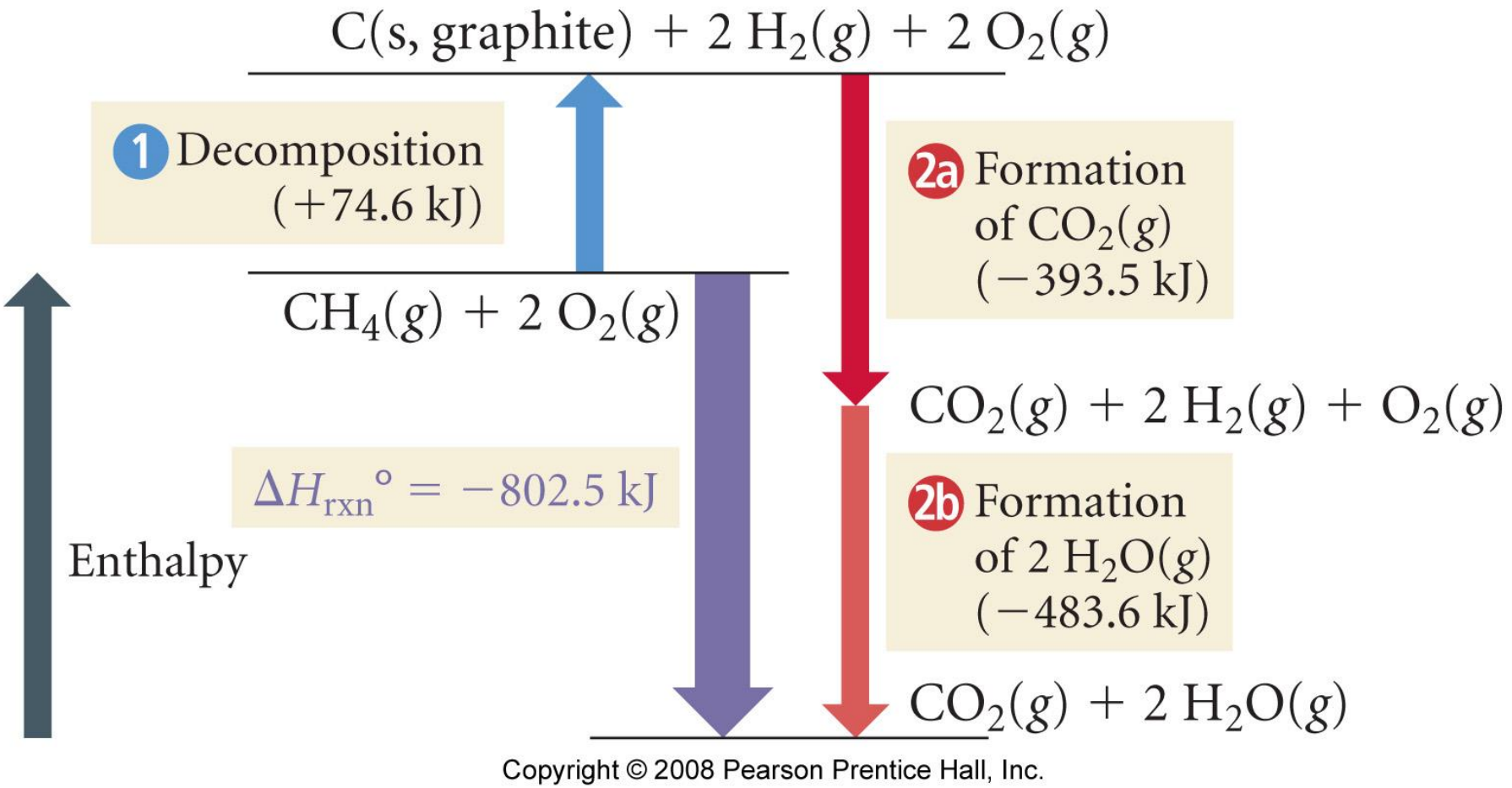
Calculating Standard Enthalpy Change for a Reaction

- any reaction can be written as the sum of formation reactions (or the reverse of formation reactions) for the reactants and products
- the $\Delta H°$ for the reaction is then the sum of the $\Delta H_f°$ for the component reactions

$$\mathbf{\Delta H°_{reaction} = \Sigma\ n\ \Delta H_f°(products) - \Sigma\ n\ \Delta H_f°(reactants)}$$

- ✓Σ means sum
- ✓n is the coefficient of the reaction

Calculating the Enthalpy Change for the Combustion of Methane



Sample - Calculate the Enthalpy Change in the Reaction

$$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$$

1. Write formation reactions for each compound and determine the $\Delta H_f°$ for each

$2\ C(s, gr) + H_2(g) \rightarrow C_2H_2(g)$ $\quad \Delta H_f° = +227.4$ kJ/mol

$C(s, gr) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H_f° = -393.5$ kJ/mol

$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$ $\quad \Delta H_f° = -285.8$ kJ/mol

Sample - Calculate the Enthalpy Change in the Reaction

$$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$$

2. Arrange equations so they add up to desired reaction

$2\ C_2H_2(g) \rightarrow 4\ C(s) + 2\ H_2(g)$ $\Delta H° = 2(-227.4)$ kJ

$4\ C(s) + 4\ O_2(g) \rightarrow 4CO_2(g)$ $\Delta H° = 4(-393.5)$ kJ

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ $\Delta H° = 2(-285.8)$ kJ

$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$ $\Delta H = -2600.4$ kJ

Sample - Calculate the Enthalpy Change in the Reaction

$$2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$$

$\Delta H°_{reaction} = \Sigma\ n\ \Delta H_f°(products) - \Sigma\ n\ \Delta H_f°(reactants)$

$$\Delta H_{rxn} = [(4 \bullet \Delta H_{CO2} + 2 \bullet \Delta H_{H2O}) - (2 \bullet \Delta H_{C2H2} + 5 \bullet \Delta H_{O2})]$$

$$\Delta H_{rxn} = [(4 \bullet (-393.5) + 2 \bullet (-285.8)) - (2 \bullet (+227.4) + 5 \bullet (0))]$$

$$\Delta H_{rxn} = -2600.4\ kJ$$

Example 6.11 – How many kg of octane must be combusted to supply 1.0 x 10^{11} kJ of energy?

Given: 1.0 x 10^{11} kJ

Find: mass octane, kg

Concept Plan:

Write the balanced equation per mole of octane

$\Delta H_f°$'s → $\Delta H_{rxn}°$

$$\Delta H°_{rxn} = \Sigma n\Delta H°_{f\,products} - \Sigma n\Delta H°_{f\,reactants}$$

kJ → (from above) mol C_8H_{18} → ($\frac{114.2\text{ g}}{1\text{ mol}}$) g C_8H_{18} → ($\frac{1\text{ kg}}{1000\text{ g}}$) kg C_8H_{18}

Relationships: MM_{octane} = 114.2 g/mol, 1 kg = 1000 g

Solution:

$$C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8\ CO_2(g) + 9\ H_2O(g)$$

$$-1.0\times10^{11}\text{ kJ} \times \frac{1\text{ mol } C_8H_{18}}{-5074.1\text{ kJ}} \times \frac{114.2\text{ g } C_8H_{18}}{1\text{ mol } C_8H_{18}} \times \frac{1\text{ kg}}{1000\text{ g}} = 2.3\times10^{6}\text{ kg } C_8H_{18}$$

$$\Delta H°_{rxn} = \left[8\left(-393.5\text{ kJ}\right) + 9\left(-241.8\text{ kJ}\right)\right] - \left[\left(-250.1\text{ kJ}\right) + \frac{25}{2}\left(0\text{ kJ}\right)\right]$$

$$= -5074.1\text{ kJ}$$

Look up the $\Delta H_f°$ for each material

Material	$\Delta H_f°$, kJ/mol
$C_8H_{18}(l)$	-250.1
$O_2(g)$	0
$CO_2(g)$	-393.5
$H_2O(g)$	-241.8

Check: the units and sign are correct; the large value is expected

Energy Use and the Environment

- in the U.S., each person uses over 10^5 kWh of energy per year
- most comes from the combustion of fossil fuels
  - ✓ combustible materials that originate from ancient life

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H°_{rxn} = -393.5$ kJ

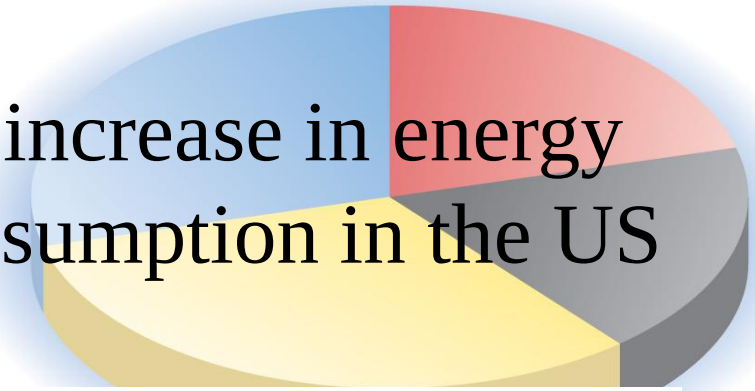
$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$ $\quad \Delta H°_{rxn} = -802.3$ kJ

$C_8H_{18}(g) + 12.5\ O_2(g) \rightarrow 8\ CO_2(g) + 9\ H_2O(g)$ $\quad \Delta H°_{rxn} = -5074.1$ kJ

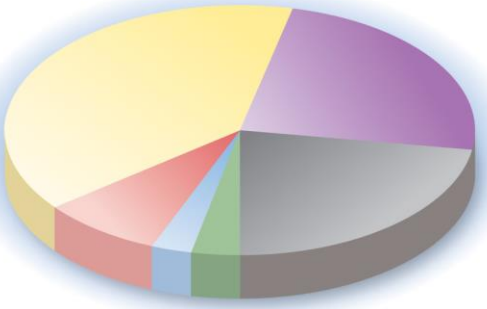
- fossil fuels cannot be replenished
- at current rates of consumption, oil and natural gas supplies will be depleted in 50 – 100 yrs.

Energy Consumption

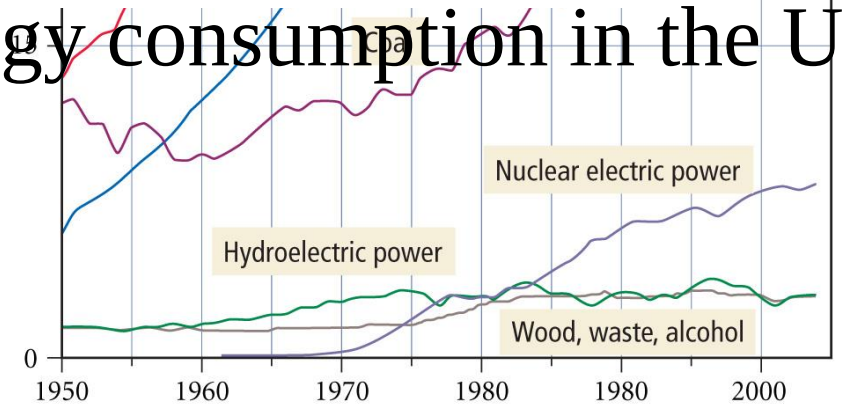
- the increase in energy consumption in the US



U.S. Energy Use by Source



rgy consumption in the US



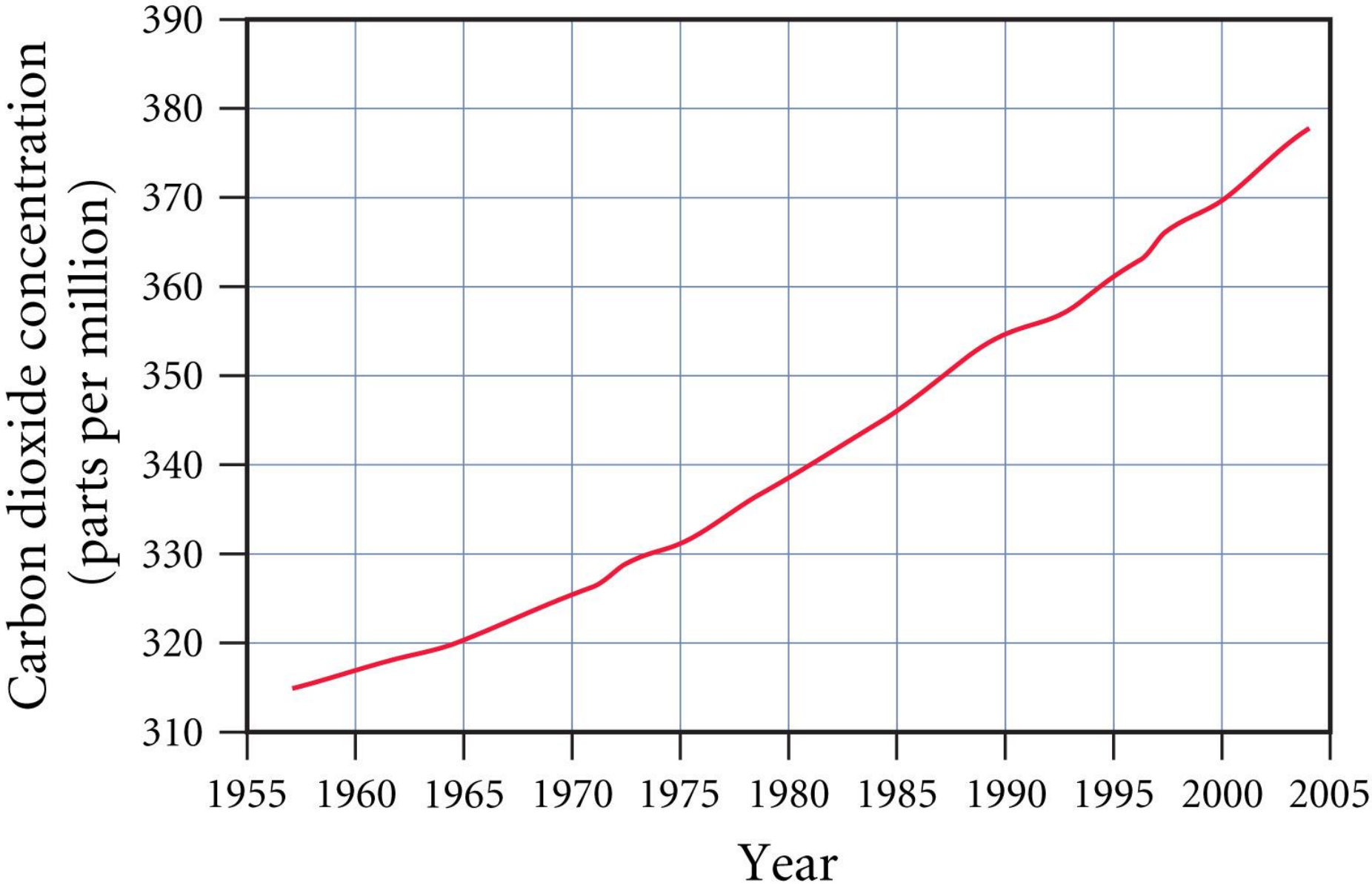
The Effect of Combustion Products on Our Environment

- because of additives and impurities in the fossil fuel, incomplete combustion and side reactions, harmful materials are added to the atmosphere when fossil fuels are burned for energy
- therefore fossil fuel emissions contribute to air pollution, acid rain, and global warming

Global Warming

- CO_2 is a greenhouse gas
  - ✓ it allows light from the sun to reach the earth, but does not allow the heat (infrared light) reflected off the earth to escape into outer space
    - ➢ it acts like a blanket
- CO_2 levels in the atmosphere have been steadily increasing
- current observations suggest that the average global air temperature has risen 0.6°C in the past 100 yrs.
- atmospheric models suggest that the warming effect could worsen if CO_2 levels are not curbed
- some models predict that the result will be more severe storms, more floods and droughts, shifts in agricultural zones, rising sea levels, and changes in habitats

Atmospheric Carbon Dioxide



Renewable Energy

- our greatest unlimited supply of energy is the sun
- new technologies are being developed to capture the energy of sunlight
  - ✓parabolic troughs, solar power towers, and dish engines concentrate the sun's light to generate electricity
  - ✓solar energy used to decompose water into $H_2(g)$ and $O_2(g)$; the H_2 can then be used by fuel cells to generate electricity

$$H_2(g) + \tfrac{1}{2}\, O_2(g) \rightarrow H_2O(l) \qquad \Delta H^\circ_{rxn} = -285.8 \text{ kJ}$$

- hydroelectric power
- wind power