Petrucci • Harwood • Herring • Madura

Ninth Edition

# GENERAL CHEMISTRY

Principles and Modern Applications

# Chapter 7: Thermochemistry
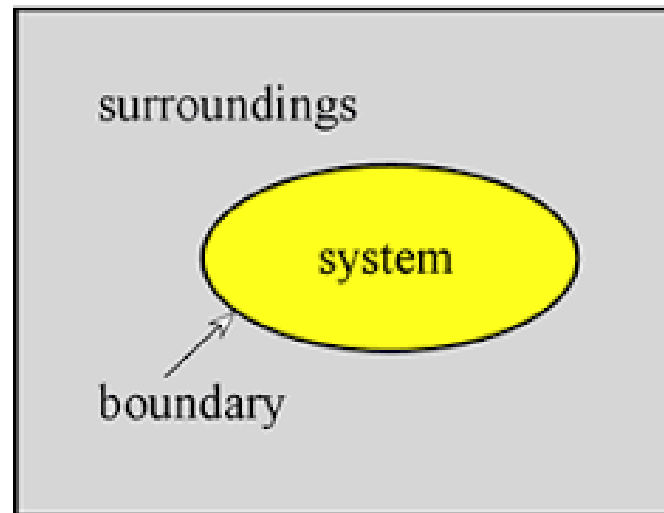
# Contents

# 6-1 Getting Started: Some Terminology

♦ A **system** is the part of the universe chosen for study, and it can be as large as all the oceans on Earth or as small as the contents of a beaker.

♦ The **surroundings** are that part of the universe outside the system with which the system interacts.



"The universe"

surroundings

system

boundary

# 6-1 Getting Started: Some Terminology

♦ An **open system** freely exchanges energy and matter with its surroundings. A **closed system** can exchange energy, but not matter, with its surroundings. An **isolated system** does not interact with its surroundings.

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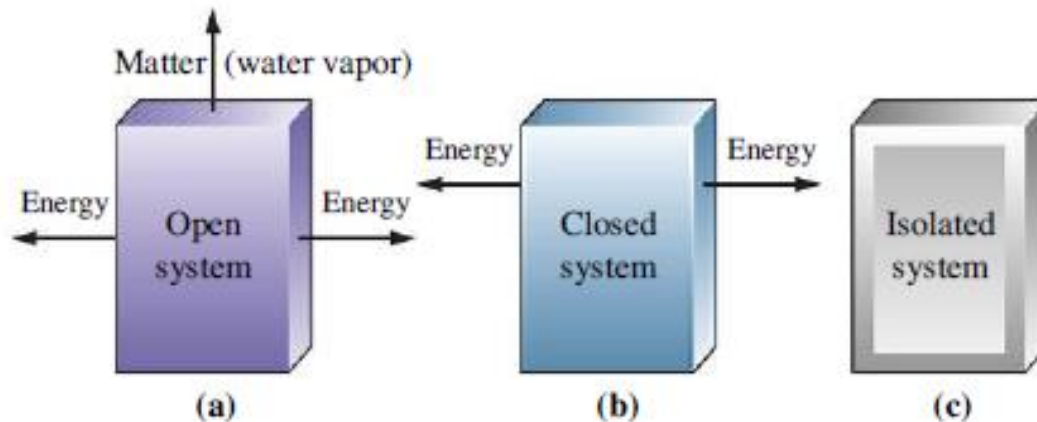
## Thermodynamic Systems

**OPEN SYSTEM**

Heat Transfer

Mass Transfer

**CLOSED SYSTEM**

Heat Transfer

No Mass Transfer

**ISOLATED SYSTEM**

No Heat Transfer

No Mass Transfer

# Terminology

♦ Energy (E): the capacity to do work or transfer heat

♦ Work (w): the energy used to move something against a force. A work's magnitude equals the product of the force, F, and the distance, d, that the object moves:

$$\mathbf{w = F \times d}$$

$$[w] = \left( \frac{\mathrm{kg\ m}}{\mathrm{s}^2} \right) \mathrm{m} = \mathrm{J}$$

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# Energy

♦ Kinetic Energy: the energy of motion. If a system is actively producing or exerting energy, we call it kinetic energy. An object's kinetic energy ($E_k$) is described by the following formula:

$$e_k = \frac{1}{2} mv^2 \quad [e_k] = kg \left(\frac{m}{s}\right)^2 = J$$

♦ Potential energy: Energy due to condition, position, or composition. Associated with forces of attraction or repulsion between objects.
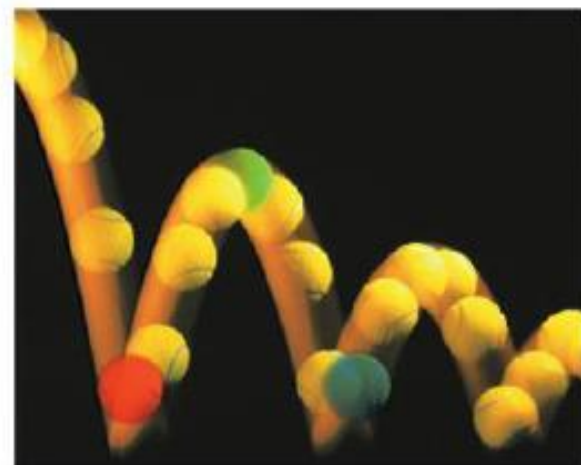
# Energy

◆ Energy can change from potential to kinetic.

◆ Thermal Energy: Kinetic energy associated with random molecular motion.

- In general proportional to temperature.
- An intensive property.

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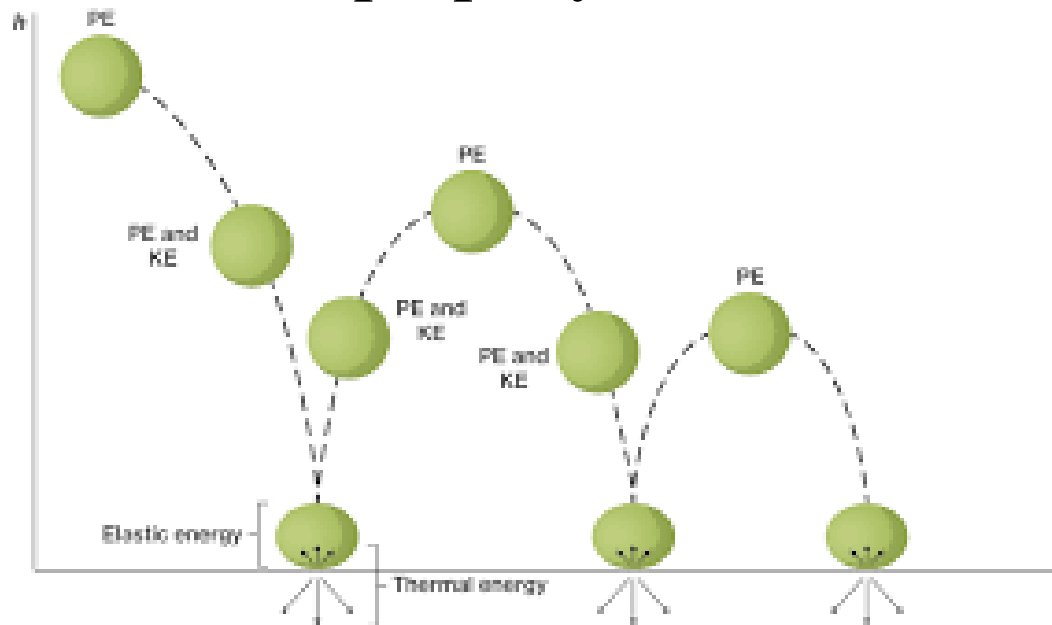
# Heat

◆ Energy transferred between a system and its surroundings as a result of a temperature difference.

◆ Heat *flows* from hotter to colder.

- Temperature may change.
- Phase may change (an isothermal process).

◆ A process occurring at a constant temperature is said to be *isothermal.*

◆ It is reasonable to expect that the quantity of heat, $q$, required to change the temperature of a substance depends on

- how much the temperature is to be changed
- the quantity of substance
- the nature of the substance (type of atoms or molecules)

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# Units of Heat

♦ Calorie (cal)

- The quantity of heat required to change the temperature of one gram of water by one degree Celsius.

♦ Joule (J)

- SI unit for heat

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

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# Heat Capacity

◆ The quantity of heat required to change the temperature of a system by one degree.

- Molar heat capacity.
  - ◦ System is one mole of substance.
- Specific heat capacity, c.      $q = mc\Delta T$
  - ◦ System is one gram of substance
- Heat capacity      $q = C\Delta T$
  - ◦ Mass ⬚ specific heat.

# EXAMPLE 7-1

How much heat is required to raise the temperature of 7.35 g of water from 21.0 to 98.0 °C? (Assume the specific heat of water is 4.18 J g$^{-1}$ °C$^{-1}$ throughout this temperature range.)

$$q = mc\Delta T$$

$$q = 7.35 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ °C}^{-1} \times (98.0-21.0) \text{ °C}$$
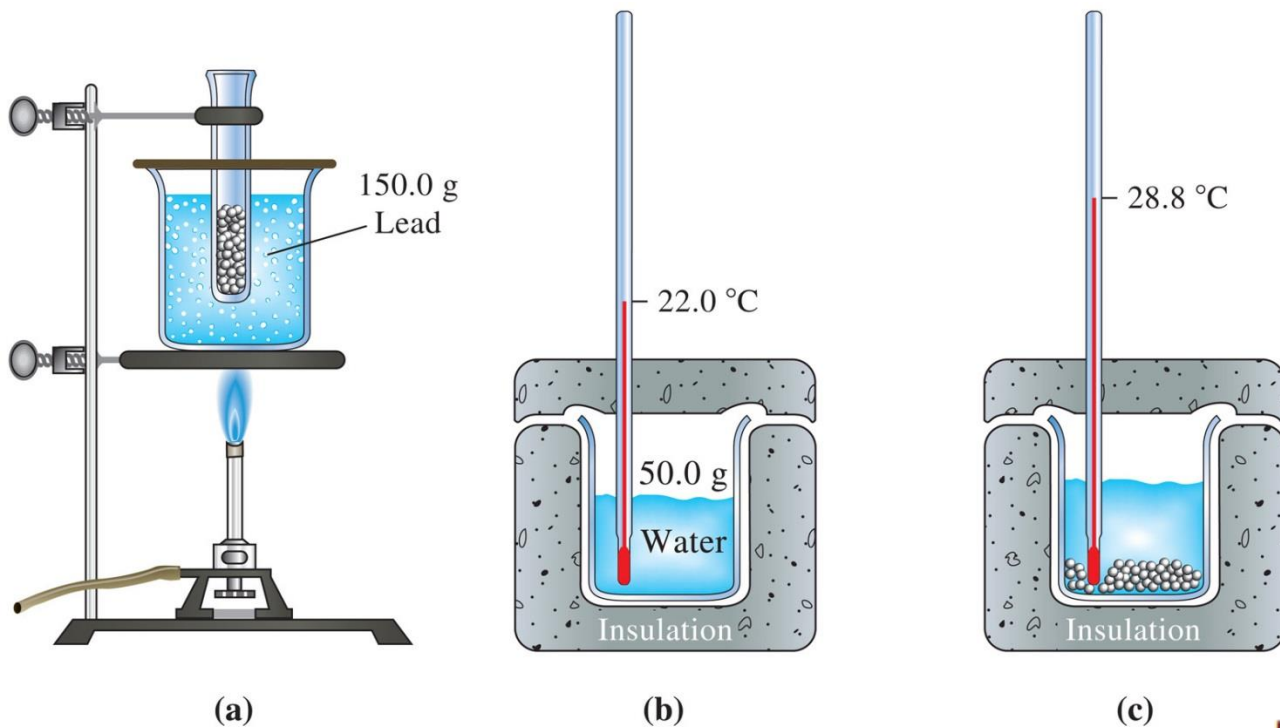
$$q = 2.36 \times 10^3 \text{ J}$$

# Conservation of Energy

♦ In interactions between a system and its surroundings the total energy remains *constant— energy is neither created nor destroyed.*

$$q_{system} + q_{surroundings} = 0$$

♦ Thus, heat gained by a system is lost by its surroundings, and vice versa.

$$q_{system} = -q_{surroundings}$$

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# Determination of Specific Heat



(a)  (b)  (c)

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150.0 g Lead

22.0 °C

50.0 g Water

Insulation

28.8 °C

Insulation

$$q_{lead} = q_{system}$$

$$q_{water} = q_{surroundings}$$

$$q_{lead} = -q_{water}$$

**Determining the specific heat of lead—Example 7-2 illustrated**
(a) A 150.0 g sample of lead is heated to the temperature of boiling water (100.0 °C). (b) A 50.0 g sample of water is added to a thermally insulated beaker, and its temperature is found to be 22.0 °C. (c) The hot lead is dumped into the cold water, and the temperature of the final lead–water mixture is 28.8 °C.

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# EXAMPLE 7-2

**Determining Specific Heat from Experimental Data.** Use the data presented on the last slide to calculate the specific heat of lead.

$$q_{lead} = -q_{water}$$

$$q_{water} = mc\Delta T = (50.0 \text{ g})(4.184 \text{ J/g °C})(28.8 - 22.0)°C$$

$$q_{water} = 1.4 \times 10^3 \text{ J}$$

$$q_{lead} = -1.4 \times 10^3 \text{ J} = mc\Delta T = (150.0 \text{ g})(c_{lead})(28.8 - 100.0)°C$$

$$c_{lead} = 0.13 \text{ Jg}^{-1}°C^{-1}$$

# 7-3 Heats of Reaction and Calorimetry

♦ Chemical energy.

- Contributes to the internal energy of a system.

♦ Heat of reaction, $q_{rxn}$.

- The quantity of heat exchanged between a system and its surroundings when a chemical reaction occurs within the system, at *constant temperature*.

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# Heats of Reaction

♦ Exothermic reactions.

- Produces heat, $q_{rxn} < 0$.

♦ Endothermic reactions.

- Consumes heat, $q_{rxn} > 0$.

♦ Calorimeter

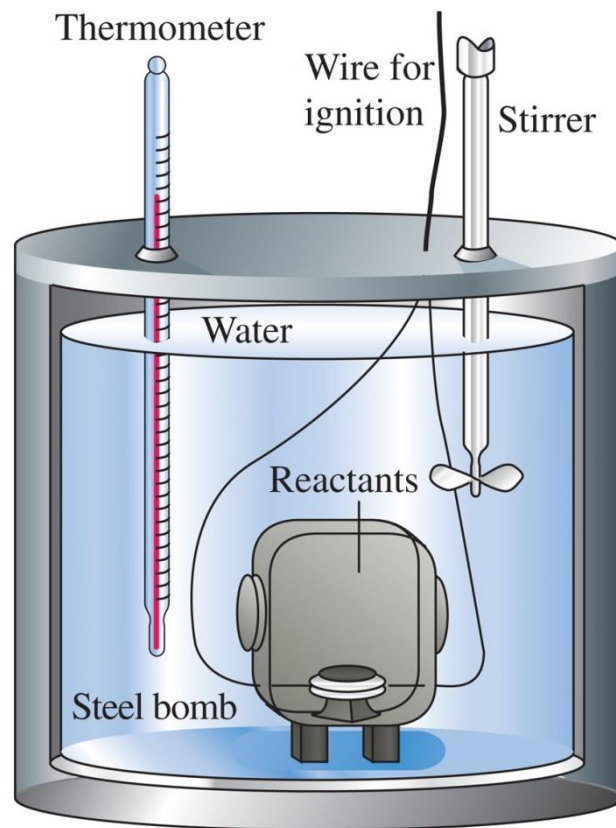- A device for measuring quantities of heat.



(a)



(b)

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# Bomb Calorimeter

$$q_{rxn} = -q_{cal}$$

$$q_{cal} = q_{\text{bomb}} + q_{\text{water}} + q_{\text{wires}} + \ldots$$

*Define the heat capacity of the calorimeter:*

$$q_{cal} = \sum_{\text{all i}} m_i c_i \Delta T = C \Delta T$$



Thermometer

Wire for ignition

Stirrer

Water

Reactants

Steel bomb

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# EXAMPLE 7-3

**Using Bomb Calorimetry Data to Determine a Heat of Reaction.** The combustion of 1.010 g sucrose, in a bomb calorimeter, causes the temperature to rise from 24.92 to 28.33°C. The heat capacity of the calorimeter assembly is 4.90 kJ/°C. What is the heat of combustion of sucrose, expressed in kJ/mol $C_{12}H_{22}O_{11}$?

# EXAMPLE 7-3

*Calculate q*<sub>*calorimeter*</sub>:

$$q_{cal} = C\Delta T = (4.90 \text{ kJ/°C})(28.33\text{-}24.92)\text{°C} = (4.90)(3.41) \text{ kJ}$$

$$= 16.7 \text{ kJ}$$

*Calculate q*<sub>*rxn*</sub>:

$$q_{rxn} = -q_{cal} = -16.7 \text{ kJ} \quad \textit{per 1.010 g}$$

# EXAMPLE 7-3

*Calculate $q_{rxn}$ in the required units:*

$$q_{rxn} = -q_{cal} = \frac{-16.7 \text{ kJ}}{1.010 \text{ g}} = \text{-16.5 kJ/g}$$

$$q_{rxn} = \text{-16.5 kJ/g} \; \frac{343.3 \text{ g}}{1.00 \text{ mol}}$$

$$= \text{-5.65} \times 10^3 \text{ kJ/mol} \qquad \text{(a)}$$

# Coffee Cup Calorimeter
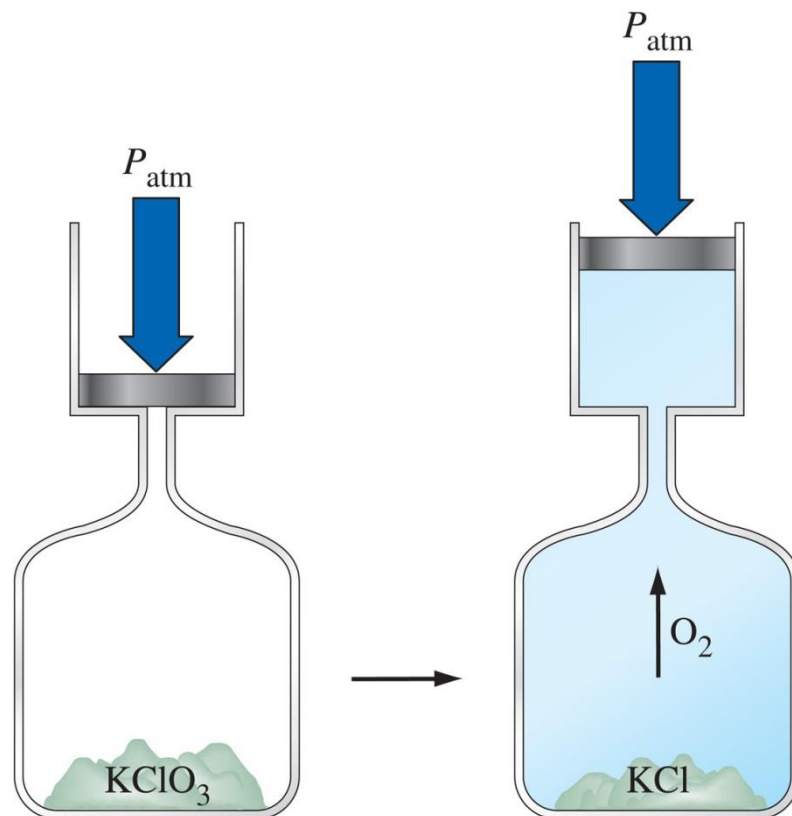
♦ A simple calorimeter.

- Well insulated and therefore *isolated*.

- Measure temperature change.

$$q_{rxn} = -q_{cal}$$

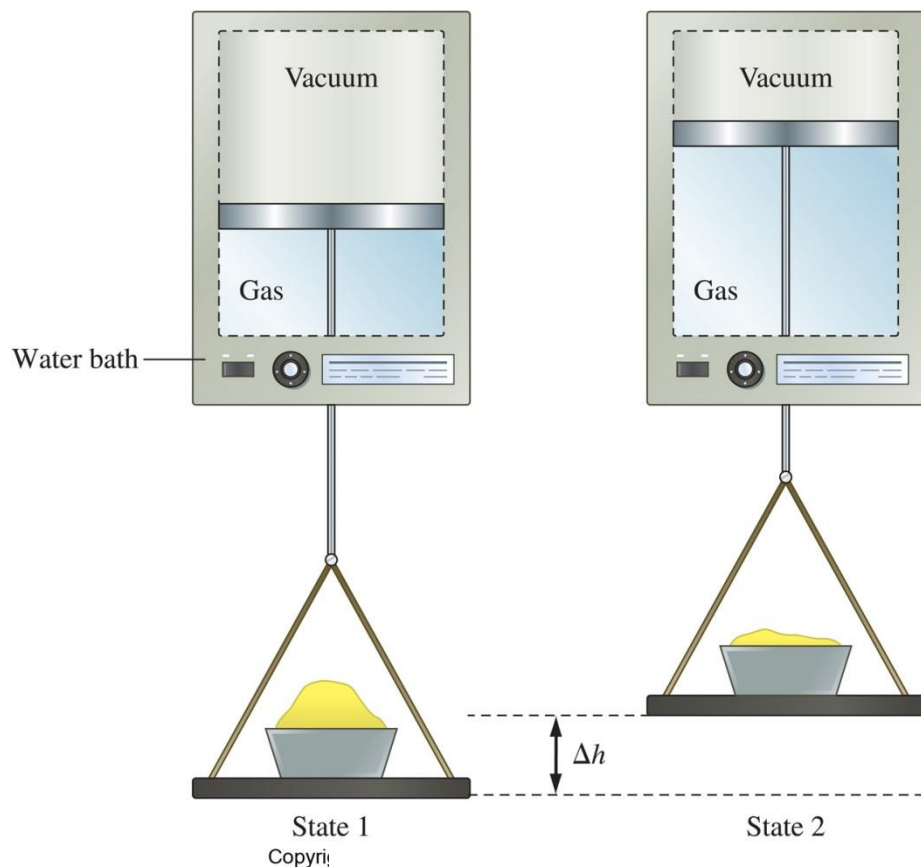General Chemistry: Chapter 7                    Prentice-Hall © 2007

# 7-4 Work

◆ Heat effects generally accompany chemical reactions. In some reactions, work is also involved- that is, the system may do work on its surroundings or vice versa.

◆ Work involved in the expansion or compression of gases is called **pressure-volume work**.

$P_{atm}$

$P_{atm}$

$P_{atm}$

$O_2$

KClO$_3$

KCl

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# Pressure Volume Work

$$\text{work } (w) = \text{force } (M \times g) \times \text{distance } (\Delta h) = -M \times g \times \Delta h$$



Vacuum

Vacuum

Gas

Gas

Water bath

$\Delta h$

State 1

State 2

Copyri

$$w = F \times d$$

$$= (m \times g) \times \Delta h$$

$$= \frac{(m \times g)}{A} \times \Delta h \times A$$

$$= P\Delta V$$

$$w = -P_{ext}\Delta V$$

# EXAMPLE 7-5

**Calculating Pressure-Volume Work.** Suppose the gas in the previous figure is 0.100 mol He at 298 K and the each mass in the figure corresponds to an external pressure of 1.20 atm. How much work, in Joules, is associated with its expansion at constant pressure.

*Assume an ideal gas and calculate the volume change:*

$V_i = nRT/P$

$\quad = (0.100 \text{ mol})(0.08201 \text{ L atm mol}^{-1} \text{ K}^{-1})(298K)/(2.40 \text{ atm})$

$\quad = 1.02 \text{ L}$

$V_f = 2.04 \text{ L}$

$\Delta V = 2.04 \text{ L-}1.02 \text{ L} = 1.02 \text{ L}$

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# EXAMPLE 7-5

*Calculate the work done by the system:*

w = -PΔV

$\qquad$ = -(1.20 atm)(1.02 L)( $\dfrac{\text{-101 J}}{\text{1 L atm}}$ )

$\qquad$ = -1.24 × 10$^2$ J

*Hint: If you use pressure in kPa you get Joules directly.*

<u>**A negative value signifies that work is done ON the surroundings**</u>

*Where did the conversion factor come from?*

Compare two versions of the gas constant and calculate.

8.3145 J/mol K ≡ 0.082057 L atm/mol K

1 ≡ 101.33 J/L atm

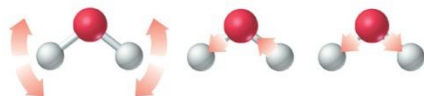# 7-5 The First Law of Thermodynamics

◆ Internal Energy, U.

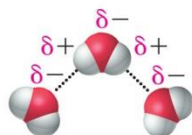  ● Total energy (potential and kinetic) in a system.



Translational

Rotational

Vibrational

Electrostatic
(Intermolecular attractions)

• Translational kinetic energy.

• Molecular rotation.

• Bond vibration.

• Intermolecular attractions.

• Chemical bonds.

• Electrons.

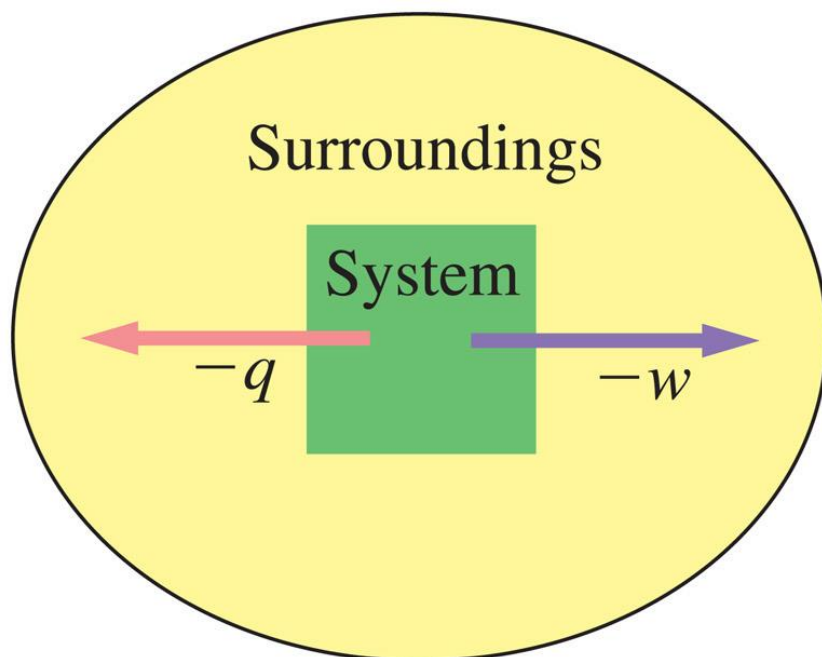General Chemistry: Chapter 7         Prentice-Hall © 2007

# First Law of Thermodynamics

♦ A system contains *only* internal energy.

  • A system does not contain heat or work.

  • These only occur during a *change* in the system.
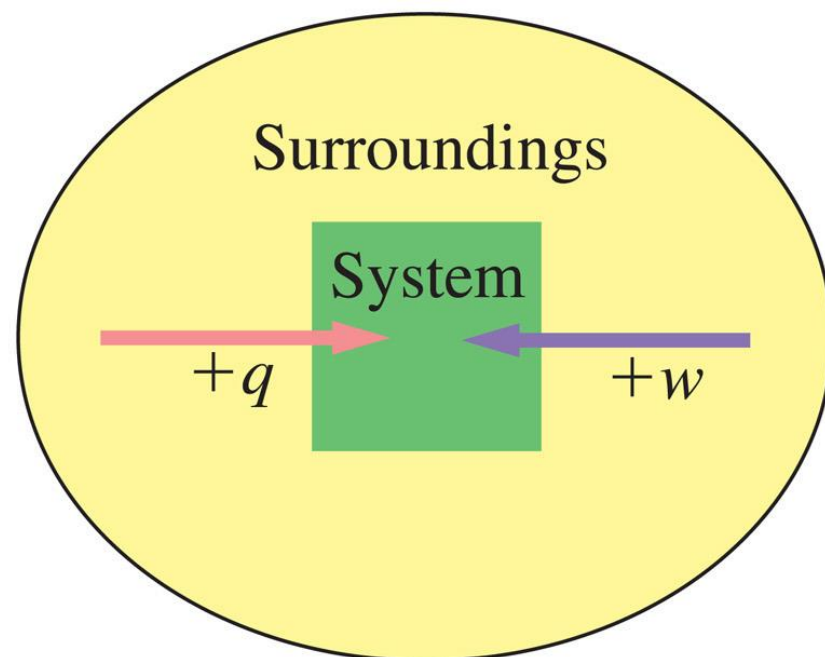
$$\Delta U = q + w$$

♦ Law of Conservation of Energy

  • The energy of an isolated system is constant

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# First Law of Thermodynamics



**Any energy *leaving* the system carries a *negative* sign.**

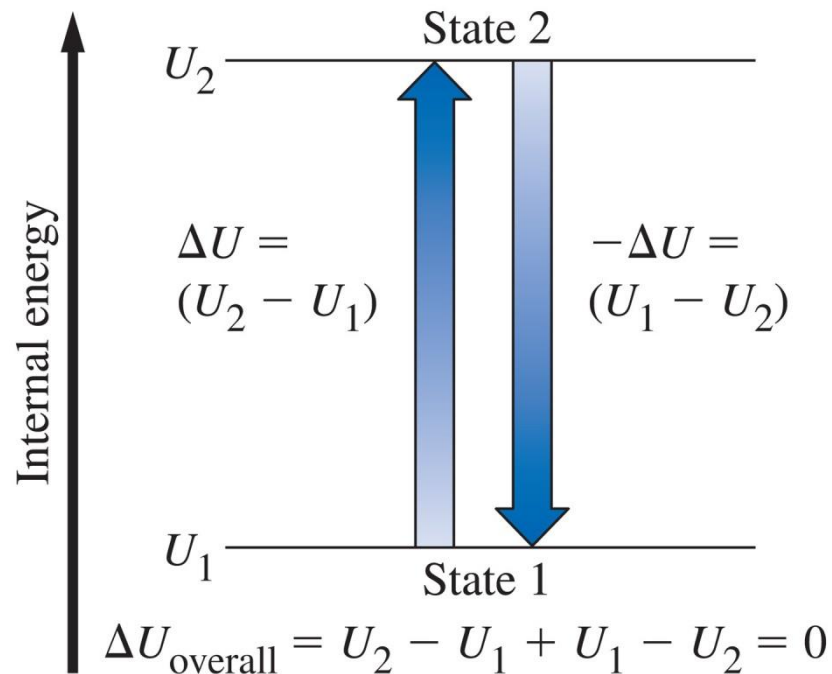**Any energy *entering* the system carries a *positive* sign.**

$$\Delta U = q + w$$

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# Functions of State

◆ Any property that has a unique value for a specified state of a system is said to be a State Function.

- ○ Water at 293.15 K and 1.00 atm is in a specified state.
- ○ d = 0.99820 g/mL
- ○ This density is a unique function of the state.
- ○ It does not matter *how* the state was established.

# Functions of State

♦ U is a function of state.

  • Not easily measured.

♦ ΔU has a unique value between two states.

  • Is easily measured.



State 2

$U_2$ ———

$\Delta U = (U_2 - U_1)$

$-\Delta U = (U_1 - U_2)$

Internal energy

$U_1$ ———

State 1

$\Delta U_{overall} = U_2 - U_1 + U_1 - U_2 = 0$

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# Path Dependent Functions

♦ Changes in heat and work are not functions of state.

- Remember example 7-5, $w = -1.24 \times 10^2$ J in a one step expansion of gas:

- Consider 2.40 atm to 1.80 atm and finally to 1.20 atm.
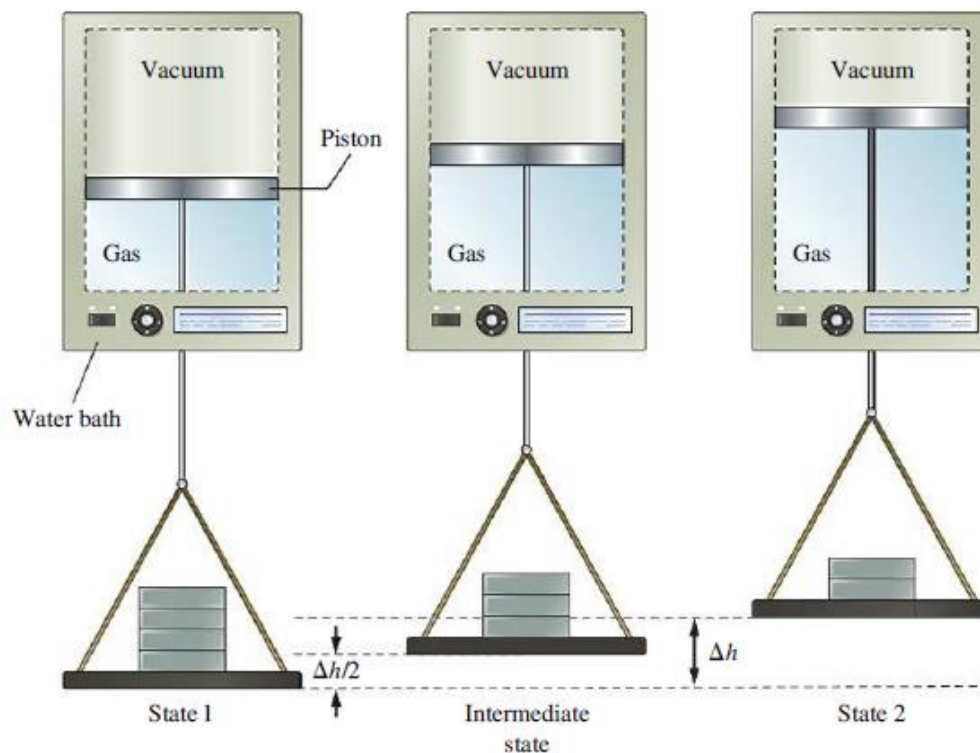
# 7-6 Heats of Reaction: $\Delta U$ and $\Delta H$

Reactants $\rightarrow$ Products

$$U_i \qquad\qquad U_f$$

$$\Delta U = U_f - U_i$$

$$\Delta U = q_{rxn} + w$$

*In a system at constant volume:*

$$\Delta U = q_{rxn} + 0 = q_{rxn} = q_v$$

The heat of reaction measured in a bomb calorimeter is equal to $\Delta U$.

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# Heats of Reaction

$$q_V = q_P + w$$

We know that $w = -P\Delta V$ and $\Delta U = q_P$, therefore:

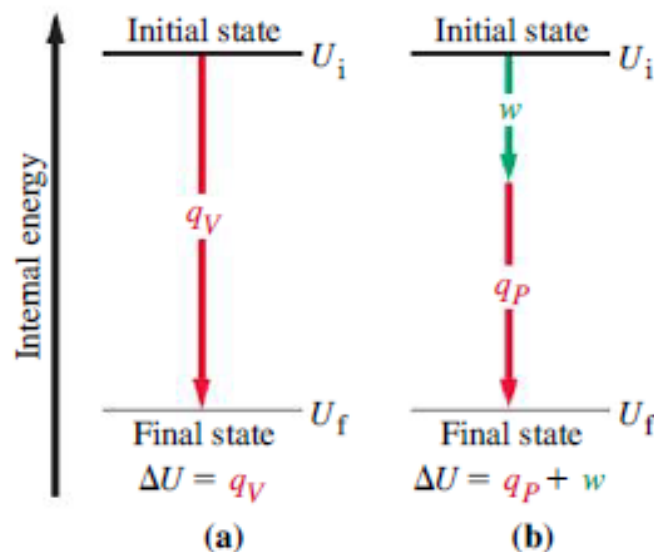$$\Delta U = q_P - P\Delta V$$

$$q_P = \Delta U + P\Delta V$$

These are all state functions, so define a new function.

Let $\qquad\qquad H = U + PV$

Then $\qquad\qquad \Delta H = H_f - H_i = \Delta U + \Delta PV$

If we work at constant pressure and temperature:

$$\Delta H = \Delta U + P\Delta V = q_P$$

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# Changes of State of Matter

*Molar enthalpy of vaporization:* The heat required to vaporize a fixed quantity of liquid is called the enthalpy (or heat) of vaporization. Usually the fixed quantity of liquid chosen is one mole, and we can call this quantity the *molar enthalpy of vaporization*. For example,

$$H_2O\ (l) \rightarrow H_2O(g) \qquad \Delta H = 44.0 \text{ kJ at 298 K}$$

*Molar enthalpy of fusion:* We described the melting of a solid in a similar fashion. The energy requirement in this case is called the enthalpy (or heat) of fusion. For the melting of one mole of ice, we can write

$$H_2O\ (s) \rightarrow H_2O(l) \qquad \Delta H = 6.01 \text{ kJ at 273.15 K}$$

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# EXAMPLE 7-8

**Enthalpy Changes Accompanying Changes in States of Matter.** Calculate $\Delta H$ for the process in which 50.0 g of water is converted from liquid at 10.0°C to vapor at 25.0°C.

*Break the problem into two steps:* Raise the temperature of the liquid first then completely vaporize it. The total enthalpy change is the sum of the changes in each step.
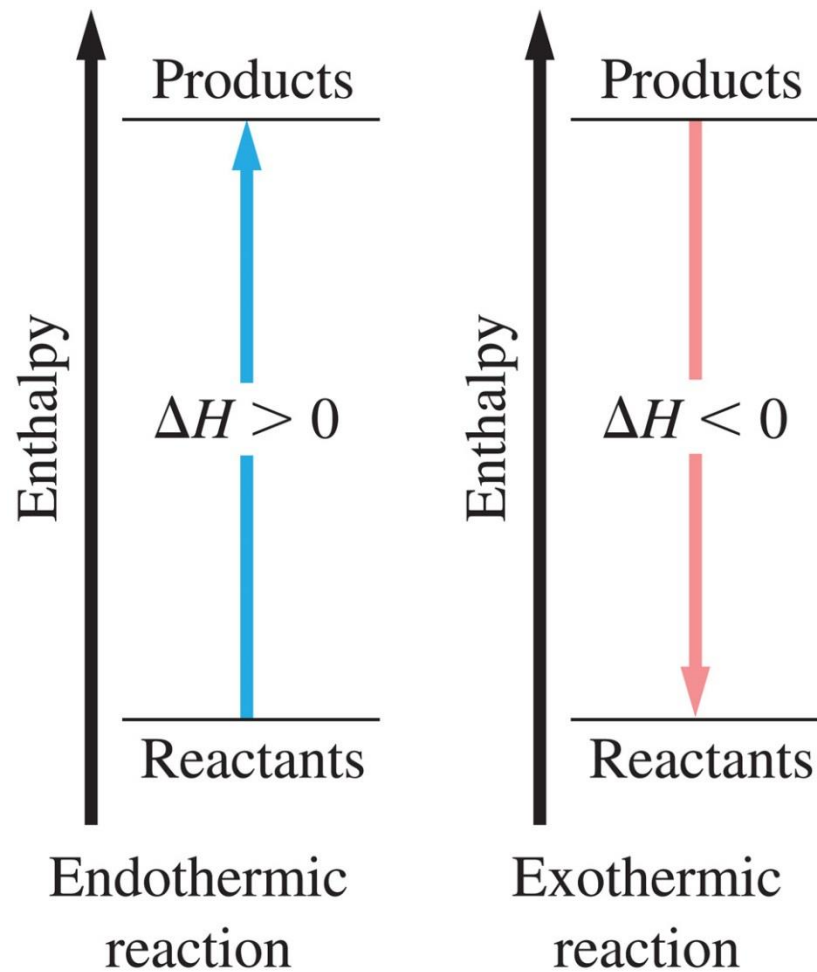
*Set up the equation and calculate:*

$$q_P = mc_{H_2O}\Delta T + n\Delta H_{vap}$$

$$= (50.0 \text{ g})(4.184 \text{ J/g °C})(25.0\text{-}10.0)°\text{C} + \frac{50.0 \text{ g}}{18.0 \text{ g/mol}} 44.0 \text{ kJ/mol}$$

$$= 3.14 \text{ kJ} + 122 \text{ kJ} = 125 \text{ kJ}$$

# Standard States and Standard Enthalpy Changes

♦ Define a particular state as a standard state.

♦ Standard enthalpy of reaction, $\Delta H°$

- The enthalpy change of a reaction in which all reactants and products are in their standard states.

♦ Standard State

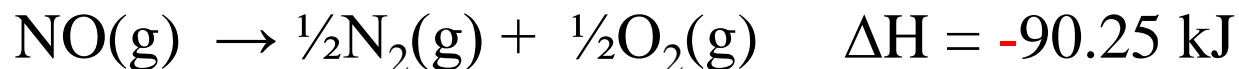- The pure element or compound at a pressure of 1 bar and at the temperature of interest.

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# Enthalpy Diagrams

$N_2(g) + O_2(g) \rightarrow 2\,NO(g)\ \Delta H = +180.50\ kJ$



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# 7-7 Indirect Determination of ΔH: Hess's Law

♦ ΔH is an extensive property.

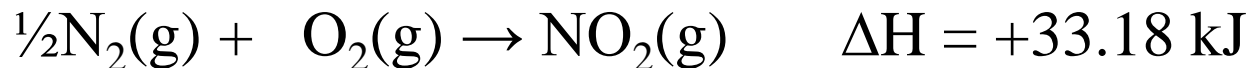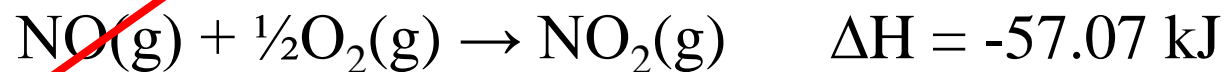- Enthalpy change is directly proportional to the amount of substance in a system.

$$N_2(g) + O_2(g) \rightarrow 2\ NO(g) \qquad \Delta H = +180.50\ kJ$$

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta H = +90.25\ kJ$$

♦ ΔH changes sign when a process is reversed

$$NO(g) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H = -90.25\ kJ$$

# Hess's Law

♦ Hess's law of constant heat summation

- If a process occurs in stages or steps (even hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.
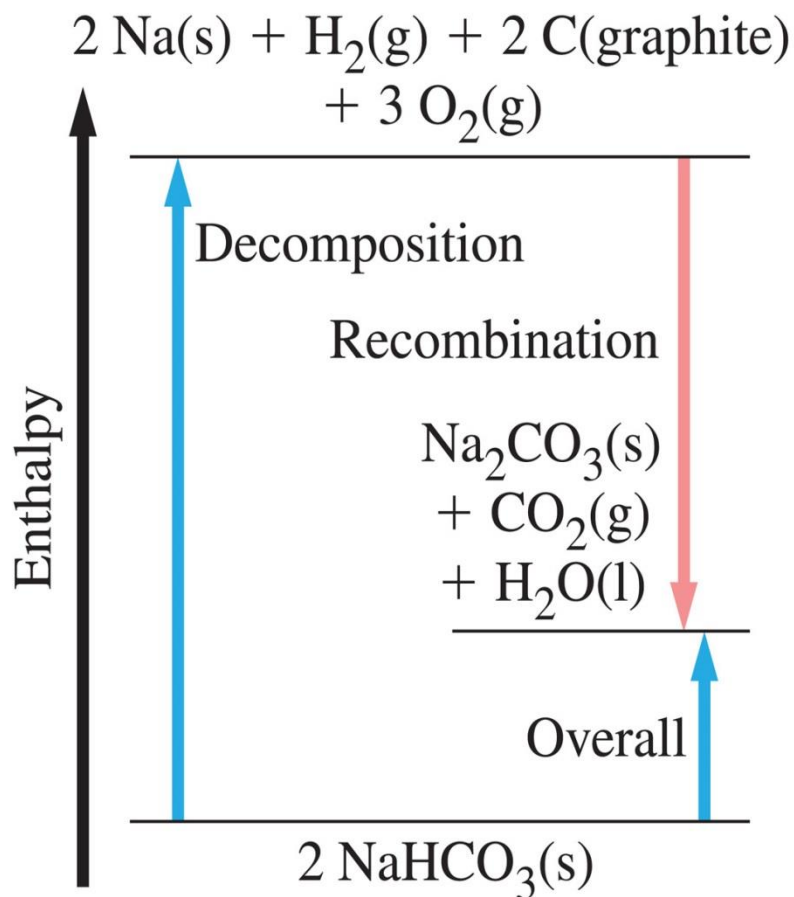
$$½N_2(g) + ½O_2(g) \rightarrow NO(g) \qquad \Delta H = +90.25 \text{ kJ}$$

$$NO(g) + ½O_2(g) \rightarrow NO_2(g) \qquad \Delta H = -57.07 \text{ kJ}$$

---

$$½N_2(g) + \ O_2(g) \rightarrow NO_2(g) \qquad \Delta H = +33.18 \text{ kJ}$$

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# 7-8 Standard Enthalpies of Formation

$\Delta H_f^\circ$

♦ The enthalpy change that occurs in the formation of one mole of a substance in the standard state from the reference forms of the elements in their standard states.

♦ Because the formation of the most stable form of an element from itself is no change at all, the standard enthalpy of formation of a pure element in its reference state is 0.
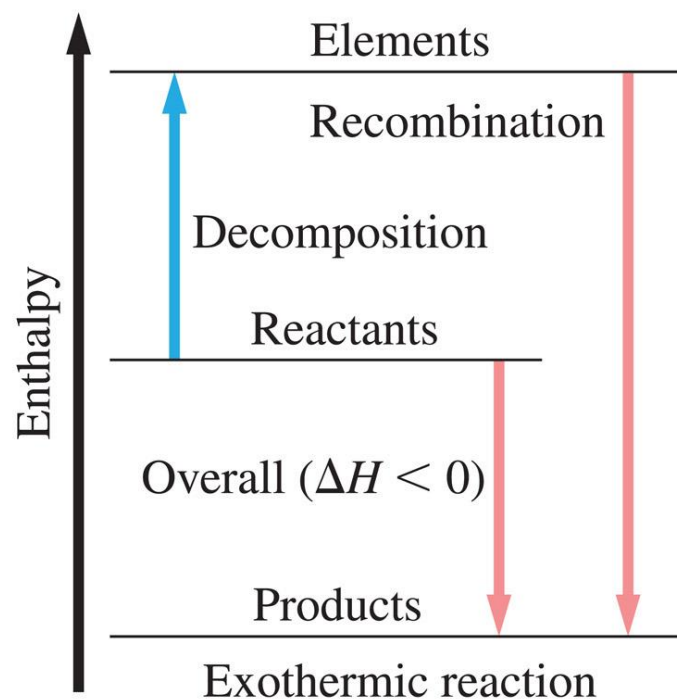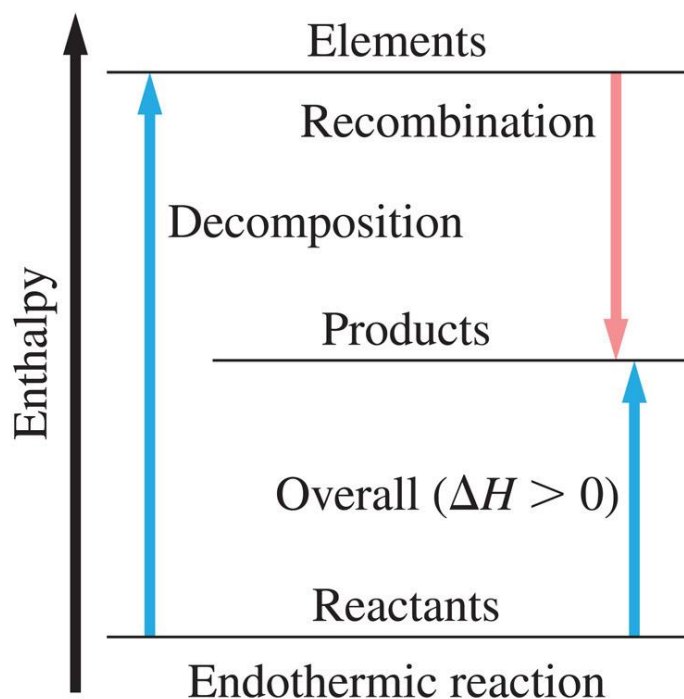
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2 Na(s) + H₂(g) + 2 C(graphite) + 3 O₂(g)

Decomposition

Recombination

Na₂CO₃(s) + CO₂(g) + H₂O(l)

Enthalpy

Overall

2 NaHCO₃(s)

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$$\Delta H_{overall} = -2\Delta H^{\circ}_{f\ NaHCO_3} + \Delta H^{\circ}_{f\ Na_2CO_3}$$
$$+ \Delta H^{\circ}_{f\ CO_2} + \Delta H^{\circ}_{f\ H_2O}$$

# Enthalpy of Reaction

$$\Delta H_{rxn} = \Sigma \Delta H_{f\ products}^{\circ} - \Sigma \Delta H_{f\ reactants}^{\circ}$$

# EXAMPLE 7-11

Calculate the standard enthalpy of combustion of ethane, $C_2H_6$ a component of natural gas.

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$$
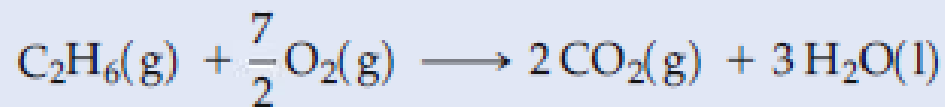
$$\Delta H^\circ = \{2\,mol\,CO_2 \times \Delta H_f^\circ[CO_2(g)] + 3\,mol\,H_2O \times \Delta H_f^\circ[H_2O(l)]\}$$

$$- \{1\,mol\,C_2H_6 \times \Delta H_f^\circ[C_2H_6(g)] + \frac{7}{2}mol\,O_2 \times \Delta H_f^\circ[O_2(g)]\}$$

$$= 2\,mol\,CO_2 \times (-393.5\,kJ/mol\,CO_2) + 3\,mol\,H_2O \times (-285.8\,kJ/mol\,H_2O)$$

$$- 1\,mol\,C_2H_6 \times (-84.7\,kJ/mol\,C_2H_6) - \frac{7}{2}mol\,O_2 \times 0\,kJ/mol\,O_2$$

$$= -787.0\,kJ - 857.4\,kJ + 84.7\,kJ = -1559.7\,kJ$$

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