

Chapter 6

Thermochemistry

# Chapter 6 *Table of Contents*

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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
  - Energy of the universe is constant

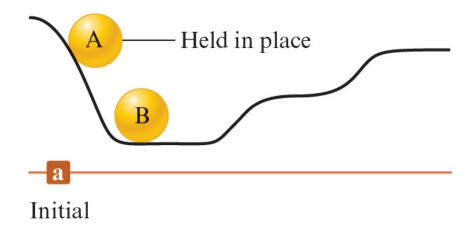
### Classification of Energy

- Potential energy (PE): Energy due to position or composition
  - Can result from attractive and repulsive forces
- Kinetic energy (KE): Energy due to the motion of an object
  - Depends on the mass of the object (m) and its velocity
     (v)

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

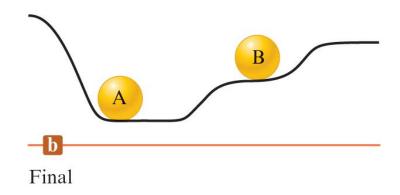
#### Conversion of Energy

Consider the following image:



Because of its higher initial position, ball A has more PE than ball B

#### Conversion of Energy (continued 1)



- PE of A is changed to KE as the ball rolls down the hill
- Part of this KE is then transferred to B, causing it to be raised to a higher final position
  - Thus, PE of B has been increased

#### Conversion of Energy (continued 2)

- Since the final position of B is lower than the original position of A, some of the energy is still unaccounted for
- Part of the original energy stored as PE in A has been transferred through work to B, thereby increasing B's PE

### Methods of Transferring Energy

- Heat: Transfer of energy between two objects due to a temperature difference
  - Temperature is a property that reflects random motion of particles in a substance
- Work: Force acting over a distance

### **Pathway**

- Specific conditions that define the path by which energy is transferred
- Energy change is independent of the pathway
- Work and heat are dependent on the pathway

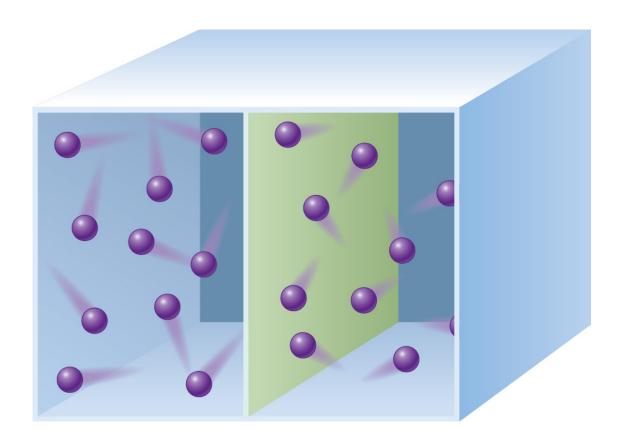
#### Energy as a State Function

- State function (state property): Property that does not depend in any way on the system's past or future
  - Value depends on the characteristics of the present state
  - While transitioning from one state to another, the change in state property is independent of the pathway taken between the two states

#### The Process of Heat

- Energy is always transferred from the hot body to the cold body
  - Temperature is a measure of the average KE of particles in solids, liquids, and gases
  - Energy is transferred as the initially faster particles decrease in motion and the initially slower molecules increase in motion
    - Particles will have the same average KE and thus the same temperature

# Figure 6.2 - Particles at Different Temperatures in Adjoining Chambers



#### Parts of the Universe

- System: Part of the universe on which one wishes to focus his/her attention
  - Example System can be defined as the reactants and products of a reaction
- Surroundings: Include everything else in the universe
  - Example Surroundings consist of anything else other than the reactants and products

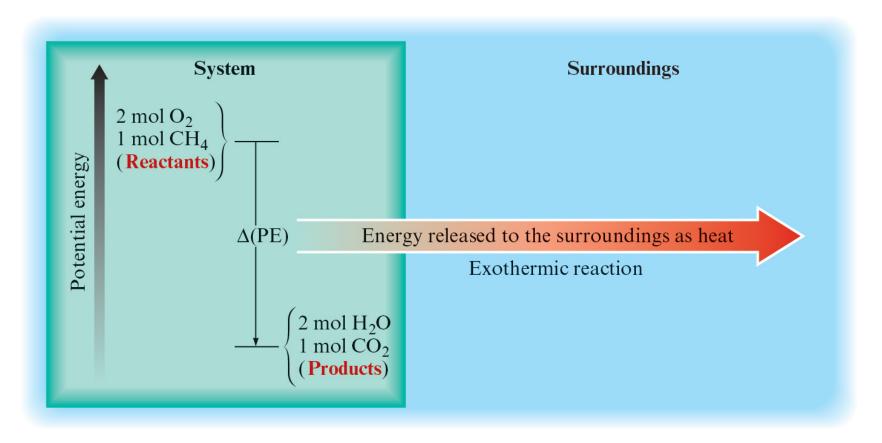
### Types of Reactions

- Exothermic: Reaction that results in the evolution of heat
  - Energy flows out of the system
  - Example Combustion of methane
- Endothermic: Reaction that results in the absorption of energy from the surroundings
  - Heat flows into a system
  - Example Formation of nitric oxide

#### **Reaction Mechanism**

- Energy gained by the surroundings must be equal to the energy lost by the system
- Exothermic reactions
  - PE stored in chemical bonds is converted to thermal energy via heat
    - Bonds in the products are stronger than those of the reactants
  - Net result Quantity of energy Δ(PE) is transferred to the surroundings through heat

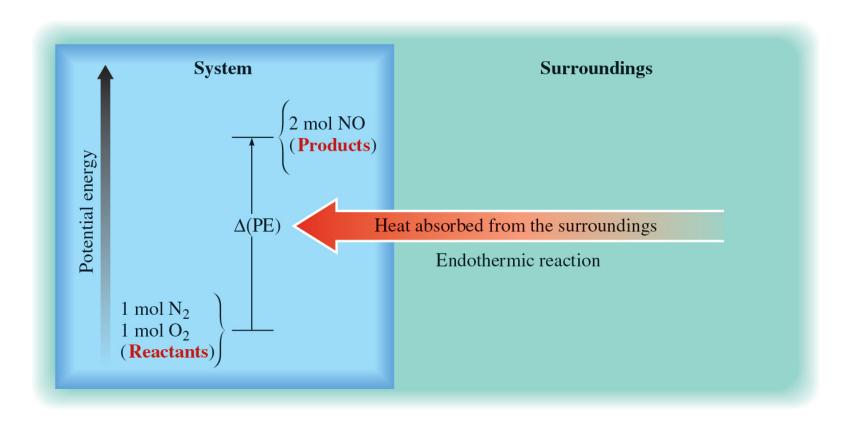
**Figure 6.3** - Energy Diagram for the Combustion of Methane, an Exothermic Process



#### Reaction Mechanism (continued)

- Endothermic reactions
  - Energy that flows into the system as heat is used to increase the PE of the system
  - Products have higher PE than reactants

**Figure 6.4** - Energy Diagram for the Formation of Nitric Oxide, an Endothermic Process



### Thermodynamics

- Study of energy and its interconversions
- First law of thermodynamics: Energy of the universe is constant
  - Known as the law of conservation of energy

### Internal Energy (E)

- Sum of kinetic and potential energies of all particles in the system
- E of a system can be changed by flow of work, heat, or both

$$\Delta E = q + w$$

- lacktriangle  $\Delta E$  Change in the system's internal energy
- *q* Heat
- w Work

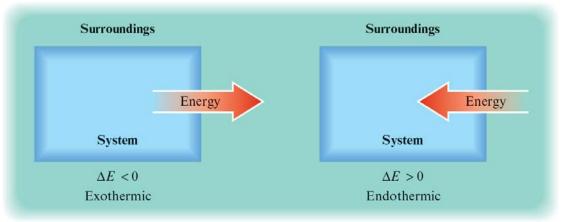
### Parts of Thermodynamic Quantities

- Number Gives the magnitude of change
- Sign Indicates the direction of flow and reflects the system's point of view
  - In an endothermic system, q = +x
    - Positive sign indicates that the system's energy is increasing
  - In an exothermic system, q = -x
    - Negative sign indicates that the system's energy is decreasing

#### Parts of Thermodynamic Quantities (continued)

- Conventions that apply to the flow of work
  - When a system does work on the surroundings, w is negative
  - When the surroundings do work on the system, w is

positive



### Interactive Example 6.1 - Internal Energy

 Calculate ΔE for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system

#### Interactive Example 6.1 - Solution

We use the following equation:

$$\Delta E = q + w$$

- q = +15.6 kJ, since the process is endothermic
- w = + 1.4 kJ, since work is done on the system

$$\Delta E = 15.6 \text{ kJ} + 1.4 \text{ kJ} = 17.0 \text{ kJ}$$

Thus, the system has gained 17.0 kJ of energy

#### Work

- Types of work associated with a chemical process
  - Work done by a gas through expansion
  - Work done to a gas through compression
- Example
  - In an automobile engine, heat from the combustion of gasoline expands the gases in the cylinder to push back the piston
    - This motion is then translated to the motion of the car

### Deriving the Equation for Work

- Consider a gas confined to a cylindrical container with a movable piston
  - F is the force acting on the piston of area A
  - Pressure is defined as force per unit area

$$P = \frac{F}{A}$$

#### Deriving the Equation for Work (continued 1)

- Work is defined as force applied over a distance
  - If the piston moves a distance of  $\Delta h$ , work done is

Work = force 
$$\times$$
 distance =  $F \times \Delta h$ 

• Since P = F/A or  $F = P \times A$ ,

Work = 
$$F \times \Delta h = P \times A \times \Delta h$$

 Volume of the cylinder equals the area of the piston times the height of the cylinder

#### Deriving the Equation for Work (continued 2)

• Change in volume  $\Delta V$  resulting from the piston moving a distance  $\Delta h$  is

$$\Delta V = \text{final volume} - \text{initial volume} = A \times \Delta h$$

• Substituting  $\Delta V = A \times \Delta h$  into the expression for work gives the magnitude of the work required to expand a gas  $\Delta V$  against a pressure P

Work = 
$$P \times A \times \Delta h = P \Delta V$$

#### Deriving the Equation for Work (continued 3)

- Since the system is doing work on the surroundings, the sign of work should be negative
  - For an expanding gas,  $\Delta V$  is a positive quantity because the V is increasing

$$w = -P\Delta V$$

• When a gas is compressed,  $\Delta V$  is a negative quantity because V decreases, which makes w a positive quantity

### **Critical Thinking**

- You are calculating  $\Delta E$  in a chemistry problem
  - What if you confuse the system and the surroundings?
    - How would this affect the magnitude of the answer you calculate? The sign?

#### Interactive Example 6.2 - PV Work

 Calculate the work associated with the expansion of a gas from 46 L to 64 L at a constant external pressure of 15 atm

### Interactive Example 6.2 - Solution

For a gas at constant pressure,

$$w = -P\Delta V$$

■ In this case P = 15 atm and  $\Delta V = 64 - 46 = 18$  L

$$w = -15$$
 atm × 18 L = -270 L · atm

- Note that since the gas expands, it does work on its surroundings
- Reality check
  - Energy flows out of the gas, so w is a negative quantity

Interactive Example 6.3 - Internal Energy, Heat, and Work

- A balloon is being inflated to its full extent by heating the air inside it
  - In the final stages of this process, the volume of the balloon changes from  $4.00 \times 10^6$  L to  $4.50 \times 10^6$  L by the addition of  $1.3 \times 10^8$  J of energy as heat
  - Assuming that the balloon expands against a constant pressure of 1.0 atm, calculate  $\Delta E$  for the process
    - To convert between L · atm and J, use 1 L · atm = 101.3 J

### Interactive Example 6.3 - Solution

- Where are we going?
  - To calculate ΔE
  - What do we know?

$$V_1 = 4.00 \times 10^6 \, \text{L}$$

$$q = +1.3 \times 10^8 \, J$$

• 
$$P = 1.0$$
 atm

$$V_2 = 4.50 \times 10^6 \, \text{L}$$

#### Interactive Example 6.3 - Solution (continued 1)

What do we need?

$$\Delta E = q + w$$

- How do we get there?
  - What is the work done on the gas?

$$w = -P\Delta V$$

• What is  $\Delta V$ ?

$$\Delta V = V_2 - V_1 = 4.50 \times 10^6 \text{ L} - 4.00 \times 10^6 \text{ L} = 5.0 \times 10^5 \text{ L}$$

### Interactive Example 6.3 - Solution (continued 2)

What is the work?

$$w = -P\Delta V = -1.0 \text{ atm} \times 5.0 \times 10^5 \text{ L} = -5.0 \times 10^5 \text{ L} \cdot \text{atm}$$

- The negative sign makes sense because the gas is expanding and doing work on the surroundings
- To calculate  $\Delta E$ , we must sum q and w
  - However, since q is given in units of J and w is given in units of L · atm, we must change the work to units of joules

$$w = -5.0 \times 10^5 \text{ Latm} \times \frac{101.3 \text{ J}}{\text{Latm}} = -5.1 \times 10^7 \text{ J}$$

### Section 6.1 The Nature of Energy

#### Interactive Example 6.3 - Solution (continued 3)

Then,

$$\Delta E = q + w = (+1.3 \times 10^8 \text{ J}) + (-5.1 \times 10^7 \text{ J}) = 8 \times 10^7 \text{ J}$$

- Reality check
  - Since more energy is added through heating than the gas expends doing work, there is a net increase in the internal energy of the gas in the balloon
    - Hence ΔE is positive

# Section 6.1 The Nature of Energy

#### example

- Label the following process as exothermic or endothermic: Ice increases in temperature when you touch it
  - a. Exothermic
  - b. Endothermic

# Section 6.1 The Nature of Energy

#### Join In (6)

- Gas A<sub>2</sub> reacts with gas B<sub>2</sub> to form gas AB
  - The bond energy of AB is much greater than the bond energy of either A<sub>2</sub> or B<sub>2</sub>
  - Is the reaction for the formation of AB exothermic or endothermic?
    - a. Exothermic
    - b. Endothermic

#### Enthalpy (H)

A state function that is defined as:

$$H = E + PV$$

- E Internal energy of the system
- P Pressure of the system
- V Volume of the system

#### Change in Enthalpy ( $\Delta H$ )

For a process carried out at constant pressure and where the only work allowed is that from a volume change:

$$\Delta H = q_P$$

- $q_p$  is the heat at constant pressure
- At constant pressure, the change in enthalpy  $\Delta H$  of the system is equal to the energy flow as heat

#### Enthalpy and PV Work

For a chemical reaction, the enthalpy change is given by the following equation:

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

- When  $H_{\text{products}} > H_{\text{reactants}}$ ,  $\Delta H$  is positive
  - Heat is absorbed by the system, and the reaction is endothermic
- When  $H_{\text{products}} < H_{\text{reactants}}$ ,  $\Delta H$  is negative
  - Overall decrease in enthalpy is achieved by the generation of heat, and the reaction is exothermic

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#### Interactive Example 6.4 - Enthalpy

- When 1 mole of methane (CH<sub>4</sub>) is burned at constant pressure, 890 kJ of energy is released as heat
  - Calculate  $\Delta H$  for a process in which a 5.8-g sample of methane is burned at constant pressure

#### Interactive Example 6.4 - Solution

- Where are we going?
  - To calculate ΔH
  - What do we know?
    - $q_P = \Delta H = -890 \text{ kJ/mol CH}_4$
    - Mass =  $5.8 \text{ g CH}_{4}$
    - Molar mass  $CH_4 = 16.04 g$

#### Interactive Example 6.4 - Solution (continued 1)

- How do we get there?
  - What are the moles of CH<sub>4</sub> burned?

$$5.8 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} = 0.36 \text{ mol CH}_4$$

• What is  $\Delta H$ ?

$$\Delta H = 0.36 \text{ mol-eH}_4 \times \frac{-890 \text{ kJ}}{\text{mol-eH}_4} = -320 \text{ kJ}$$

#### Interactive Example 6.4 - Solution (continued 2)

 Thus, when a 5.8-g sample of CH<sub>4</sub> is burned at constant pressure,

$$\Delta H = \text{heat flow} = -320 \text{ kJ}$$

- Reality check
  - In this case, a 5.8-g sample of CH<sub>4</sub> is burned
    - Since this amount is smaller than 1 mole, less than 890 kJ
       will be released as heat

#### Exercise

 The overall reaction in a commercial heat pack can be represented as

$$4\text{Fe}(s) + 3\text{O}_{2}(g) \rightarrow 2\text{Fe}_{2}\text{O}_{3}(s)$$
  $\Delta H = -1652 \text{ kJ}$ 

a. How much heat is released when 4.00 moles of iron are reacted with excess  $O_2$ ?

1650 kJ is released

#### Exercise (continued)

b. How much heat is released when 1.00 mole of Fe<sub>2</sub>O<sub>3</sub> is produced?

#### 826 kJ released

b. How much heat is released when 1.00 g iron is reacted with excess  $O_2$ ?

#### 7.39 kJ released

b. How much heat is released when 10.0 g Fe and 2.00 g  $O_2$  are reacted?

34.4 kJ released

#### Calorimetry

- Science of measuring heat
  - Based on observations of temperature change when a body absorbs or discharges energy as heat
- Calorimeter: Device used experimentally to determine the heat associated with a chemical reaction

#### Heat Capacity (C)

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$$

- Specific heat capacity: Energy required to raise the temperature of one gram of a substance by one degree Celsius
  - Units  $J/^{\circ}$  C · g or  $J/K \cdot g$

#### **Table 6.1** - The Specific Heat Capacities of Some Common Substances

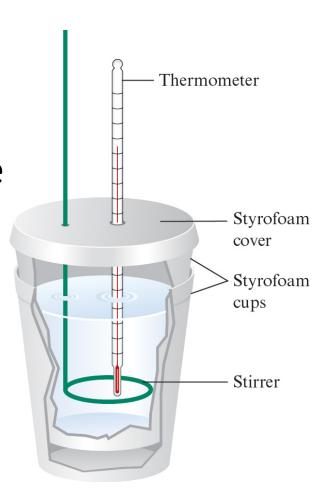
Substance	Specific Heat Capacity (J/°C · g)
$H_2O(I)$	4.18
$H_2O(s)$	2.03
Al(s)	0.89
Fe(s)	0.45
Hg( <i>l</i> )	0.14
C(s)	0.71

#### Heat Capacity (C) (continued)

- Molar heat capacity: Energy required to raise the temperature of one mole of a substance by one degree Celsius
  - Units J/° C · mol or J/K · mol
- Heat capacities of metals are different from that of water
  - It takes less energy to change the temperature of a gram of a metal by 1° C than for a gram of water

#### Coffee-Cup Calorimeter

- Contains two nested Styrofoam cups with a cover through which a stirrer and thermometer can be inserted
  - Outer cup is used to provide extra insulation
  - Inner cup holds the solution in which the reaction occurs



#### **Constant-Pressure Calorimetry**

- Atmospheric pressure remains constant during the process
- Used to determine changes in enthalpy for reactions that occur in solution
  - $\Delta H = q_{\rm P}$

#### Constant-Pressure Calorimetry (continued 1)

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

# Constant-Pressure Calorimetry: Determining Change in Enthalpy for a Neutralization Reaction

Energy (as heat) released by the reaction

- = energy (as heat) absorbed by the solution
- = specific heat capacity ? mass of solution ? increase in temperature
- $= s \times m \times \Delta T$
- When twice the amount of solution has been mixed, twice as much heat would be produced
  - Heat of a reaction is an extensive property
    - Depends directly on the amount of substance

# Interactive Example 6.5 - Constant-Pressure Calorimetry

• When 1.00 L of 1.00 M Ba(NO<sub>3</sub>)<sub>2</sub> solution at 25.0° C is mixed with 1.00 L of 1.00 M Na<sub>2</sub>SO<sub>4</sub> solution at 25.0° C in a calorimeter, the white solid BaSO<sub>4</sub> forms, and the temperature of the mixture increases to 28.1° C

### Interactive Example 6.5 - Constant-Pressure Calorimetry (continued)

- Assume that:
  - The calorimeter absorbs only a negligible quantity of heat
  - The specific heat capacity of the solution is  $4.18 \, \text{J/}^{\circ} \, \, \, \text{C} \cdot \text{g}$
  - The density of the final solution is 1.0 g/mL
- Calculate the enthalpy change per mole of BaSO<sub>4</sub>
   formed

#### Interactive Example 6.5 - Solution

- Where are we going?
  - To calculate ΔH per mole of BaSO<sub>4</sub> formed
  - What do we know?
    - 1.00 L of 1.00 M Ba(NO<sub>3</sub>)<sub>2</sub>
    - 1.00 L of 1.00 M Na<sub>2</sub>SO<sub>4</sub>
    - $T_{\text{initial}} = 25.0^{\circ}$  C and  $T_{\text{final}} = 28.1^{\circ}$  C
    - Heat capacity of solution =  $4.18 \text{ J/}^{\circ} \text{ C} \cdot \text{g}$
    - Density of final solution = 1.0 g/mL

#### Interactive Example 6.5 - Solution (continued 1)

- What do we need?
  - Net ionic equation for the reaction
    - The ions present before any reaction occurs are  $Ba^{2+}$ ,  $NO_3^-$ ,  $Na^+$ , and  $SO_4^{2-}$
    - The Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions are spectator ions, since NaNO<sub>3</sub> is very soluble in water and will not precipitate under these conditions
    - The net ionic equation for the reaction is:

$$\operatorname{Ba}^{2+}(aq) + \operatorname{SO}_{4}^{2-}(aq) \to \operatorname{BaSO}_{4}(s)$$

#### Interactive Example 6.5 - Solution (continued 2)

- How do we get there?
  - What is  $\Delta H$ ?
    - Since the temperature increases, formation of solid BaSO<sub>4</sub> must be exothermic;  $\Delta H$  is negative

#### Heat evolved by the reaction

- = heat absorbed by the solution
- = specific heat capacity? mass of solution? increase in temperature

#### Interactive Example 6.5 - Solution (continued 3)

What is the mass of the final solution?

Mass of solution = 2.00 
$$\cancel{L}$$
 ×  $\frac{1000 \cancel{mL}}{1 \cancel{L}}$  ×  $\frac{1.0 \cancel{g}}{\cancel{mL}}$  = 2.0 × 10<sup>3</sup> g

• What is the temperature increase?

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 28.1^{\circ}\text{C} - 25.0^{\circ}\text{C} = 3.1^{\circ}\text{C}$$

• How much heat is evolved by the reaction?

Heat evolved = 
$$(4.18 \text{ J/°} \cancel{\cancel{C}} \cdot \cancel{\cancel{g}})(2.0 \times 10^3 \cancel{\cancel{g}})(3.1 \circ \cancel{\cancel{C}}) = 2.6 \times 10^4 \text{ J}$$

#### Interactive Example 6.5 - Solution (continued 4)

Thus,

$$q = q_P = \Delta H = -2.6 \times 10^4 \text{ J}$$

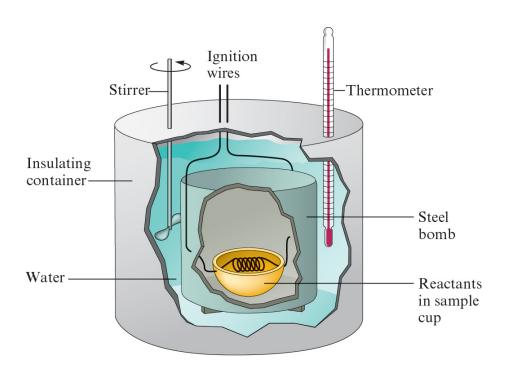
- What is ΔH per mole of BaSO<sub>4</sub> formed?
  - Since 1.0 L of 1.0 M Ba(NO<sub>3</sub>)<sub>2</sub> contains 1 mole of Ba<sup>2+</sup> ions and 1.0 L of 1.0 M Na<sub>2</sub>SO<sub>4</sub> contains 1.0 mole of SO<sub>4</sub><sup>2-</sup> ions, 1.0 mole of solid BaSO<sub>4</sub> is formed in this experiment
  - Thus the enthalpy change per mole of BaSO₄ formed is

$$\Delta H = -2.6 \times 10^4 \text{ J/mol} = -26 \text{ kJ/mol}$$

#### **Constant-Volume Calorimetry**

- Used to study the energy changes in reactions under conditions of constant volume
  - No work is done because V must change for pressure– volume work to be performed
- Device used Bomb calorimeter
  - Weighed reactants are placed within a rigid steel container and ignited
  - Energy change is determined by the increase in temperature of the water and other calorimeter parts

#### Figure 6.7 - A Bomb Calorimeter





#### Constant-Volume Calorimetry (continued 1)

- For a constant-volume process,  $\Delta V = 0$ 
  - Therefore,  $w = -P\Delta V = 0$

$$\Delta E = q + w = q = q_V$$
 (constant volume)

- Energy released by the reaction
  - = temperature increase × energy required to change the temperature by 1° C
  - $= \Delta T \times$  heat capacity of calorimeter

#### Constant-Volume Calorimetry (continued 2)

• Since no work is done in this case,  $\Delta E$  is equal to the heat

$$\Delta E = q + w = q$$
 since  $w = 0$ 

#### Example 6.6 - Constant-Volume Calorimetry

- It has been suggested that hydrogen gas obtained by the decomposition of water might be a substitute for natural gas (principally methane)
  - To compare the energies of combustion of these fuels, the following experiment was carried out using a bomb calorimeter with a heat capacity of 11.3 kJ/° C

#### Example 6.6 - Constant-Volume Calorimetry (continued)

- When a 1.50-g sample of methane gas was burned with excess oxygen in the calorimeter, the temperature increased by 7.3° C
- When a 1.15-g sample of hydrogen gas was burned with excess oxygen, the temperature increase was 14.3° C
  - Compare the energies of combustion (per gram) for hydrogen and methane

#### Example 6.6 - Solution

- Where are we going?
  - To calculate ΔH of combustion per gram for H<sub>2</sub> and CH<sub>4</sub>
  - What do we know?
    - 1.50 g CH<sub>4</sub>  $\Rightarrow \Delta T = 7.3^{\circ}$  C
    - 1.15 g  $H_2 \Rightarrow \Delta T = 14.3^{\circ}$  C
    - Heat capacity of calorimeter =  $11.3 \text{ kJ/}^{\circ}$  C
  - What do we need?
    - $\Delta E = \Delta T \times$  heat capacity of calorimeter

Example 6.6 - Solution (continued 1)

- How do we get there?
  - What is the energy released for each combustion?
    - For  $CH_4$ , we calculate the energy of combustion for methane using the heat capacity of the calorimeter (11.3 kJ/ $^{\circ}$  C) and the observed temperature increase of 7.3 $^{\circ}$  C

Energy released in the combustion of 1.5 g CH<sub>4</sub> = 
$$(11.3 \text{ kJ/°C})(7.3 \text{°C})$$
  
= 83 kJ

Example 6.6 - Solution (continued 2)

Energy released in the combustion of 1 g CH<sub>4</sub> =  $\frac{83 \text{ kJ}}{1.5 \text{ g}}$  = 55 kJ/g

For H<sub>2</sub>,

Energy released in the combustion of 1.15 g  $H_2 = (11.3 \text{ kJ/°C})(14.3 \text{°C})$ = 162 kJ

Energy released in the combustion of 1 g H<sub>2</sub> =  $\frac{162 \text{ kJ}}{1.15 \text{ g}}$  = 141 kJ/g

# Section 6.2 Enthalpy and Calorimetry

Example 6.6 - Solution (continued 3)

- How do the energies of combustion compare?
  - The energy released in the combustion of 1 g hydrogen is approximately 2.5 times that for 1 g methane, indicating that hydrogen gas is a potentially useful fuel

# Section 6.2 Enthalpy and Calorimetry

### Join In (11)

- If 5.0 kJ of energy is added to a 15.5-g sample of water at 10.° C, the water is:
  - a. boiling
  - b. completely vaporized
  - c. frozen solid
  - d. still a liquid

# Section 6.2 Enthalpy and Calorimetry

### Join In (12)

- A 50.0-g sample of water at 80° C is added to a 50.0-g sample of water at 20° C
  - The final temperature of the water should be:
    - a. between 20° C and 50° C
    - b. 50° C
    - c. between 50° C and 80° C

#### Hess's Law

• 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

### Characteristics of Enthalpy Changes

- If a reaction is reversed, the sign of ΔH is also reversed
- Magnitude of  $\Delta H$  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

### **Critical Thinking**

- What if Hess's law were not true?
  - What are some possible repercussions this would have?

#### Problem-Solving Strategy - Hess's Law

- Work backward from the required reaction
  - Use 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

#### Interactive Example 6.8 - Hess's Law II

- Diborane (B<sub>2</sub>H<sub>6</sub>) is a highly reactive boron hydride that was once considered as a possible rocket fuel for the U.S. space program
  - Calculate  $\Delta H$  for the synthesis of diborane from its elements, according to the following equation:

$$2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$$

#### Interactive Example 6.8 - Hess's Law II (continued)

Use the following data:

Reaction

$$\Delta H$$

a. 
$$2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s)$$

b. 
$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$

c. 
$$H_2(g) + \frac{1}{2}O_2(g) \to H_2O(l)$$

d. 
$$H_2O(l) \rightarrow H_2O(g)$$

44 kJ

#### Interactive Example 6.8 - Solution

- To obtain ΔH for the required reaction, we must somehow combine equations (a), (b), (c), and (d) to produce that reaction and add the corresponding ΔH values
  - This can best be done by focusing on the reactants and products of the required reaction
    - The reactants are B(s) and  $H_2(g)$ , and the product is  $B_2H_6(g)$

#### Interactive Example 6.8 - Solution (continued 1)

- How can we obtain the correct equation?
  - Reaction (a) has B(s) as a reactant, as needed in the required equation
    - Thus reaction (a) will be used as it is
  - Reaction (b) has B<sub>2</sub>H<sub>6</sub>(g) as a reactant, but this substance is needed as a product
    - Thus reaction (b) must be reversed, and the sign of  $\Delta H$  must be changed accordingly

#### Interactive Example 6.8 - Solution (continued 2)

Up to this point we have:

(a) 
$$2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s)$$
  $\Delta H = -1273 \text{ kJ}$   
-(b)  $B_2O_3(s) + 3H_2O(g) \rightarrow B_2H_6(g) + 3O_2(g)$   $\Delta H = -(-2035 \text{ kJ})$ 

Sum: 
$$B_2O_3(s) + 2B(s) + \frac{3}{2}O_2(g) + 3H_2O(g) \rightarrow$$
  
 $B_2O_3(s) + B_2H_6(g) + 3O_2(g) \qquad \Delta H = 762 \text{ kJ}$ 

Deleting the species that occur on both sides gives

$$2B(s) + 3H_2O(g) \rightarrow B_2H_6(g) + \frac{3}{2}O_2(g) \quad \Delta H = 762 \text{ kJ}$$

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#### Interactive Example 6.8 - Solution (continued 3)

- We are closer to the required reaction, but we still need to remove  $H_2O(g)$  and  $O_2(g)$  and introduce  $H_2(g)$  as a reactant
  - We can do this using reactions (c) and (d)
    - Multiply reaction (c) and its  $\Delta H$  value by 3 and add the result to the preceding equation

#### Interactive Example 6.8 - Solution (continued 4)

$$2B(s) + 3H_2O(g) \to B_2H_6(g) + \frac{3}{2}O_2(g) \qquad \Delta H = 762 \text{ kJ}$$

$$3 \times (c) \quad 3\left[H_2(g) + \frac{1}{2}O_2(g) \to H_2O(l)\right] \qquad \Delta H = 3(-286 \text{ kJ})$$

Sum: 
$$2B(s) + 3H_2(g) + \frac{3}{2}O_2(g) + 3H_2O(g) \rightarrow$$
  

$$B_2H_6(g) + \frac{3}{2}O_2(g) + 3H_2O(l) \quad \Delta H = -96 \text{ kJ}$$

#### Interactive Example 6.8 - Solution (continued 5)

- We can cancel the 3/2  $O_2(g)$  on both sides, but we cannot cancel the  $H_2O$  because it is gaseous on one side and liquid on the other
  - This can be solved by adding reaction (d), multiplied by 3:

$$2B(s) + 3H_{2}(g) + 3H_{2}O(g) \rightarrow B_{2}H_{6}(g) + 3H_{2}O(l) \quad \Delta H = -96 \text{ kJ}$$

$$3 \times (d) \quad 3[H_{2}O(l) \rightarrow H_{2}O(g)] \quad \Delta H = 3(44 \text{ kJ})$$

$$2B(s) + 3H_{2}(g) + 3H_{2}O(g) + 3H_{2}O(l) \rightarrow$$

$$B_{2}H_{6}(g) + 3H_{2}O(l) + 3H_{2}O(g) \qquad \Delta H = +36 \text{ kJ}$$

#### Interactive Example 6.8 - Solution (continued 6)

This gives the reaction required by the problem

$$2B(s) + 3H_2(g) \rightarrow B_2H_6(g)$$
  $\Delta H = +36 \text{ kJ}$ 

 Thus ΔH for the synthesis of 1 mole of diborane from the elements is +36 kJ

### Join In (15)

• Given the following equation, which of the following statement(s) is (are) true?

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$
  $\Delta H = ? 96 \text{ kJ}$ 

- I. The reaction is exothermic
- II. When 0.500 mol sulfur is reacted, 148 kJ of energy is released
- III. When 32.0 g of sulfur is burned,  $2.96 \times 10^5$  J of energy is released

#### Homework

- 1. Which has the greater kinetic energy, an object with a mass of 2.0 kg and a velocity of 1.0 m/s or an object with a mass of 1.0 kg and a velocity of 2.0 m/s?
- 2. For the process  $H_2O(l) \longrightarrow H_2O(g)$  at 298 K and 1.0 atm,  $\Delta H$  is more positive than  $\Delta E$  by 2.5 kJ/mol. What does the 2.5 kJ/mol quantity represent?

### Thank you