Chapter 6

Thermochemistry

Chapter 6: Thermochemistry
Objectives

- Define energy, work, potential energy, kinetic energy, system and surroundings, endothermic and exothermic.
- Be able to identify each of the above.
- Understand $\Delta E = q + w$ and use the equation to find the sign of E.
- Know $\Delta H = H_{products} - H_{reactants}$.
- Use calorimetry to solve for a variable or estimate a temperature of a system.
- Use Hess's law to calculate enthalpy of a reaction.
- Use Standard enthalpy of formation to solve for enthalpy of reaction: $\Delta H = \Sigma nH_{reactants} - \Sigma nH_{products}$.

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Energy

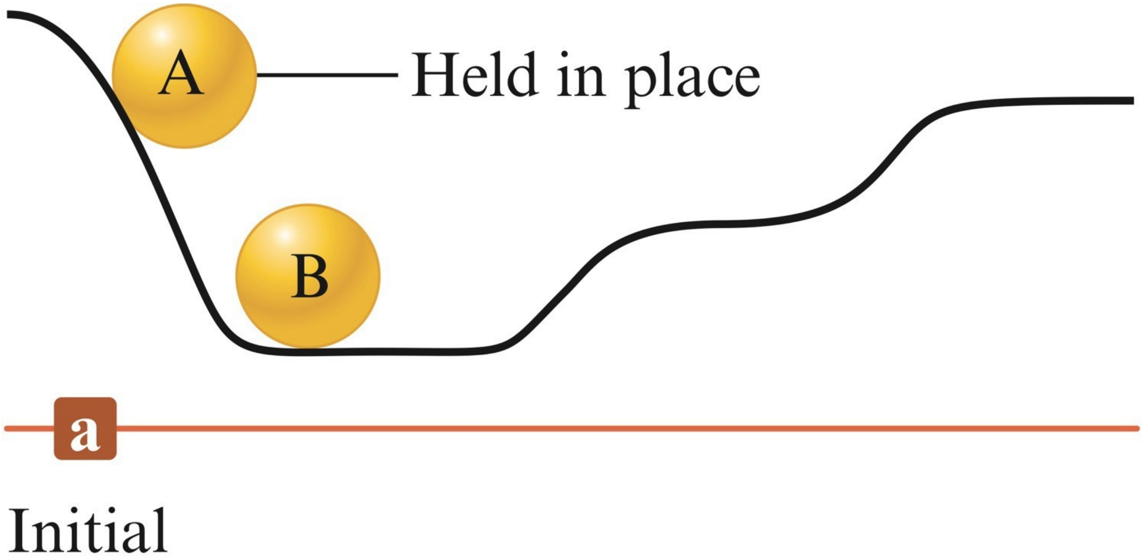
- Capacity to do work or to produce heat.
- Law of conservation of energy – energy can be converted from one form to another but can be neither created nor destroyed.
  - The total energy content of the universe is constant.

Energy

- Potential energy – energy due to position or composition.
- Kinetic energy – energy due to motion of the object and depends on the mass of the object and its velocity.

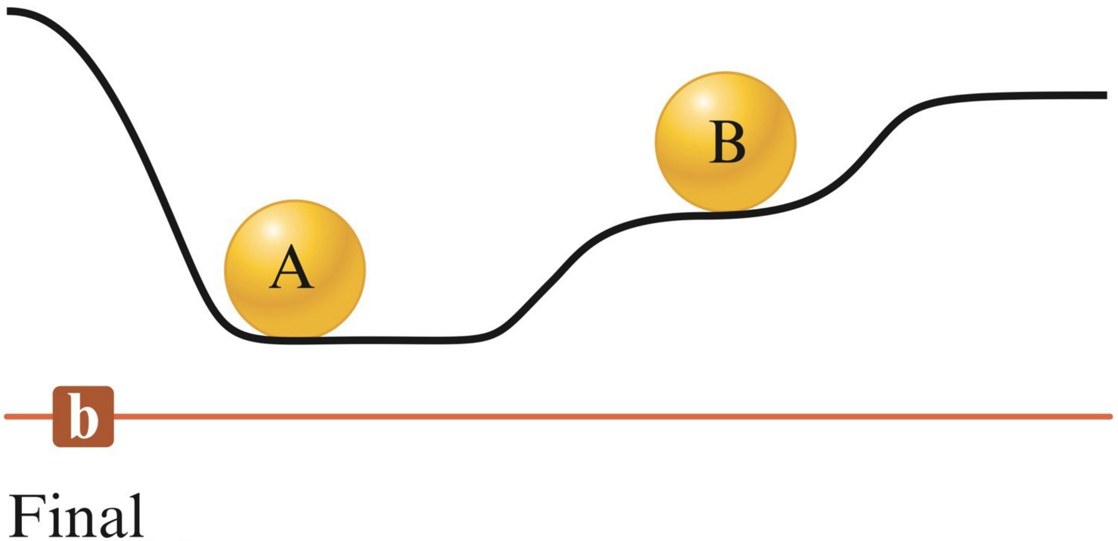
Initial Position

- In the initial position, ball A has a higher potential energy than ball B.



Final Position

- After A has rolled down the hill, the potential energy lost by A has been converted to random motions of the components of the hill (frictional heating) and to the increase in the potential energy of B.



Energy

- Heat involves the transfer of energy between two objects due to a temperature difference.
- Work – force acting over a distance.
- Energy is a state function; work and heat are not
  - State Function – property that does not depend in any way on the system’s past or future (only depends on *present* state).

Chemical Energy

- System – part of the universe on which we wish to focus attention.
- Surroundings – include everything else in the universe.

Chemical Energy

- Endothermic Reaction:
  - Heat flow is into a system.
  - Absorb energy from the surroundings.
- Exothermic Reaction:
  - Energy flows out of the system.
- Energy gained by the surroundings must be equal to the energy lost by the system.

CONCEPT CHECK!

Is the freezing of water an endothermic or exothermic process? Explain.

CONCEPT CHECK!

Classify each process as exothermic or endothermic. Explain. The system is underlined in each example.

Exo	a)	Your hand gets cold when you touch ice.
Endo	b)	The ice gets warmer when you touch it.
Endo	c)	Water boils in a kettle being heated on a stove.
Exo	d)	Water vapor condenses on a cold pipe.
Endo	e)	Ice cream melts.

CONCEPT CHECK!

For each of the following, define a system and its surroundings and give the direction of energy transfer.

a) Methane is burning in a Bunsen burner in a laboratory.
b) Water drops, sitting on your skin after swimming, evaporate.

CONCEPT CHECK!

Hydrogen gas and oxygen gas react violently to form water. Explain.

- Which is lower in energy: a mixture of hydrogen and oxygen gases, or water?

Thermodynamics

- The study of energy and its interconversions is called thermodynamics.
- Law of conservation of energy is often called the first law of thermodynamics.

Internal Energy

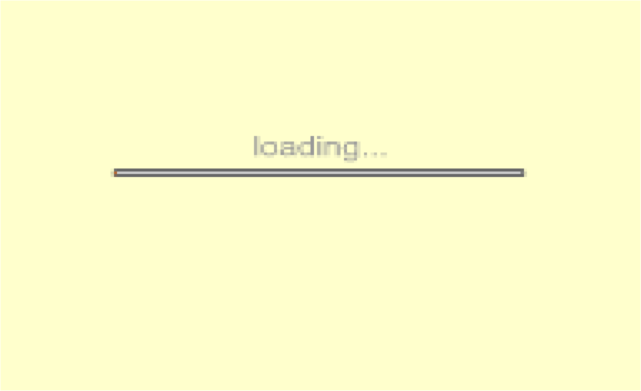
- Internal energy *E* of a system is the sum of the kinetic and potential energies of all the "particles" in the system.
- To change the internal energy of a system:

  $$\Delta E = q + w$$

  q represents heat

  w represents work

Work vs Energy Flow



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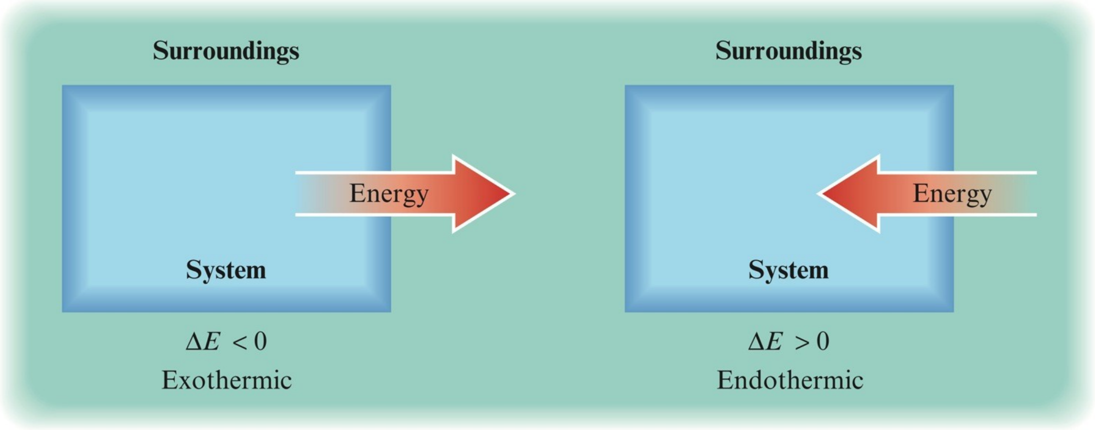
Internal Energy

- Thermodynamic quantities consist of two parts:
  - Number gives the magnitude of the change.
  - Sign indicates the direction of the flow.

Internal Energy

- Sign reflects the system's point of view.
- Endothermic Process:
  - *q* is positive
- Exothermic Process:
  - *q* is negative

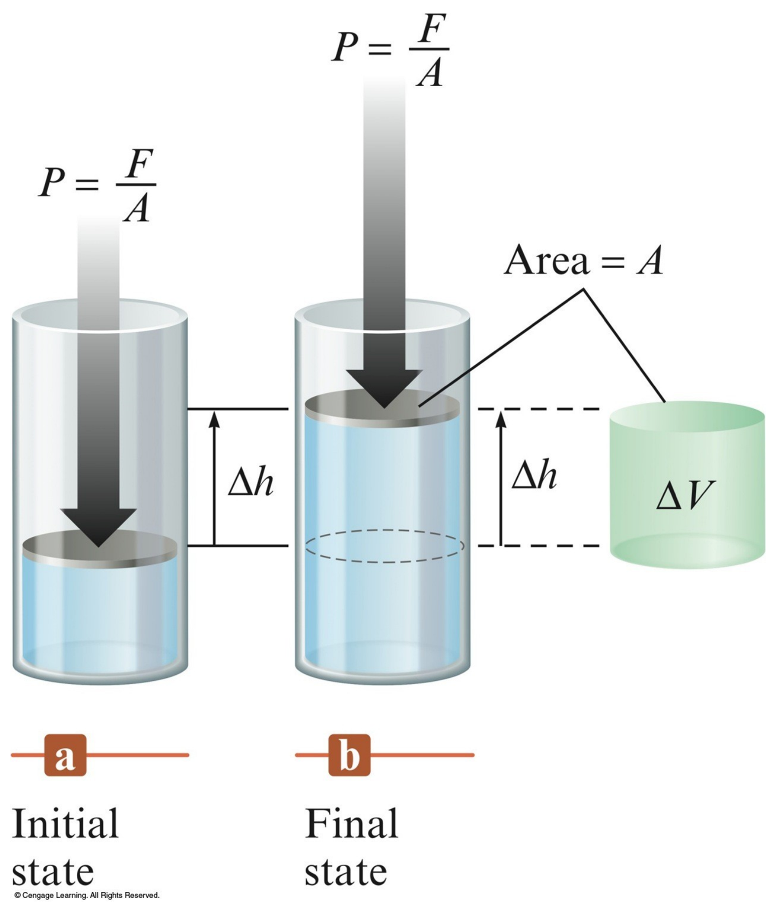


Internal Energy

- Sign reflects the system’s point of view.
- System does work on surroundings:
  - w is negative
- Surroundings do work on the system:
  - w is positive

Work

- Work = $P \times A \times \Delta h = P\Delta V$
  - P is pressure.
  - A is area.
  - Δh is the piston moving a distance.
  - ΔV is the change in volume.



Work

- For an expanding gas, ΔV is a positive quantity because the volume is increasing. Thus ΔV and w must have opposite signs:

$$w = -P\Delta V$$

- To convert between L·atm and Joules, use 1 L·atm = 101.3 J.

EXERCISE!

Which of the following performs more work?

a) A gas expanding against a pressure of 2 atm from 1.0 L to 4.0 L.
b) A gas expanding against a pressure of 3 atm from 1.0 L to 3.0 L.

They perform the same amount of work.

CONCEPT CHECK!

Determine the sign of ΔE for each of the following with the listed conditions:

a) An endothermic process that performs work.

- |work| > |heat| ΔE = negative
- |work| < |heat| ΔE = positive

b) Work is done on a gas and the process is exothermic.

- |work| > |heat| ΔE = positive
- |work| < |heat| ΔE = negative

Change in Enthalpy

- State function
- $\Delta H = q$ at constant pressure
- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$

EXERCISE!

Consider the combustion of propane:

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

$\Delta H = -2221$ kJ

Assume that all of the heat comes from the combustion of propane. Calculate ΔH in which 5.00 g of propane is burned in excess oxygen at constant pressure.

–252 kJ

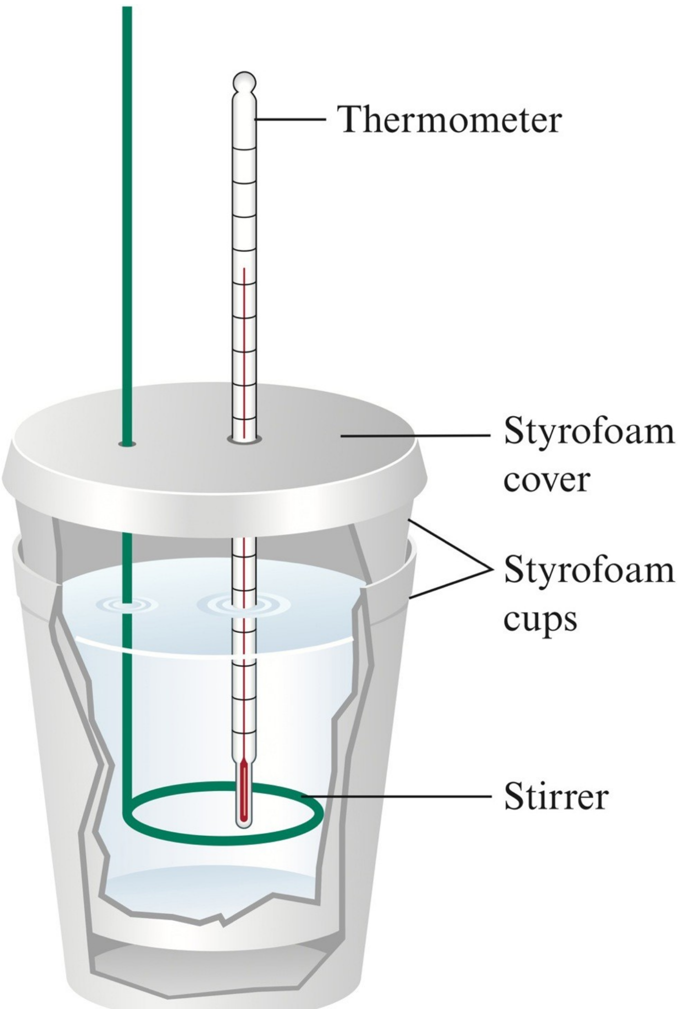
Calorimetry

- Science of measuring heat
- Specific heat capacity:
  - The energy required to raise the temperature of one gram of a substance by one degree Celsius.
- Molar heat capacity:
  - The energy required to raise the temperature of one mole of substance by one degree Celsius.

Calorimetry

- If two reactants at the same temperature are mixed and the resulting solution gets warmer, this means the reaction taking place is exothermic.
- An endothermic reaction cools the solution.

A Coffee–Cup Calorimeter Made of Two Styrofoam Cups



Calorimetry

- Energy released (heat) = $m \times s \times \Delta T$

m = mass of solution (g)

s = specific heat capacity (J/°C·g)

ΔT = change in temperature (°C)

CONCEPT CHECK!

A 100.0 g sample of water at 90°C is added to a 100.0 g sample of water at 10°C.

The final temperature of the water is:

a) Between 50°C and 90°C

b) 50°C

c) Between 10°C and 50°C

CONCEPT CHECK!

A 100.0 g sample of water at 90.°C is added to a 500.0 g sample of water at 10.°C.

The final temperature of the water is:

a) Between 50°C and 90°C

b) 50°C

c) Between 10°C and 50°C

Calculate the final temperature of the water.

23°C

CONCEPT CHECK!

You have a Styrofoam cup with 50.0 g of water at 10.°C. You add a 50.0 g iron ball at 90. °C to the water. (s_{H2O} = 4.18 J/°C·g and s_{Fe} = 0.45 J/°C·g)

The final temperature of the water is:

a) Between 50°C and 90°C

b) 50°C

c) Between 10°C and 50°C

Calculate the final temperature of the water.

18°C

- In going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H_1 = 68\ \text{kJ}$

- This reaction also can be carried out in two distinct steps, with enthalpy changes designated by ΔH_2 and ΔH_3.

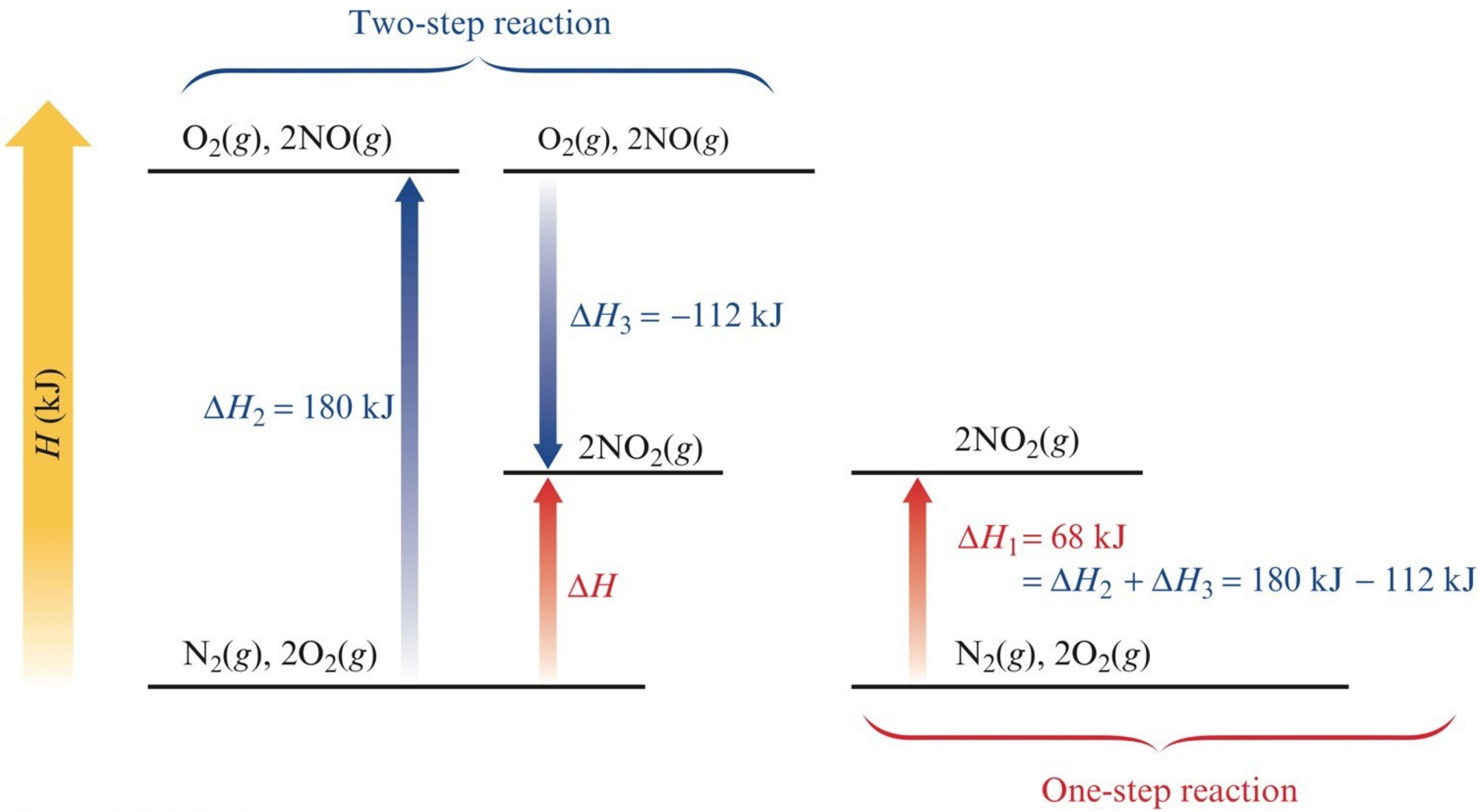
$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H_2 = 180\ \text{kJ}$

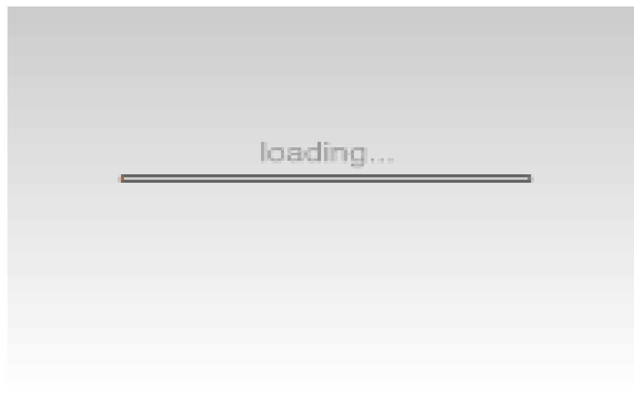
$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H_3 = -112\ \text{kJ}$

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H_2 + \Delta H_3 = 68\ \text{kJ}$

$\Delta H_1 = \Delta H_2 + \Delta H_3 = 68\ \text{kJ}$

The Principle of Hess's Law





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Characteristics of Enthalpy Changes

- If a reaction is reversed, the sign of ΔH is also reversed.
- The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

Example

- Consider the following data:

$$NH_3(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \qquad \Delta H = 46\ kJ$$

$$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g) \qquad \Delta H = -484\ kJ$$

- Calculate ΔH for the reaction

$$2\ N_2(g) + 6\ H_2O(g) \longrightarrow 3\ O_2(g) + 4\ NH_3(g)$$

Problem-Solving Strategy

- Work *backward* from the required reaction, using the reactants and products to decide how to manipulate the other given reactions at your disposal.
- Reverse any reactions as needed to give the required reactants and products.
- Multiply reactions to give the correct numbers of reactants and products.

Example

- Reverse the two reactions:

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\longrightarrow NH_3(g) \qquad \Delta H = -46\text{ kJ}$$

$$2\ H_2O(g)\longrightarrow 2\ H_2(g)+O_2(g) \qquad \Delta H = +484\text{ kJ}$$

- Desired reaction:

$$2\ N_2(g)+6\ H_2O(g)\longrightarrow 3\ O_2(g)+4\ NH_3(g)$$

Example

- Multiply reactions to give the correct numbers of reactants and products:

$$4\left(\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \longrightarrow NH_3(g)\right) \quad 4(\Delta H = -46\ \text{kJ})$$

$$3\left(2\ H_2O(g) \longrightarrow 2\ H_2(g) + O_2(g)\right) \quad 3(\Delta H = +484\ \text{kJ})$$

- Desired reaction:

$$2\ N_2(g) + 6\ H_2O(g) \longrightarrow 3\ O_2(g) + 4\ NH_3(g)$$

Example

- Final reactions:

$$2\ N_2(g) + 6\ H_2(g) \longrightarrow 4\ NH_3(g) \qquad \Delta H = -184\ kJ$$

$$6\ H_2O(g) \longrightarrow 6\ H_2(g) + 3\ O_2(g) \qquad \Delta H = +1452\ kJ$$

- Desired reaction:

$$2\ N_2(g) + 6\ H_2O(g) \longrightarrow 3\ O_2(g) + 4\ NH_3(g)$$

ΔH = +1268 kJ

Standard Enthalpy of Formation ($\Delta H_f°$)

- Change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states.

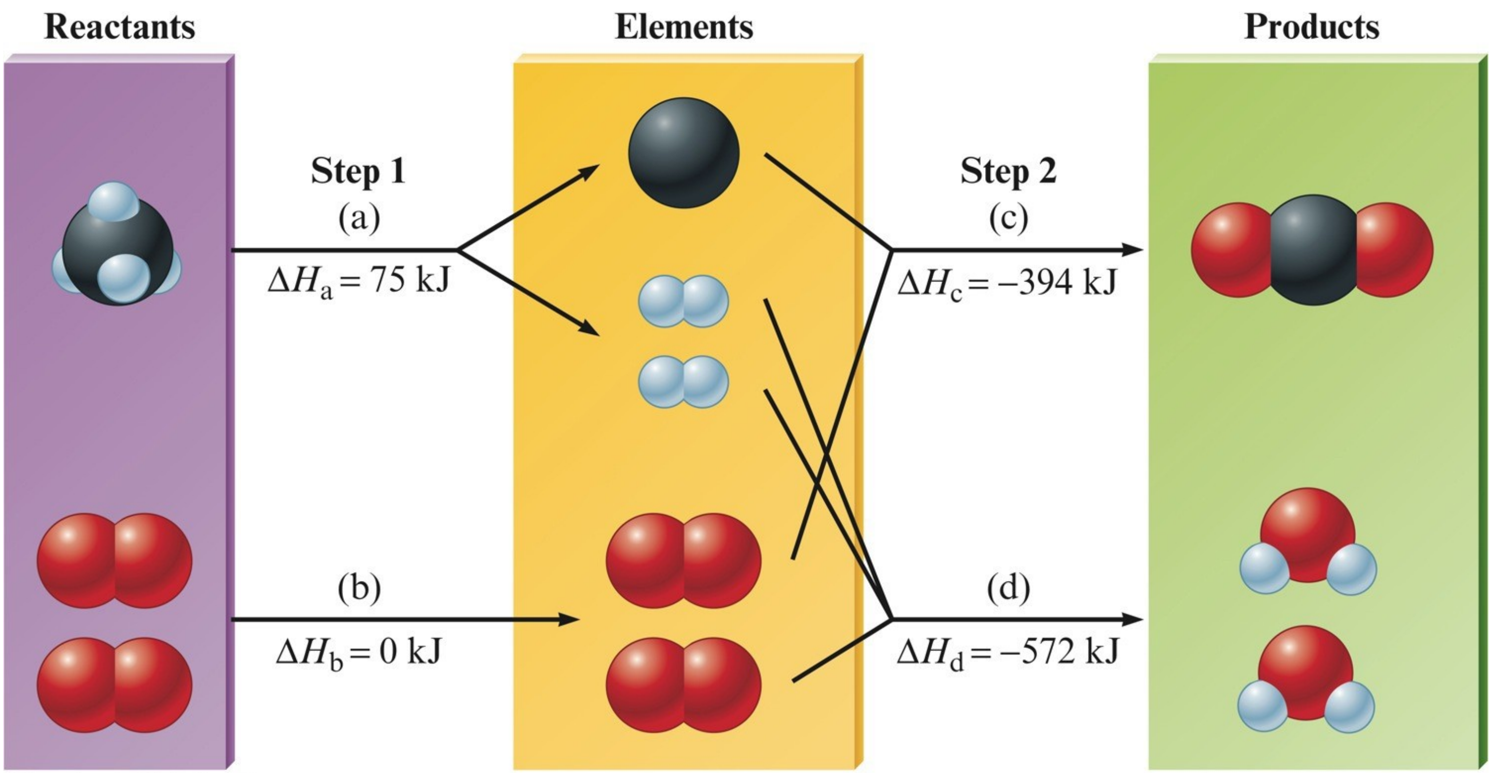
Conventional Definitions of Standard States

- For a Compound
  - For a gas, pressure is exactly 1 atm.
  - For a solution, concentration is exactly 1 *M*.
  - Pure substance (liquid or solid)
- For an Element
  - The form [$N_2(g)$, $K(s)$] in which it exists at 1 atm and 25°C.

A Schematic Diagram of the Energy Changes for the Reaction

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

$$\Delta H^\circ_{\text{reaction}} = -(-75\text{ kJ}) + 0 + (-394\text{ kJ}) + (-572\text{ kJ}) = -891\text{ kJ}$$



Problem-Solving Strategy: Enthalpy Calculations

1. When a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes.
2. When the balanced equation for a reaction is multiplied by an integer, the value of ΔH for that reaction must be multiplied by the same integer.

Problem-Solving Strategy: Enthalpy Calculations

3. The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H^\circ_{rxn} = \Sigma n_p H_f^\circ{}_{(products)} - \Sigma n_r H_f^\circ{}_{(reactants)}$$

4. Elements in their standard states are not included in the $\Delta H_{reaction}$ calculations because ΔH_f° for an element in its standard state is zero.

EXERCISE!

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

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

Given the following information:

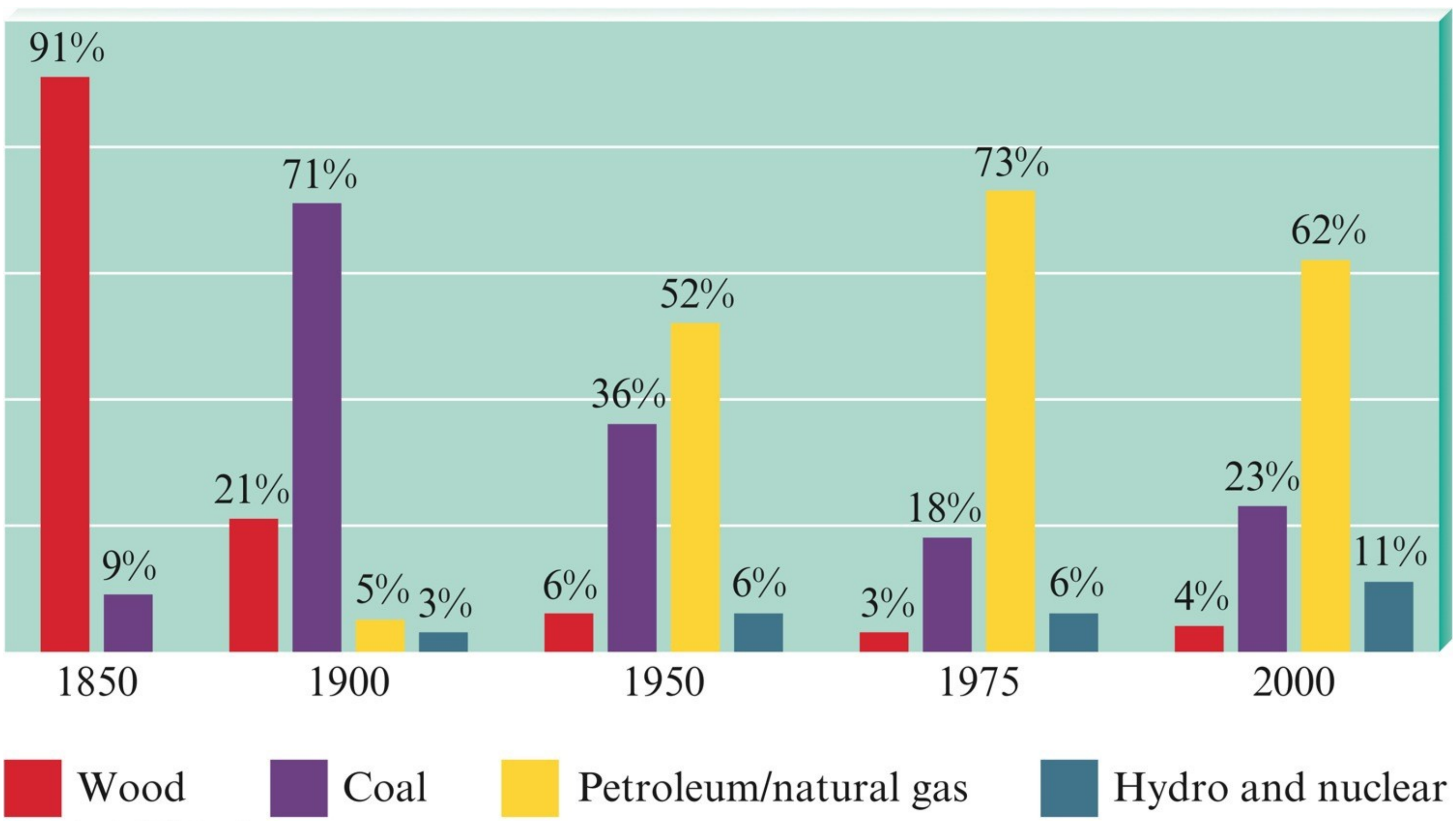
	$\Delta H_f°$ (kJ/mol)
$Na(s)$	0
$H_2O(l)$	–286
$NaOH(aq)$	–470
$H_2(g)$	0

$\Delta H° = –368$ kJ

Section 6.5
Present Sources of Energy

- Fossil Fuels
  - Petroleum, Natural Gas, and Coal
- Wood
- Hydro
- Nuclear

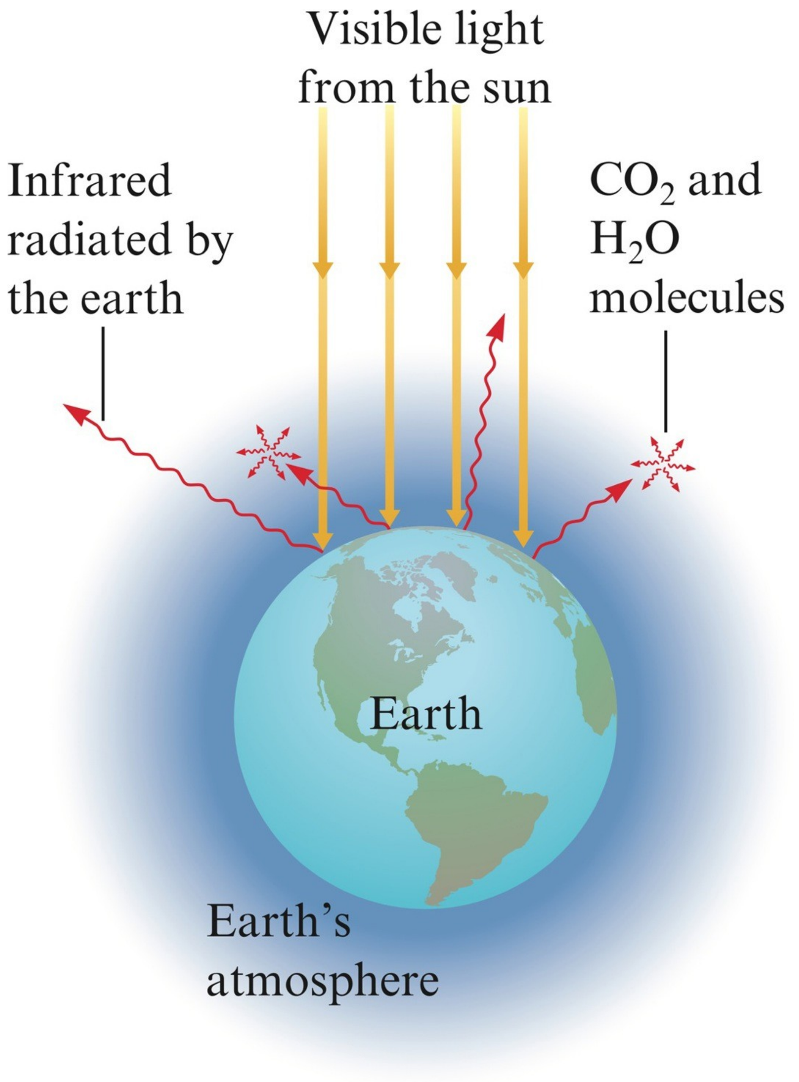
Energy Sources Used in the United States



The Earth's Atmosphere

- Transparent to visible light from the sun.
- Visible light strikes the Earth, and part of it is changed to infrared radiation.
- Infrared radiation from Earth's surface is strongly absorbed by CO_2, H_2O, and other molecules present in smaller amounts in atmosphere.
- Atmosphere traps some of the energy and keeps the Earth warmer than it would otherwise be.

The Earth's Atmosphere



- Coal Conversion
- Hydrogen as a Fuel
- Other Energy Alternatives
  - Oil shale
  - Ethanol
  - Methanol
  - Seed oil

Chapter 6 Activity