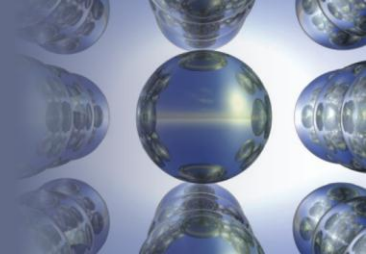


Chapter 6

Thermochemistry

Chapter 6

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- (6.5) Present sources of energy
- (6.6) New energy sources

Section 6.1

The Nature of Energy

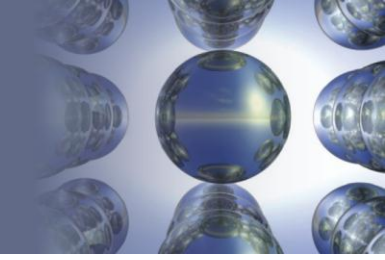


Energy

- 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
 - Total energy content of the universe is constant

Section 6.1

The Nature of Energy



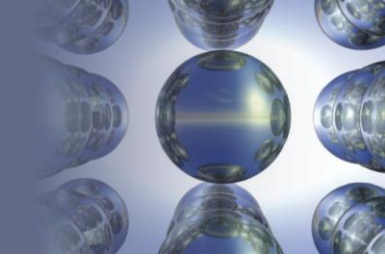
Classification of Energy

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

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

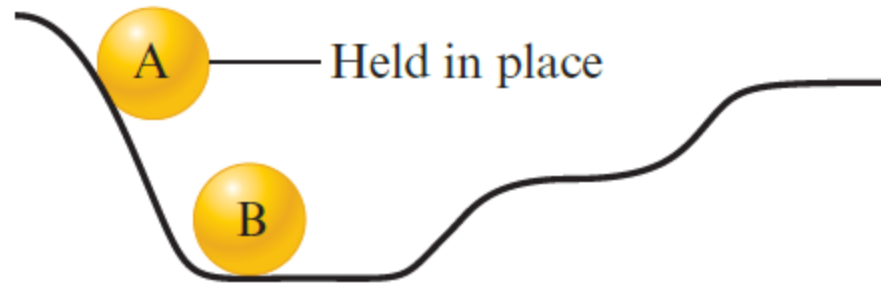
Section 6.1

The Nature of Energy



Conversion of Energy

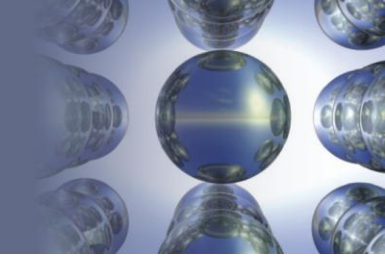
- Consider the following image:



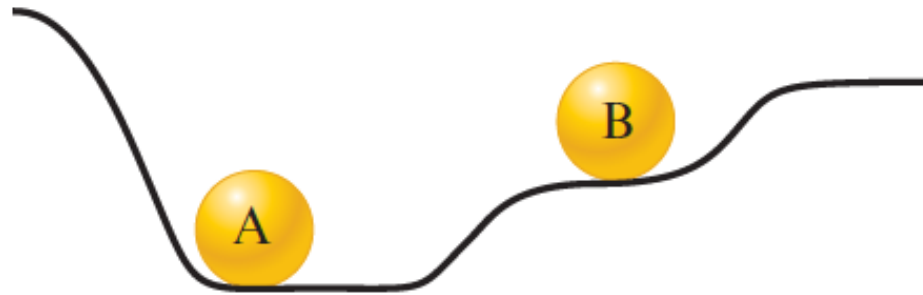
- Due to its higher initial position, ball A has more potential energy than ball B

Section 6.1

The Nature of Energy



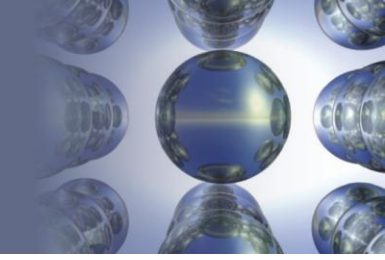
Conversion of Energy (Continued)



- 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)
 - The increase in the potential energy of B

Section 6.1

The Nature of Energy



Methods of Transferring Energy

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

Section 6.1

The Nature of Energy

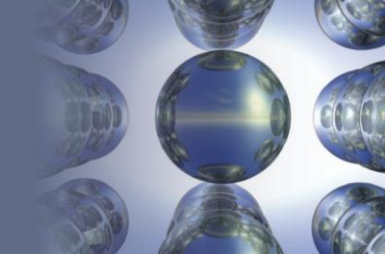


Pathway

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

Section 6.1

The Nature of Energy

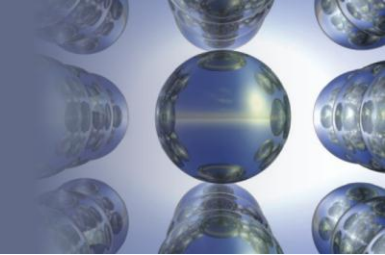


Energy as a State Function

- **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

Section 6.1

The Nature of Energy

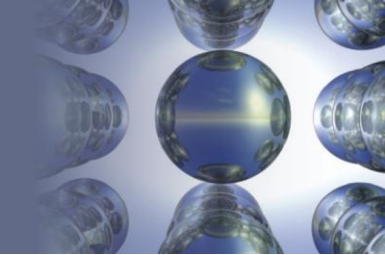


Parts of the Universe

- **System:** Part of the universe on which one wishes to focus his/her attention
 - Example - The reactants and products of a reaction
- **Surroundings:** Include everything else in the universe
 - Example - Things other than the reactants and products

Section 6.1

The Nature of Energy

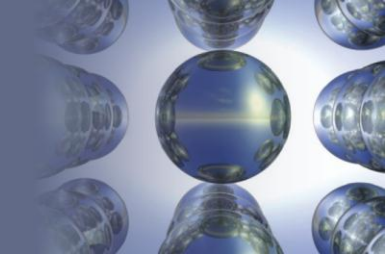


Types of Reactions

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

Section 6.1

The Nature of Energy

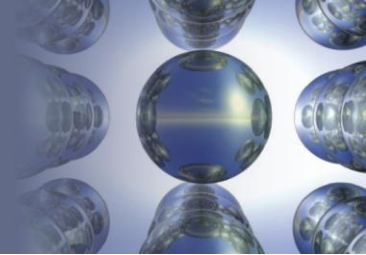


Reaction Mechanism

- Energy gained by the surroundings must be equal to the energy lost by the system
 - Endothermic reactions result from a lowered potential energy of the reaction system
 - In exothermic reactions, potential energy stored in chemical bonds is converted to thermal energy via heat

Section 6.1

The Nature of Energy



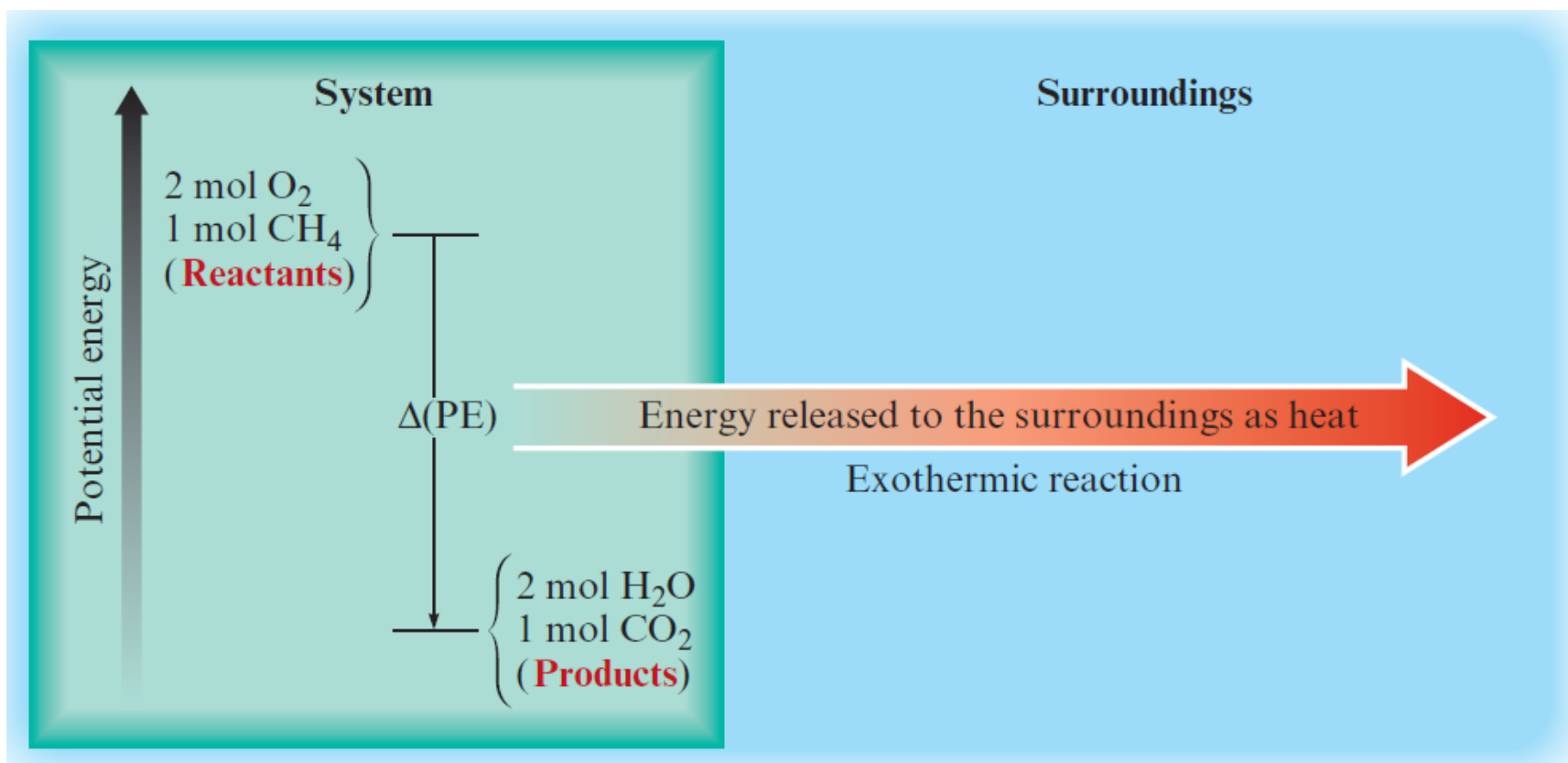
$\Delta(\text{PE})$

- Change in potential energy stored in the bonds of products as compared with the bonds of reactants
 - For an exothermic process, more energy is released while forming new bonds than is consumed while breaking the bonds in the reactants
 - In an endothermic reaction, energy that flows into the system as heat is used to increase the potential energy of the system

Section 6.1

The Nature of Energy

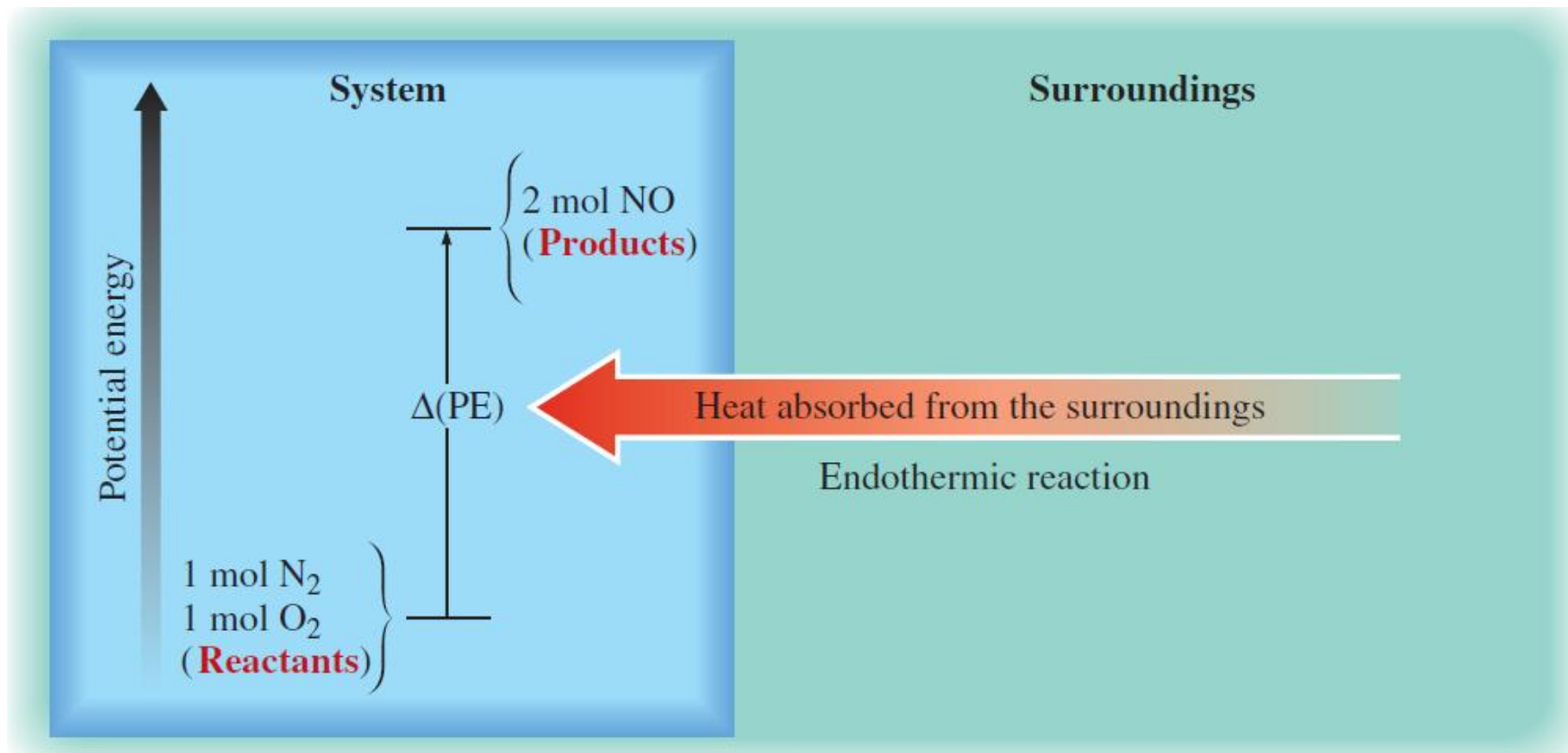
Figure 6.2 - Energy Diagram for the Combustion of Methane



Section 6.1

The Nature of Energy

Figure 6.3 - Energy Diagram for the Formation of Nitric Oxide



Section 6.1

The Nature of Energy

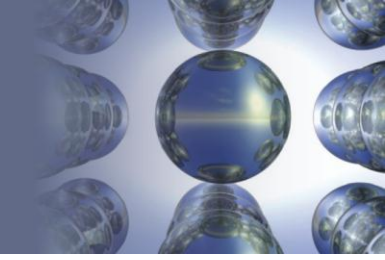


Thermodynamics

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

Section 6.1

The Nature of Energy



Internal Energy (E)

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

$$\Delta E = q + w$$

- ΔE - Change in the system's internal energy
- q - Heat
- w - Work

Section 6.1

The Nature of Energy

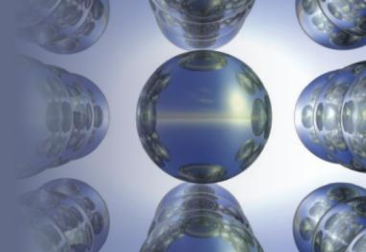


Parts of Thermodynamic Quantities

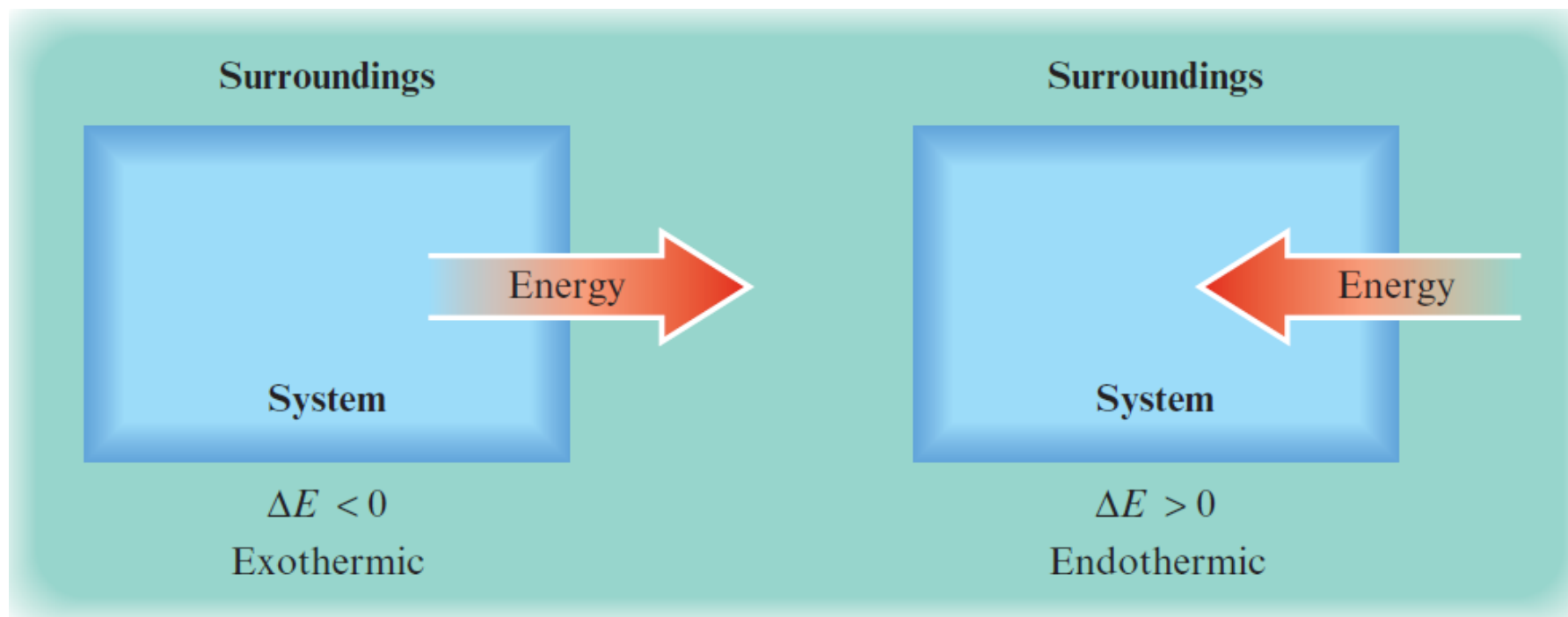
- Number - Gives the magnitude of change
- Sign - Indicates the direction of flow
 - Reflects the system's point of view
 - In an endothermic system, q is equal to $+x$
 - In an exothermic system, q is equal to $-x$
 - When a system does work on surroundings, w is negative
 - When the surroundings do work on the system, w is positive

Section 6.1

The Nature of Energy

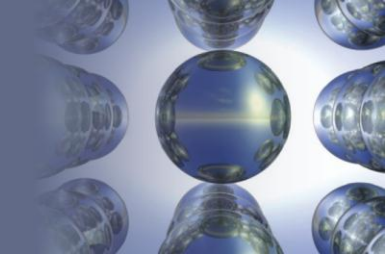


Endothermic and Exothermic Systems and Energy



Section 6.1

The Nature of Energy

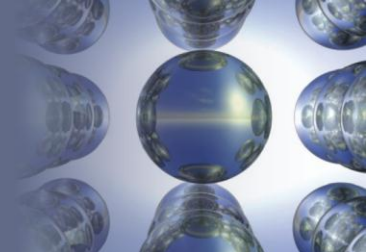


Interactive Example 6.1 - Internal Energy

- 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

Section 6.1

The Nature of Energy



Interactive Example 6.1 - Solution

- We use the following equation:

$$\Delta E = q + w$$

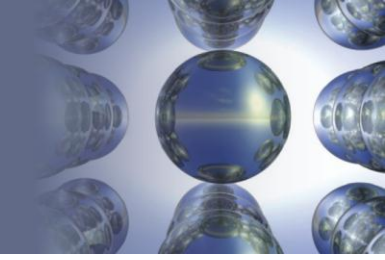
- $q = + 15.6$ kJ, since the process is endothermic
- $w = + 1.4$ kJ, since work is done on the system

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

- Thus, the system has gained 17.0 kJ of energy

Section 6.1

The Nature 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 - Motion of a car
 - In an automobile engine, heat from the combustion of gasoline expands the gases in the cylinder to push back the piston, and this results in the motion of the car

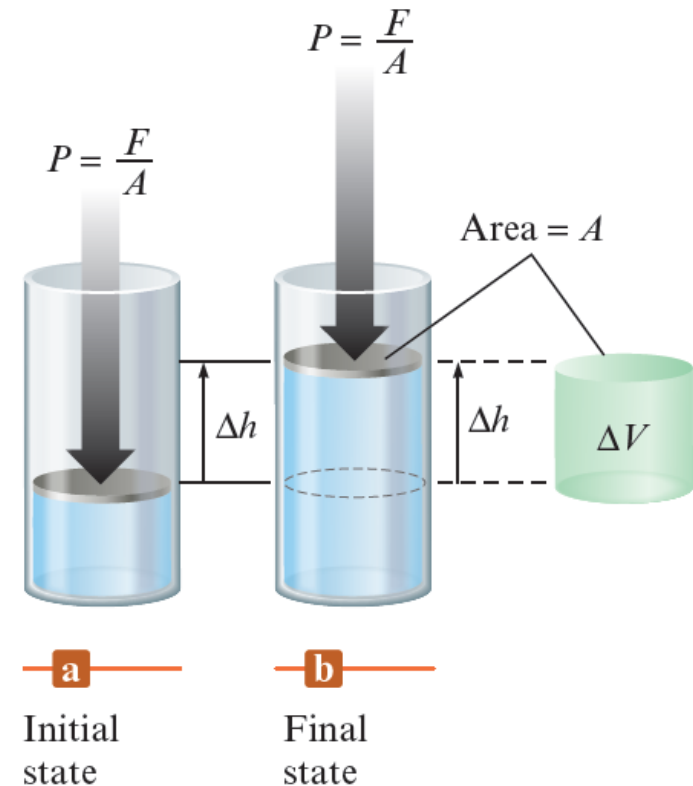
Section 6.1

The Nature of Energy

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

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



Section 6.1

The Nature of Energy



Deriving the Equation for Work (Continued 1)

- Consider that the piston moves a distance of Δh

$$\text{Work} = \text{force} \times \text{distance} = F \times \Delta h$$

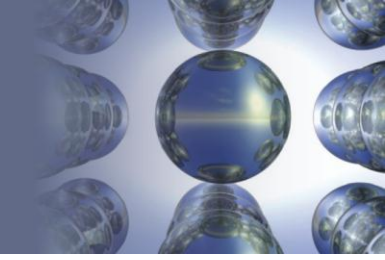
$$\text{Work} = F \times \Delta h = P \times A \times \Delta h$$

- Volume of the cylinder equals the area of the piston times the height of the cylinder
 - Change in volume ΔV resulting from the piston moving a distance Δh is:

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

Section 6.1

The Nature of Energy



Deriving the Equation for Work (Continued 2)

- Substitute the expression derived for ΔV into the expression for work

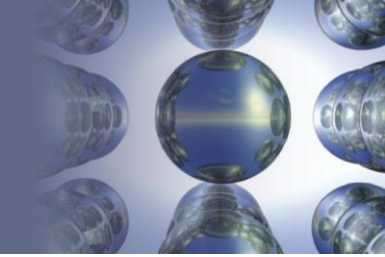
$$\text{Work} = P \times A \times \Delta h = P\Delta V$$

- Since the system is doing work on the surroundings, the sign of work should be negative
 - ΔV is a positive quantity since volume is increasing
 - Therefore,

$$w = -P\Delta V$$

Section 6.1

The Nature of Energy

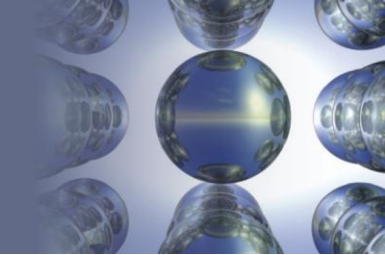


Deriving the Equation for Work (Continued 3)

- For a gas expanding against an external pressure P , w is a negative quantity as required
 - Work flows out of the system
- When a gas is compressed, ΔV is a negative quantity (the volume decreases)
 - This makes w a positive quantity (work flows into the system)

Section 6.1

The Nature of Energy

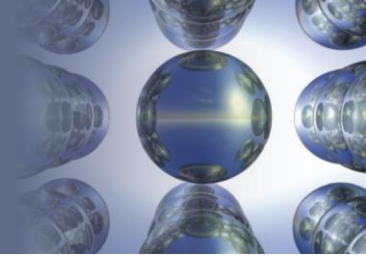


Critical Thinking

- You are calculating ΔE 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?

Section 6.1

The Nature of Energy

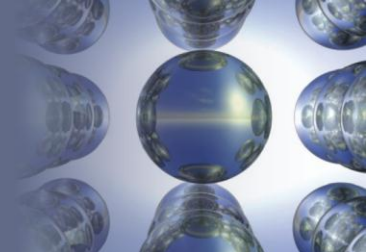


Interactive Example 6.2 - *PV* Work

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

Section 6.1

The Nature of Energy



Interactive Example 6.2 - Solution

- For a gas at constant pressure,

$$w = -P\Delta V$$

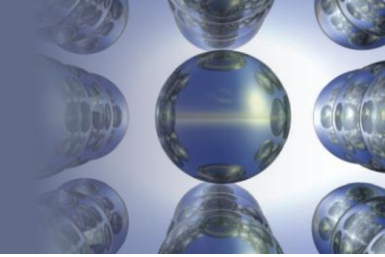
- In this case $P = 15 \text{ atm}$ and $\Delta V = 64 - 46 = 18 \text{ L}$

$$w = -15 \text{ atm} \times 18 \text{ L} = -270 \text{ L} \cdot \text{atm}$$

- 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

Section 6.1

The Nature of Energy

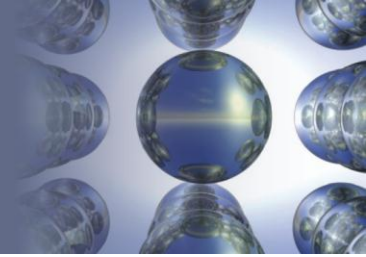


Interactive Example 6.3 - Internal Energy, Heat, and Work

- 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 4.00×10^6 L to 4.50×10^6 L by the addition of 1.3×10^8 J of energy as heat
 - Assuming that the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process
 - To convert between L · atm and J, use $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$

Section 6.1

The Nature of Energy

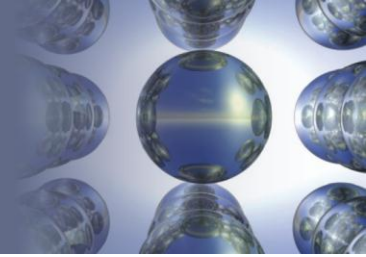


Interactive Example 6.3 - Solution

- Where are we going?
 - To calculate ΔE
- What do we know?
 - $V_1 = 4.00 \times 10^6 \text{ L}$
 - $q = +1.3 \times 10^8 \text{ J}$
 - $P = 1.0 \text{ atm}$
 - $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$
 - $V_2 = 4.50 \times 10^6 \text{ L}$

Section 6.1

The Nature of Energy



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?

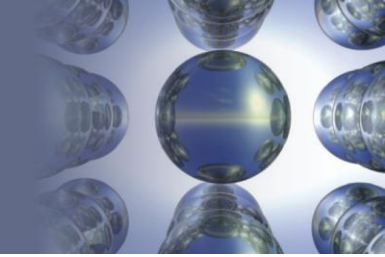
$$w = -P\Delta V$$

- What is ΔV ?

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

Section 6.1

The Nature of Energy



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 ΔE , 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

Section 6.1

The Nature of Energy



Interactive Example 6.3 - Solution (Continued 3)

$$w = -5.0 \times 10^5 \cancel{\text{ L}\cdot\text{atm}} \times \frac{101.3 \text{ J}}{\cancel{\text{ L}\cdot\text{atm}}} = -5.1 \times 10^7 \text{ J}$$

- Then,

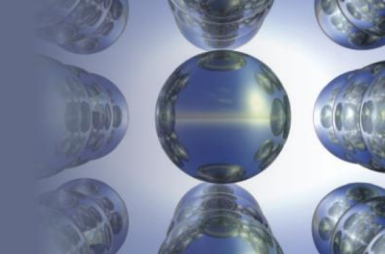
$$\Delta E = q + w = (+1.3 \times 10^8 \text{ J}) + (-5.1 \times 10^7 \text{ J}) = 8 \times 10^7 \text{ J}$$

- 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



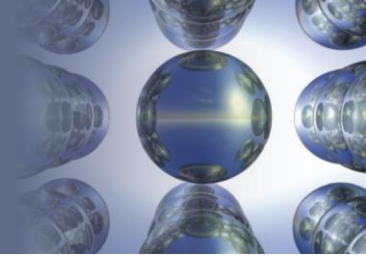
Exercise

- A balloon filled with 39.1 moles of helium has a volume of 876 L at 0.0° C and 1.00 atm pressure
 - The temperature of the balloon is increased to 38.0° C as it expands to a volume of 998 L, the pressure remaining constant
 - Calculate q , w , and ΔE for the helium in the balloon
 - The molar heat capacity for helium gas is $20.8 \text{ J}/^{\circ} \text{ C} \cdot \text{mol}$

$$q = 30.9 \text{ kJ}, w = -12.4 \text{ kJ}, \text{ and } \Delta E = 18.5 \text{ kJ}$$

Section 6.2

Enthalpy and Calorimetry



Enthalpy (H)

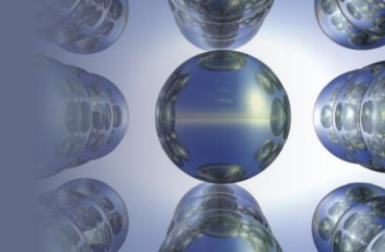
- A state function that is defined as:

$$H = E + PV$$

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

Section 6.2

Enthalpy and Calorimetry



Enthalpy and PV Work

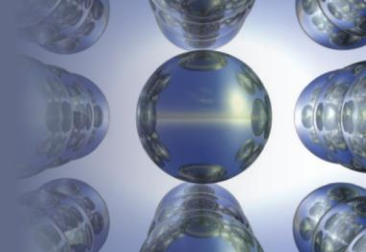
- At constant pressure, $\Delta H = q_p$
 - q_p - Heat at constant pressure
- For a chemical reaction, the enthalpy change is given by the following equation:

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

- When $H_{\text{products}} > H_{\text{reactants}}$, ΔH is positive
 - Heat is absorbed by the system
 - Reaction is endothermic

Section 6.2

Enthalpy and Calorimetry

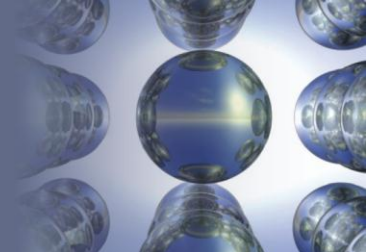


Enthalpy and PV Work (Continued)

- When $H_{\text{products}} < H_{\text{reactants}}$, ΔH is negative
 - Overall decreased in enthalpy is achieved by the generation of heat
 - Reaction is exothermic

Section 6.2

Enthalpy and Calorimetry

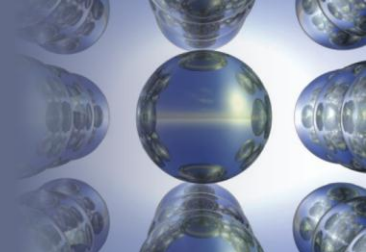


Interactive Example 6.4 - Enthalpy

- When 1 mole of methane (CH_4) is burned at constant pressure, 890 kJ of energy is released as heat
 - Calculate ΔH for a process in which a 5.8-g sample of methane is burned at constant pressure

Section 6.2

Enthalpy and Calorimetry

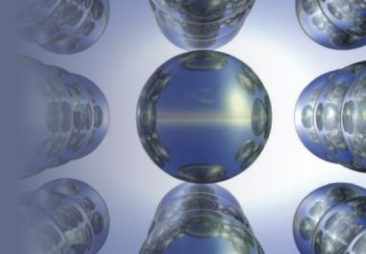


Interactive Example 6.4 - Solution

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

Section 6.2

Enthalpy and Calorimetry



Interactive Example 6.4 - Solution (Continued 1)

- How do we get there?
 - What are the moles of CH_4 burned?

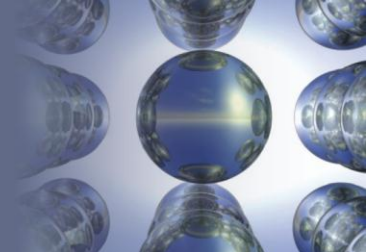
$$5.8 \cancel{\text{ g CH}_4} \times \frac{1 \text{ mol CH}_4}{16.04 \cancel{\text{ g CH}_4}} = 0.36 \text{ mol CH}_4$$

- What is ΔH ?

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

Section 6.2

Enthalpy and Calorimetry



Interactive Example 6.4 - Solution (Continued 2)

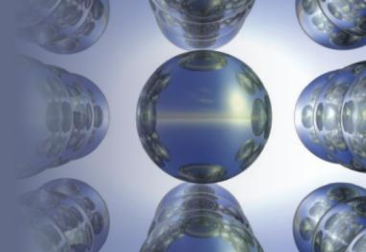
- Thus, when a 5.8-g sample of CH_4 is burned at constant pressure,

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

- Reality check
 - In this case, a 5.8-g sample of CH_4 is burned
 - Since this amount is smaller than 1 mole, less than 890 kJ will be released as heat

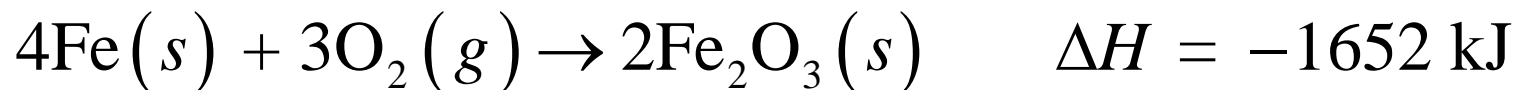
Section 6.2

Enthalpy and Calorimetry



Exercise

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

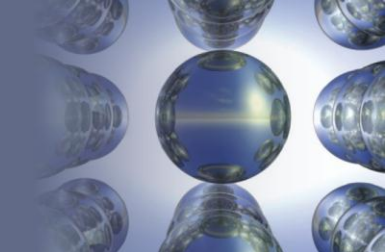


- How much heat is released when 4.00 moles of iron are reacted with excess O_2 ?

1650 kJ heat is released

Section 6.2

Enthalpy and Calorimetry



Exercise (Continued)

- How much heat is released when 1.00 mole of Fe_2O_3 is produced?

826 kJ of heat is released

- How much heat is released when 1.00 g iron is reacted with excess O_2 ?

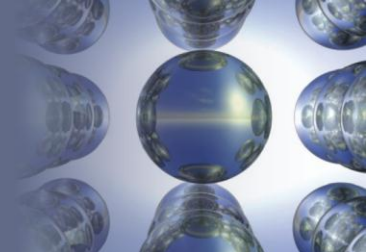
7.39 kJ of heat is released

- How much heat is released when 10.0 g Fe and 2.00 g O_2 are reacted?

34.4 kJ of heat is released

Section 6.2

Enthalpy and Calorimetry

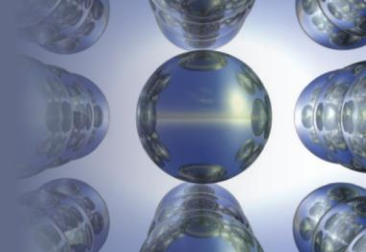


Calorimetry

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

Section 6.2

Enthalpy and Calorimetry



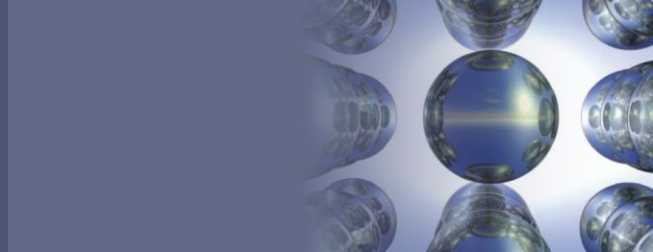
Heat Capacity (C)

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

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

Section 6.2

Enthalpy and Calorimetry



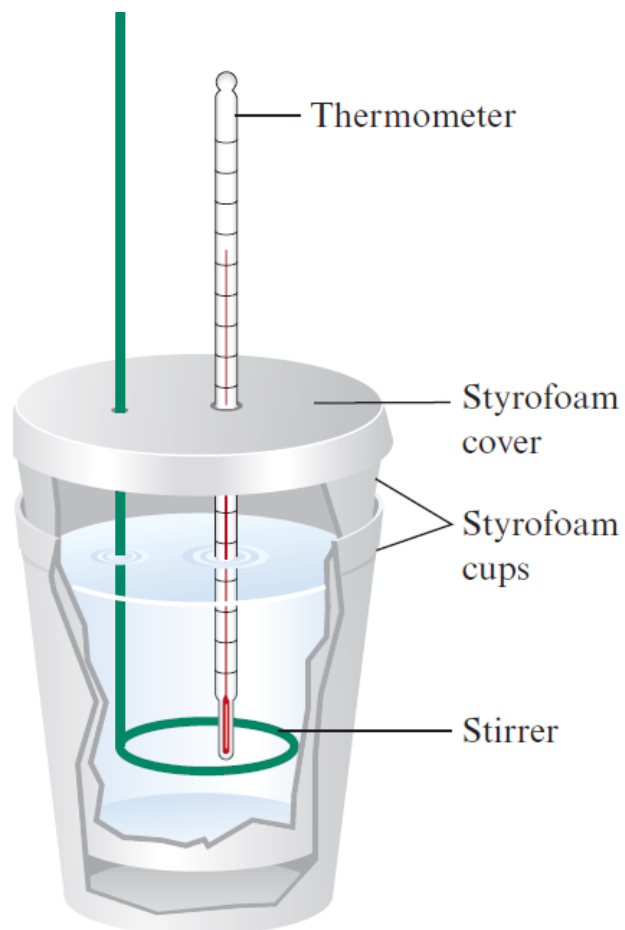
Heat Capacity (C) (Continued)

- **Molar heat capacity:** Energy required to raise the temperature of one mole of a substance by one degree Celsius
 - Units - $\text{J}/^{\circ}\text{C} \cdot \text{mol}$ or $\text{J}/\text{K} \cdot \text{mol}$
- Heat capacities of metals are different from that of water
 - Takes less energy to change the temperature of a gram of a metal by 1°C than for a gram of water

Section 6.2

Enthalpy and Calorimetry

Figure 6.5 - A Coffee-Cup Calorimeter



Section 6.2

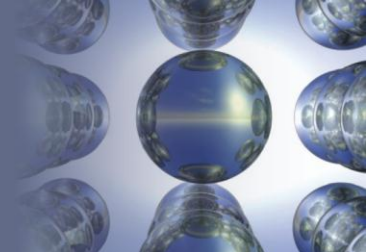
Enthalpy and Calorimetry

Table 6.1 - The Specific Heat Capacities of Some Common Substances

Substance	Specific Heat Capacity ($\text{J}/^\circ\text{C} \cdot \text{g}$)
$\text{H}_2\text{O}(l)$	4.18
$\text{H}_2\text{O}(s)$	2.03
$\text{Al}(s)$	0.89
$\text{Fe}(s)$	0.45
$\text{Hg}(l)$	0.14
$\text{C}(s)$	0.71

Section 6.2

Enthalpy and Calorimetry

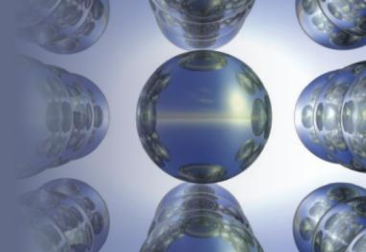


Constant-Pressure Calorimetry

- Example - Coffee-cup calorimeter
 - Atmospheric pressure remains constant during the process
- Used to determine enthalpy changes in reactions that occur in a solution
 - In a solution, $\Delta H = q_P$

Section 6.2

Enthalpy and Calorimetry

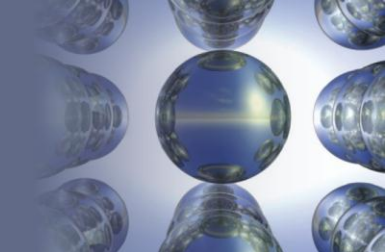


Constant-Pressure Calorimetry (Continued 1)

- When two reactants at the same temperature are mixed:
 - An exothermic reaction warms the solution
 - An endothermic reaction cools the solution

Section 6.2

Enthalpy and Calorimetry

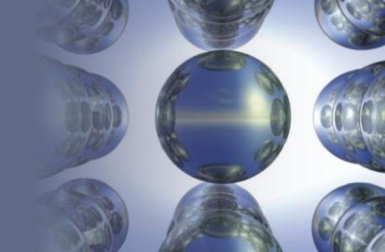


Constant-Pressure Calorimetry (Continued 2)

- Calculation of heat for a neutralization reaction
 - Energy (as heat) released by the reaction
 - = Energy (as heat) absorbed by the solution
 - = Specific heat capacity \times mass of solution
 - \times change in temperature
 - = $s \times m \times \Delta T$
- Heat of a reaction is an extensive property
 - Depends entirely on the amount of substance

Section 6.2

Enthalpy and Calorimetry

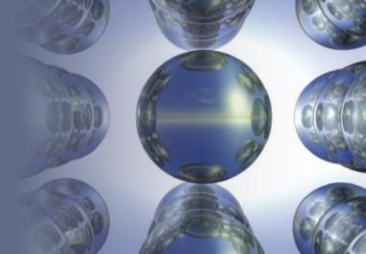


Interactive Example 6.5 - Constant-Pressure Calorimetry

- When 1.00 L of 1.00 M $\text{Ba}(\text{NO}_3)_2$ solution at 25.0°C is mixed with 1.00 L of 1.00 M Na_2SO_4 solution at 25.0°C in a calorimeter, the white solid BaSO_4 forms, and the temperature of the mixture increases to 28.1°C

Section 6.2

Enthalpy and Calorimetry

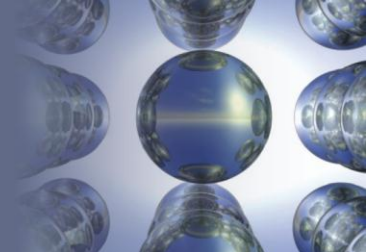


Interactive Example 6.5 - Constant-Pressure Calorimetry (Continued)

- 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_4 formed

Section 6.2

Enthalpy and Calorimetry

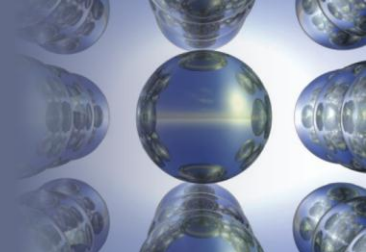


Interactive Example 6.5 - Solution

- Where are we going?
 - To calculate ΔH per mole of BaSO_4 formed
- What do we know?
 - 1.00 L of 1.00 M $\text{Ba}(\text{NO}_3)_2$
 - 1.00 L of 1.00 M Na_2SO_4
 - $T_{\text{initial}} = 25.0^\circ \text{ C}$ and $T_{\text{final}} = 28.1^\circ \text{ C}$
 - Heat capacity of solution = $4.18 \text{ J}/^\circ \text{ C} \cdot \text{g}$
 - Density of final solution = 1.0 g/mL

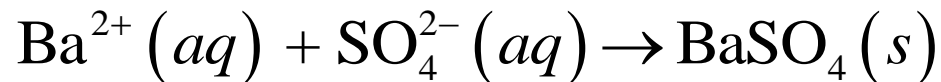
Section 6.2

Enthalpy and Calorimetry



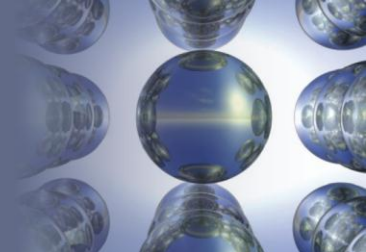
Interactive Example 6.5 - Solution (Continued 1)

- 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^+ and NO_3^- ions are spectator ions, since NaNO_3 is very soluble in water and will not precipitate under these conditions
 - The net ionic equation for the reaction is:



Section 6.2

Enthalpy and Calorimetry

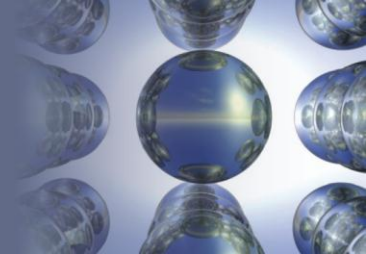


Interactive Example 6.5 - Solution (Continued 2)

- How do we get there?
 - What is ΔH ?
 - Since the temperature increases, formation of solid BaSO_4 must be exothermic
 - ΔH is negative
 - Heat evolved by the reaction
 - = heat absorbed by the solution
 - = specific heat capacity \times mass of solution \times increase in temperature

Section 6.2

Enthalpy and Calorimetry



Interactive Example 6.5 - Solution (Continued 3)

- What is the mass of the final solution?

$$\text{Mass of solution} = 2.00 \cancel{\text{ L}} \times \frac{1000 \cancel{\text{ mL}}}{1 \cancel{\text{ L}}} \times \frac{1.0 \text{ g}}{\cancel{\text{ mL}}} = 2.0 \times 10^3 \text{ g}$$

- What is the temperature increase?

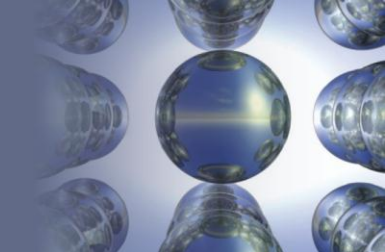
$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 28.1^\circ\text{C} - 25.0^\circ\text{C} = 3.1^\circ\text{C}$$

- How much heat is evolved by the reaction?

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

Section 6.2

Enthalpy and Calorimetry



Interactive Example 6.5 - Solution (Continued 4)

- Thus,

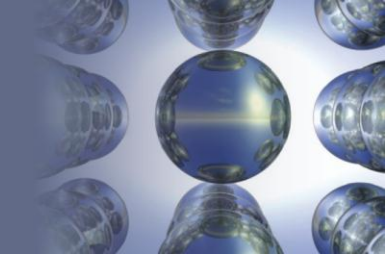
$$q = q_p = \Delta H = -2.6 \times 10^4 \text{ J}$$

- What is ΔH per mole of BaSO_4 formed?
 - Since 1.0 L of 1.0 M $\text{Ba}(\text{NO}_3)_2$ contains 1 mole of Ba^{2+} ions and 1.0 L of 1.0 M Na_2SO_4 contains 1.0 mole of SO_4^{2-} ions, 1.0 mole of solid BaSO_4 is formed in this experiment
 - Thus the enthalpy change per mole of BaSO_4 formed is

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

Section 6.2

Enthalpy and Calorimetry



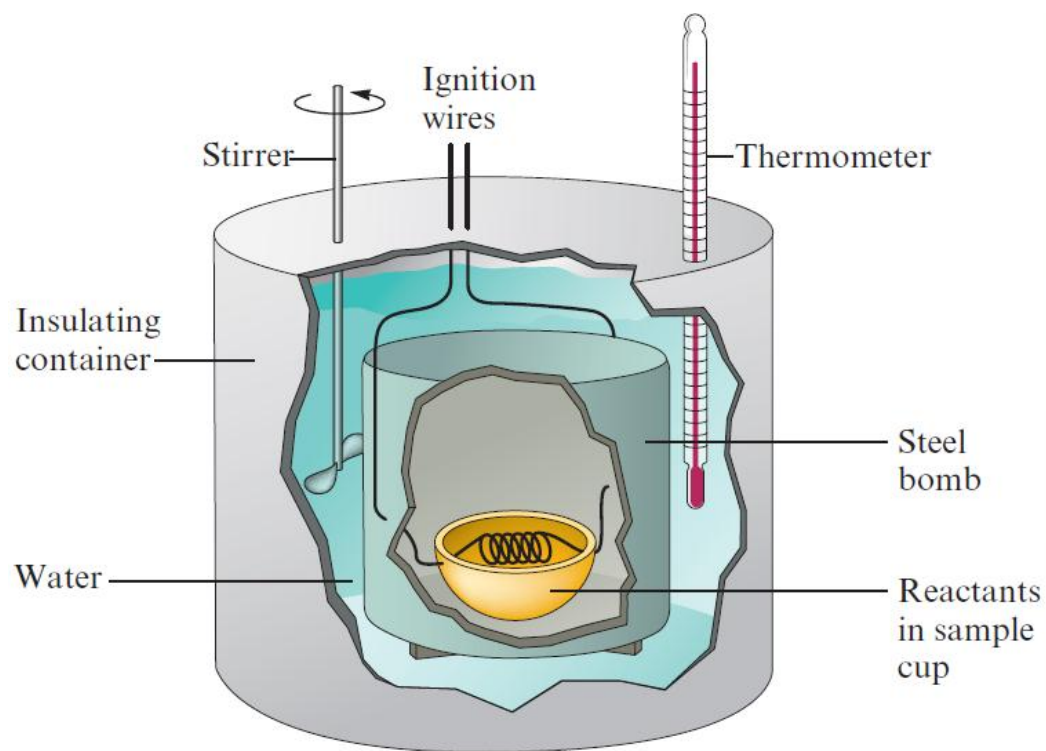
Constant-Volume Calorimetry

- Used in conditions when experiments are to be performed under constant volume
 - No work is done since V must change for PV work to be performed
- Bomb calorimeter
 - Weighed reactants are placed within a rigid steel container and ignited
 - Change in energy is determined by the increase in temperature of the water and other parts

Section 6.2

Enthalpy and Calorimetry

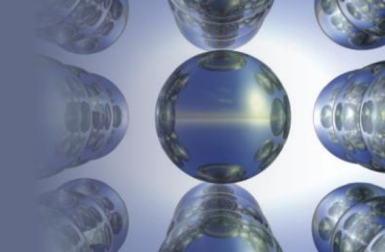
Figure 6.6 - A Bomb Calorimeter



Charles D. Winters/Photo Researchers, Inc.

Section 6.2

Enthalpy and Calorimetry



Constant-Volume Calorimetry (Continued)

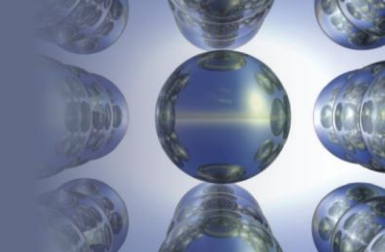
- For a constant-volume process, $\Delta V = 0$
 - Therefore, $w = -P\Delta V = 0$

$$\Delta E = q + w = q = q_V \quad (\text{constant volume})$$

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

Section 6.2

Enthalpy and Calorimetry

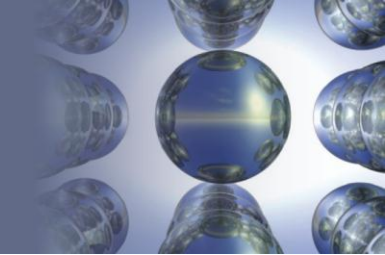


Example 6.6 - Constant-Volume Calorimetry

- 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 $11.3 \text{ kJ/}^\circ \text{C}$

Section 6.2

Enthalpy and Calorimetry

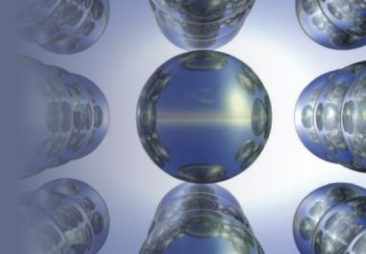


Example 6.6 - Constant-Volume Calorimetry (Continued)

- 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

Section 6.2

Enthalpy and Calorimetry

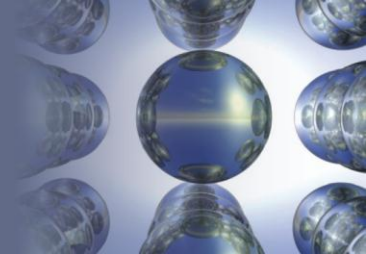


Example 6.6 - Solution

- Where are we going?
 - To calculate ΔH of combustion per gram for H_2 and CH_4
- What do we know?
 - $1.50 \text{ g } CH_4 \rightarrow \Delta T = 7.3^\circ \text{ C}$
 - $1.15 \text{ g } H_2 \rightarrow \Delta T = 14.3^\circ \text{ C}$
 - Heat capacity of calorimeter = $11.3 \text{ kJ/}^\circ \text{ C}$

Section 6.2

Enthalpy and Calorimetry



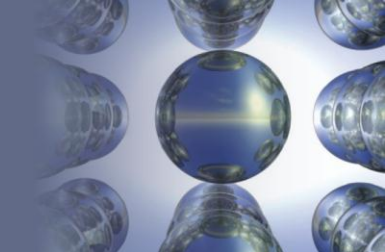
Example 6.6 - Solution (Continued 1)

- What do we need?
 - $\Delta E = \Delta T \times$ heat capacity of calorimeter
- 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 ($11.3 \text{ kJ}/^\circ \text{C}$) and the observed temperature increase of 7.3°C

$$\begin{aligned}\text{Energy released in the combustion of } 1.5 \text{ g CH}_4 &= (11.3 \text{ kJ}/^\circ\text{C})(7.3^\circ\text{C}) \\ &= 83 \text{ kJ}\end{aligned}$$

Section 6.2

Enthalpy and Calorimetry



Example 6.6 - Solution (Continued 2)

$$\text{Energy released in the combustion of 1 g CH}_4 = \frac{83 \text{ kJ}}{1.5 \text{ g}} = 55 \text{ kJ/g}$$

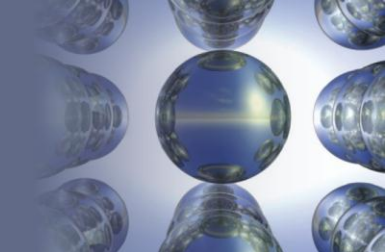
- For H₂,

$$\begin{aligned} \text{Energy released in the combustion of 1.15 g H}_2 &= (11.3 \text{ kJ/}^\circ\text{C})(14.3^\circ\text{C}) \\ &= 162 \text{ kJ} \end{aligned}$$

$$\text{Energy released in the combustion of 1 g H}_2 = \frac{162 \text{ kJ}}{1.15 \text{ g}} = 141 \text{ kJ/g}$$

Section 6.2

Enthalpy and Calorimetry

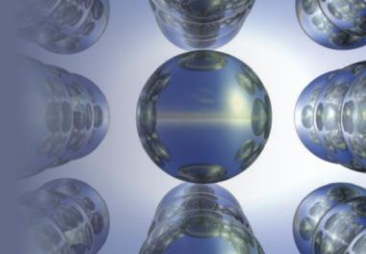


Example 6.6 - Solution (Continued 3)

- 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 6.3

Hess's Law

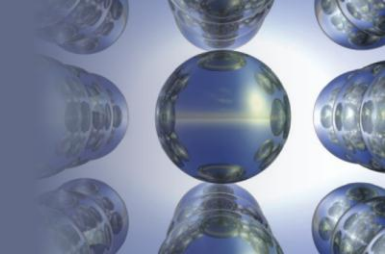


Hess's Law

- 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

Section 6.3

Hess's Law

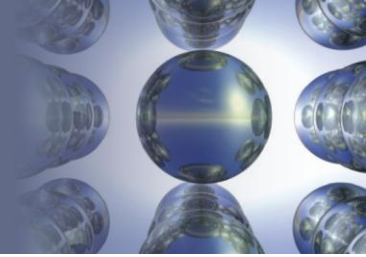


Characteristics of Enthalpy Changes

- If a reaction is reversed, the sign of ΔH is also reversed
- 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

Section 6.3

Hess's Law

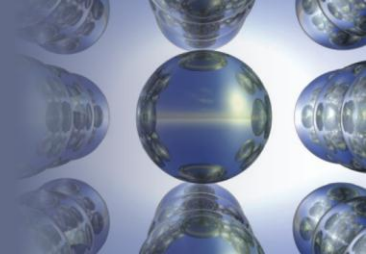


Critical Thinking

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

Section 6.3

Hess's Law

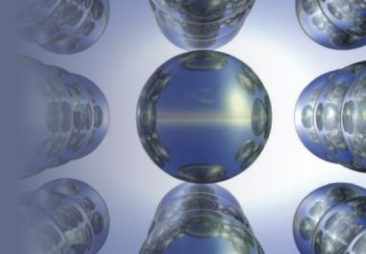


Problem-Solving Strategy - Hess's Law

- 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

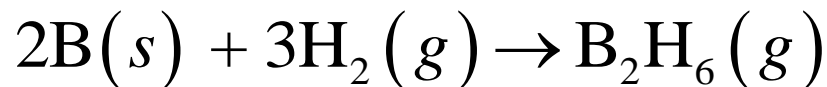
Section 6.3

Hess's Law



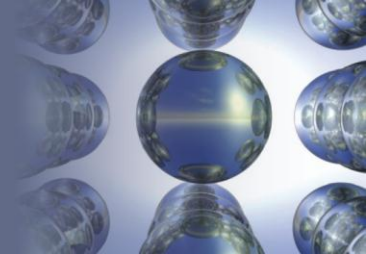
Interactive Example 6.8 - Hess's Law II

- Diborane (B_2H_6) is a highly reactive boron hydride that was once considered as a possible rocket fuel for the U.S. space program
 - Calculate ΔH for the synthesis of diborane from its elements, according to the following equation:



Section 6.3

Hess's Law



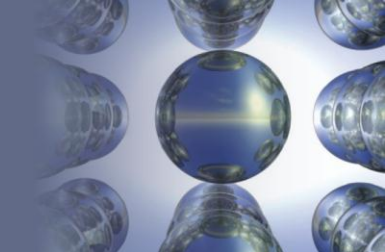
Interactive Example 6.8 - Hess's Law II (Continued)

- Use the following data:

Reaction	ΔH
a. $2\text{B}(s) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{B}_2\text{O}_3(s)$	-1273 kJ
b. $\text{B}_2\text{H}_6(g) + 3\text{O}_2(g) \rightarrow \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g)$	-2035 kJ
c. $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$	-286 kJ
d. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$	44 kJ

Section 6.3

Hess's Law

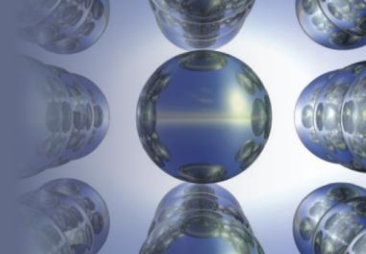


Interactive Example 6.8 - Solution

- 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 $B_2H_6(g)$

Section 6.3

Hess's Law

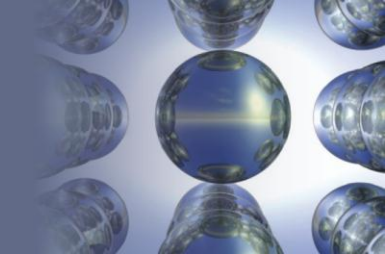


Interactive Example 6.8 - Solution (Continued 1)

- How can we obtain the correct equation?
 - Reaction (a) has $B(s)$ as a reactant, as needed in the required equation
 - Reaction (a) will be used as it is
 - Reaction (b) has $B_2H_6(g)$ as a reactant, but this substance is needed as a product
 - Reaction (b) must be reversed, and the sign of ΔH must be changed accordingly

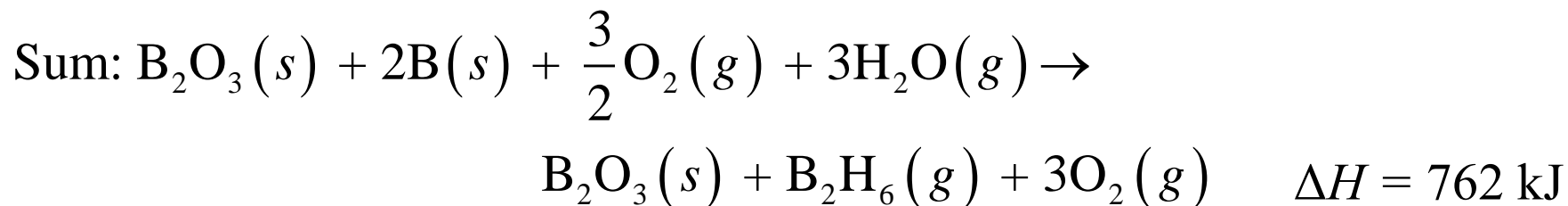
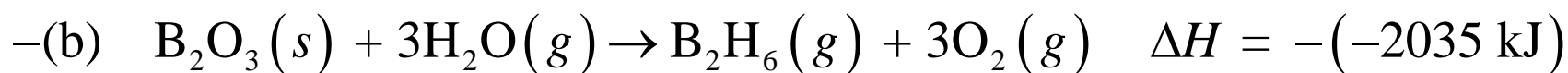
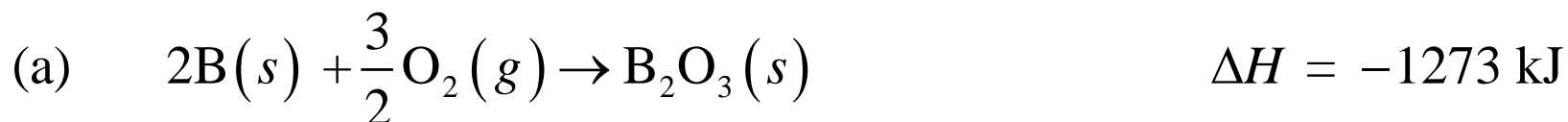
Section 6.3

Hess's Law

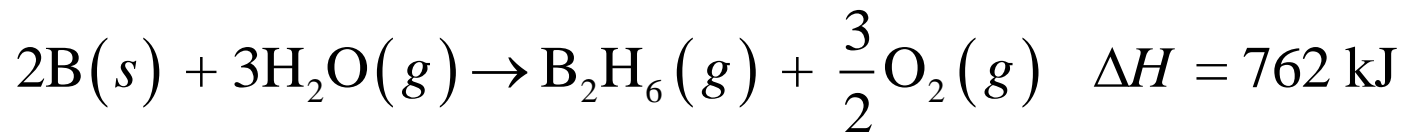


Interactive Example 6.8 - Solution (Continued 2)

- Up to this point we have:

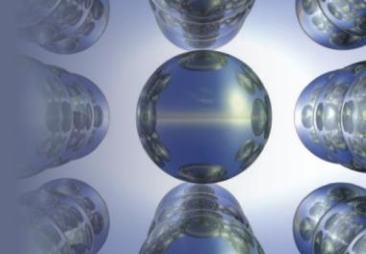


- Deleting the species that occur on both sides gives:



Section 6.3

Hess's Law

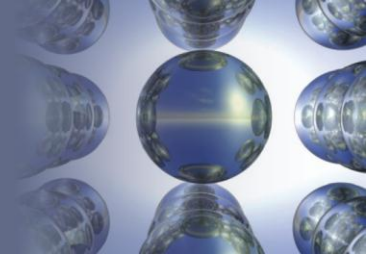


Interactive Example 6.8 - Solution (Continued 3)

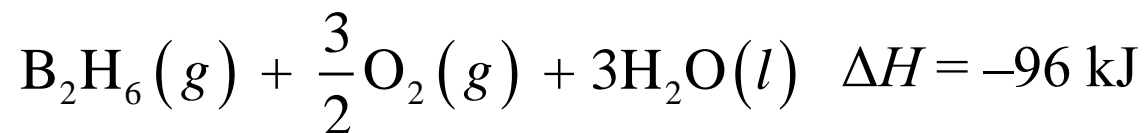
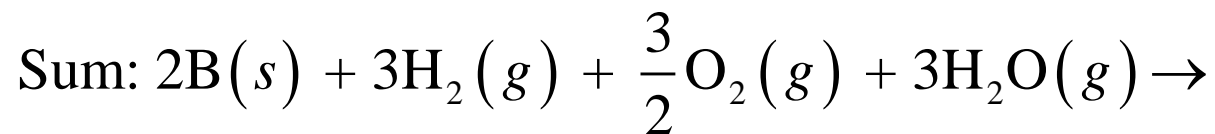
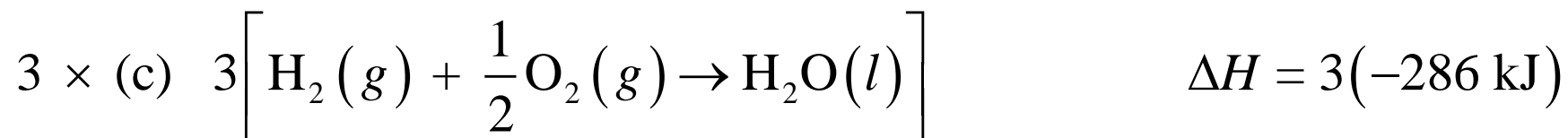
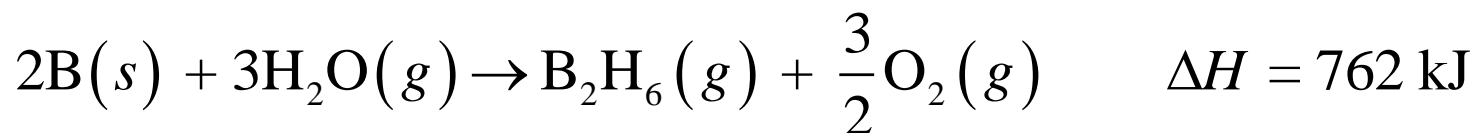
- We are closer to the required reaction, but we still need to remove $\text{H}_2\text{O}(g)$ and $\text{O}_2(g)$ and introduce $\text{H}_2(g)$ as a reactant
 - We can do this using reactions (c) and (d)
 - Multiply reaction (c) and its ΔH value by 3 and add the result to the preceding equation

Section 6.3

Hess's Law



Interactive Example 6.8 - Solution (Continued 4)

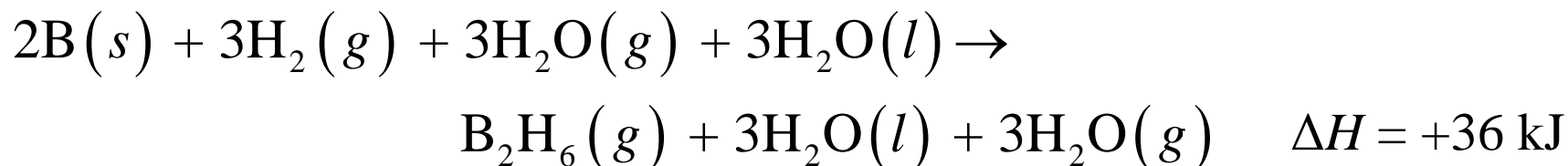
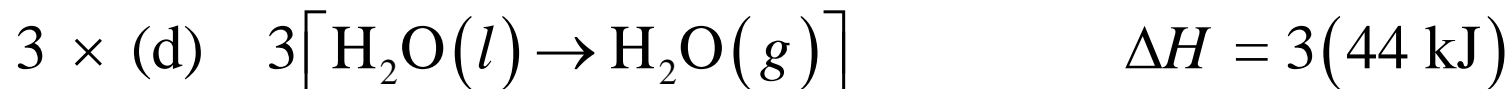


Section 6.3

Hess's Law

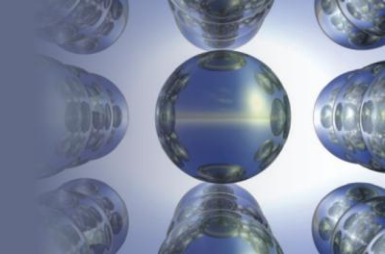
Interactive Example 6.8 - Solution (Continued 5)

- We can cancel the $3/2 \text{ O}_2(g)$ 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:



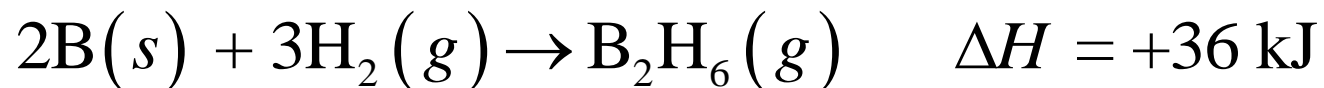
Section 6.3

Hess's Law



Interactive Example 6.8 - Solution (Continued 6)

- This gives the reaction required by the problem

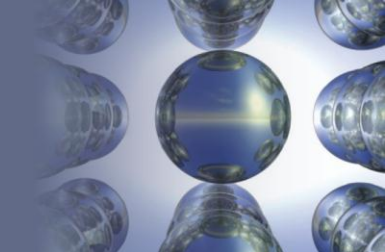


- **Conclusion**

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

Section 6.4

Standard Enthalpies of Formation

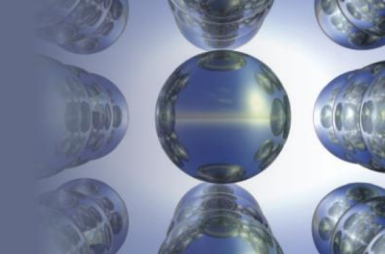


Standard Enthalpy of Formation (ΔH_f°)

- Change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states
 - **Standard state:** Precisely defined reference state
 - A degree symbol on a thermodynamic function indicates that the corresponding process that is carried out under standard conditions

Section 6.4

Standard Enthalpies of Formation

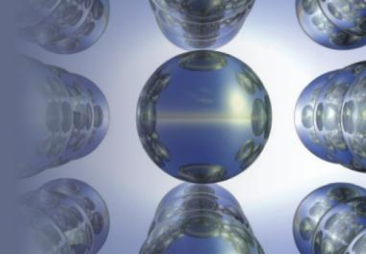


Conventional Definitions of Standard States for a Compound

- Standard state for a gaseous substance is a pressure of exactly 1 atm
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid
- For a substance in solution, the standard state is a concentration of exactly 1 *M*

Section 6.4

Standard Enthalpies of Formation



Conventional Definitions of Standard States for an Element

- Standard state of an element is the form in which that element exists under conditions of 1 atm and 25° C
 - Examples
 - Standard state for oxygen is $O_2(g)$
 - Standard state of sodium is $Na(s)$
 - Standard state of mercury is $Hg(l)$

Section 6.4

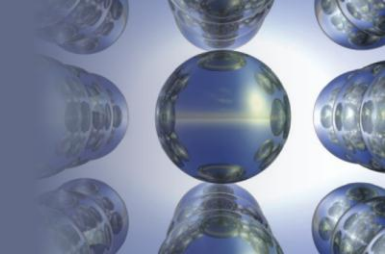
Standard Enthalpies of Formation

Table 6.2 - Standard Enthalpies of Formation for Several Compounds at 25° C

Compound	ΔH_f° (kJ/mol)
$\text{NH}_3(g)$	-46
$\text{NO}_2(g)$	34
$\text{H}_2\text{O}(l)$	-286
$\text{Al}_2\text{O}_3(s)$	-1676
$\text{Fe}_2\text{O}_3(s)$	-826
$\text{CO}_2(g)$	-394
$\text{CH}_3\text{OH}(l)$	-239
$\text{C}_8\text{H}_{18}(l)$	-269

Section 6.4

Standard Enthalpies of Formation

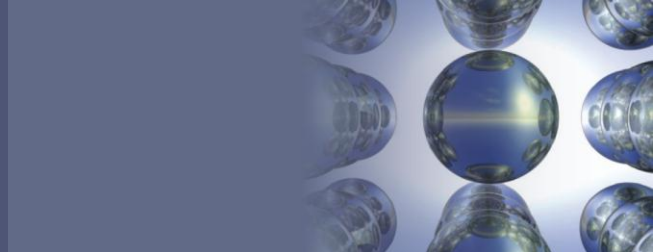


Problem-Solving Strategy - Enthalpy Calculations

- When a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes
- 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

Section 6.4

Standard Enthalpies of Formation



Problem-Solving Strategy - Enthalpy Calculations

(Continued)

- Change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H^{\circ}_{\text{reaction}} = \sum n_{\text{p}} \Delta H^{\circ}_{\text{f}} (\text{products}) - \sum n_{\text{r}} \Delta H^{\circ}_{\text{f}} (\text{reactants})$$

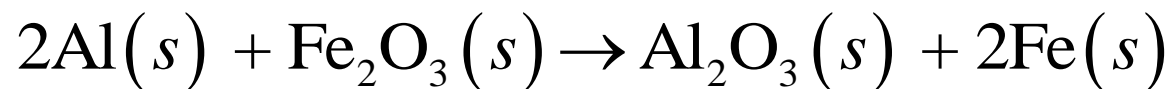
- Elements in their standard states are not included in the $\Delta H_{\text{reaction}}$ calculations
 - $\Delta H_{\text{f}}^{\circ}$ for an element in its standard state is zero

Section 6.4

Standard Enthalpies of Formation

Interactive Example 6.10 - Enthalpies from Standard Enthalpies of Formation II

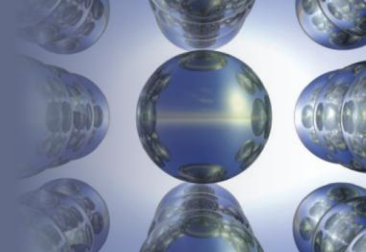
- Using enthalpies of formation, calculate the standard change in enthalpy for the thermite reaction:



- This reaction occurs when a mixture of powdered aluminum and iron(III) oxide is ignited with a magnesium fuse

Section 6.4

Standard Enthalpies of Formation



Interactive Example 6.10 - Solution

- Where are we going?
 - To calculate ΔH for the reaction
- What do we know?
 - ΔH_f° for $\text{Fe}_2\text{O}_3(s) = -826 \text{ kJ/mol}$
 - ΔH_f° for $\text{Al}_2\text{O}_3(s) = -1676 \text{ kJ/mol}$
 - ΔH_f° for $\text{Al}(s) = \Delta H_f^\circ$ for $\text{Fe}(s) = 0$

Section 6.4

Standard Enthalpies of Formation



Interactive Example 6.10 - Solution (Continued 1)

- What do we need?

- We use the following equation:

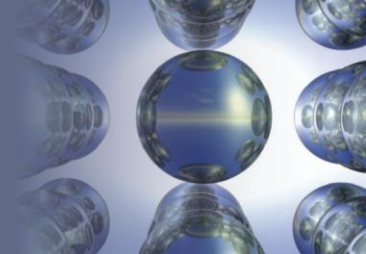
$$\Delta H^{\circ} = \sum n_p \Delta H^{\circ}_f (\text{products}) - \sum n_r \Delta H^{\circ}_f (\text{reactants})$$

- How do we get there?

$$\begin{aligned} \Delta H^{\circ}_{\text{reaction}} &= \Delta H^{\circ}_f \text{ for } \text{Al}_2\text{O}_3 (s) - \Delta H^{\circ}_f \text{ for } \text{Fe}_2\text{O}_3 (s) \\ &= -1676 \text{ kJ} - (-826 \text{ kJ}) = -850 \text{ kJ} \end{aligned}$$

Section 6.4

Standard Enthalpies of Formation

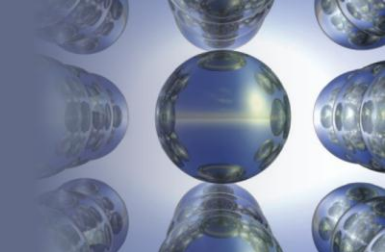


Interactive Example 6.10 - Solution (Continued 2)

- This reaction is so highly exothermic that the iron produced is initially molten
 - Used as a lecture demonstration
 - Used in welding massive steel objects such as ships' propellers

Section 6.4

Standard Enthalpies of Formation



Critical Thinking

- For $\Delta H_{\text{reaction}}$ calculations, we define ΔH_f° for an element in its standard state as zero
 - What if we define ΔH_f° for an element in its standard state as 10 kJ/mol?
 - How would this affect your determination of $\Delta H_{\text{reaction}}$?
 - Provide support for your answer with a sample calculation

Section 6.4

Standard Enthalpies of Formation

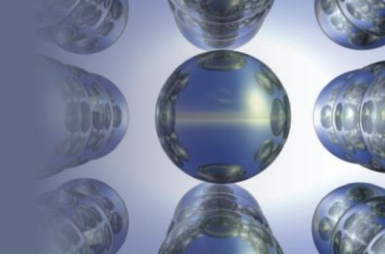


Example 6.11 - Enthalpies from Standard Enthalpies of Formation III

- Until recently, methanol (CH_3OH) was used as a fuel in high-performance engines in race cars
 - Using data from the table containing standard enthalpies of formation for several compounds at 25°C , compare the standard enthalpy of combustion per gram of methanol with that per gram of gasoline
 - Gasoline is actually a mixture of compounds, but assume for this problem that gasoline is pure liquid octane (C_8H_{18})

Section 6.4

Standard Enthalpies of Formation

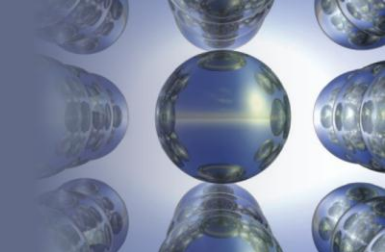


Example 6.11 - Solution

- Where are we going?
 - To compare ΔH of combustion for methanol and octane
- What do we know?
 - Standard enthalpies of formation from Table 6.2

Section 6.4

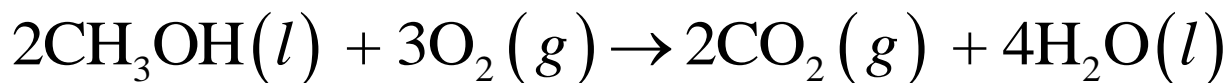
Standard Enthalpies of Formation



Example 6.11 - Solution (Continued 1)

- How do we get there? (For methanol)

- What is the combustion reaction?



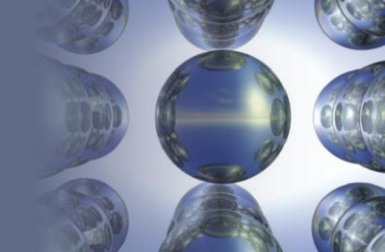
- What is the $\Delta H^\circ_{\text{reaction}}$?

- Use the standard enthalpies of formation from Table 6.2 and the following equation:

$$\Delta H^\circ_{\text{reaction}} = \sum n_p \Delta H^\circ_f (\text{products}) - \sum n_r \Delta H^\circ_f (\text{reactants})$$

Section 6.4

Standard Enthalpies of Formation

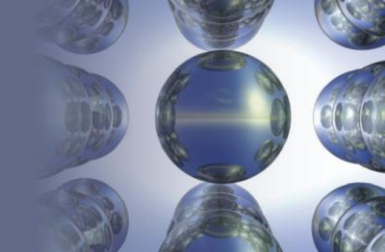


Example 6.11 - Solution (Continued 2)

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= 2 \times \Delta H^\circ_{\text{f}} \text{ for } \text{CO}_2(g) + 4 \times \Delta H^\circ_{\text{f}} \text{ for } \text{H}_2\text{O}(l) \\ &\quad - 2 \times \Delta H^\circ_{\text{f}} \text{ for } \text{CH}_3\text{OH}(l) \\ &= 2 \times (-394 \text{ kJ}) + 4 \times (-286 \text{ kJ}) - 2 \times (-239 \text{ kJ}) \\ &= -1.45 \times 10^3 \text{ kJ}\end{aligned}$$

Section 6.4

Standard Enthalpies of Formation



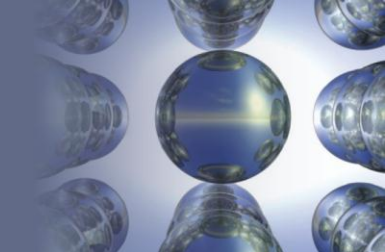
Example 6.11 - Solution (Continued 3)

- What is the enthalpy of combustion per gram?
 - 1.45×10^3 kJ of heat is evolved when 2 moles of methanol burn
 - The molar mass of methanol is 32.04 g/mol, which means that 1.45×10^3 kJ of energy is produced when 64.08 g methanol burns
 - The enthalpy of combustion per gram of methanol is:

$$\frac{-1.45 \times 10^3 \text{ kJ}}{64.08 \text{ g}} = -22.6 \text{ kJ/g}$$

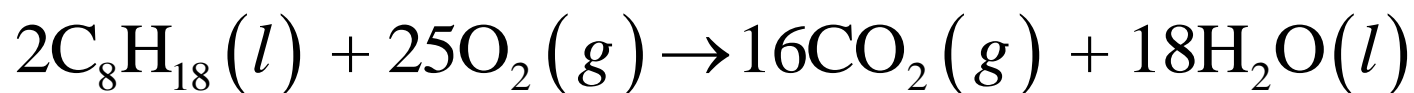
Section 6.4

Standard Enthalpies of Formation



Example 6.11 - Solution (Continued 4)

- How do we get there? (For octane)
 - What is the combustion reaction?

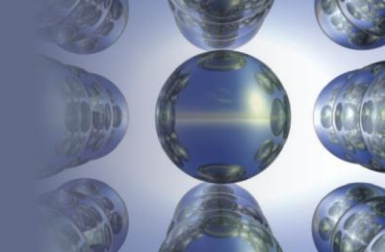


- What is the $\Delta H^\circ_{\text{reaction}}$?
 - Use the standard enthalpies of formation from Table 6.2 and the following equation:

$$\Delta H^\circ_{\text{reaction}} = \sum n_p \Delta H^\circ_f (\text{products}) - \sum n_r \Delta H^\circ_f (\text{reactants})$$

Section 6.4

Standard Enthalpies of Formation

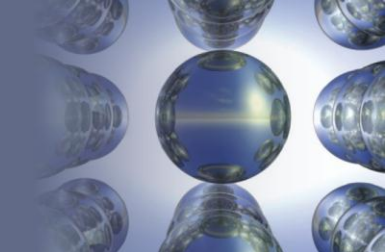


Example 6.11 - Solution (Continued 5)

$$\begin{aligned}\Delta H^{\circ}_{\text{reaction}} &= 16 \times \Delta H^{\circ}_{\text{f}} \text{ for } \text{CO}_2(g) + 18 \times \Delta H^{\circ}_{\text{f}} \text{ for } \text{H}_2\text{O}(l) \\ &\quad - 2 \times \Delta H^{\circ}_{\text{f}} \text{ for } \text{C}_8\text{H}_{18}(l) \\ &= 16 \times (-394 \text{ kJ}) + 18 \times (-286 \text{ kJ}) - 2 \times (-269 \text{ kJ}) \\ &= -1.09 \times 10^4 \text{ kJ}\end{aligned}$$

Section 6.4

Standard Enthalpies of Formation



Example 6.11 - Solution (Continued 6)

- What is the enthalpy of combustion per gram?
 - This is the amount of heat evolved when 2 moles of octane burn
 - Since the molar mass of octane is 114.22 g/mol, the enthalpy of combustion per gram of octane is

$$\frac{-1.09 \times 10^4 \text{ kJ}}{2(114.22 \text{ g})} = -47.7 \text{ kJ/g}$$

Section 6.4

Standard Enthalpies of Formation



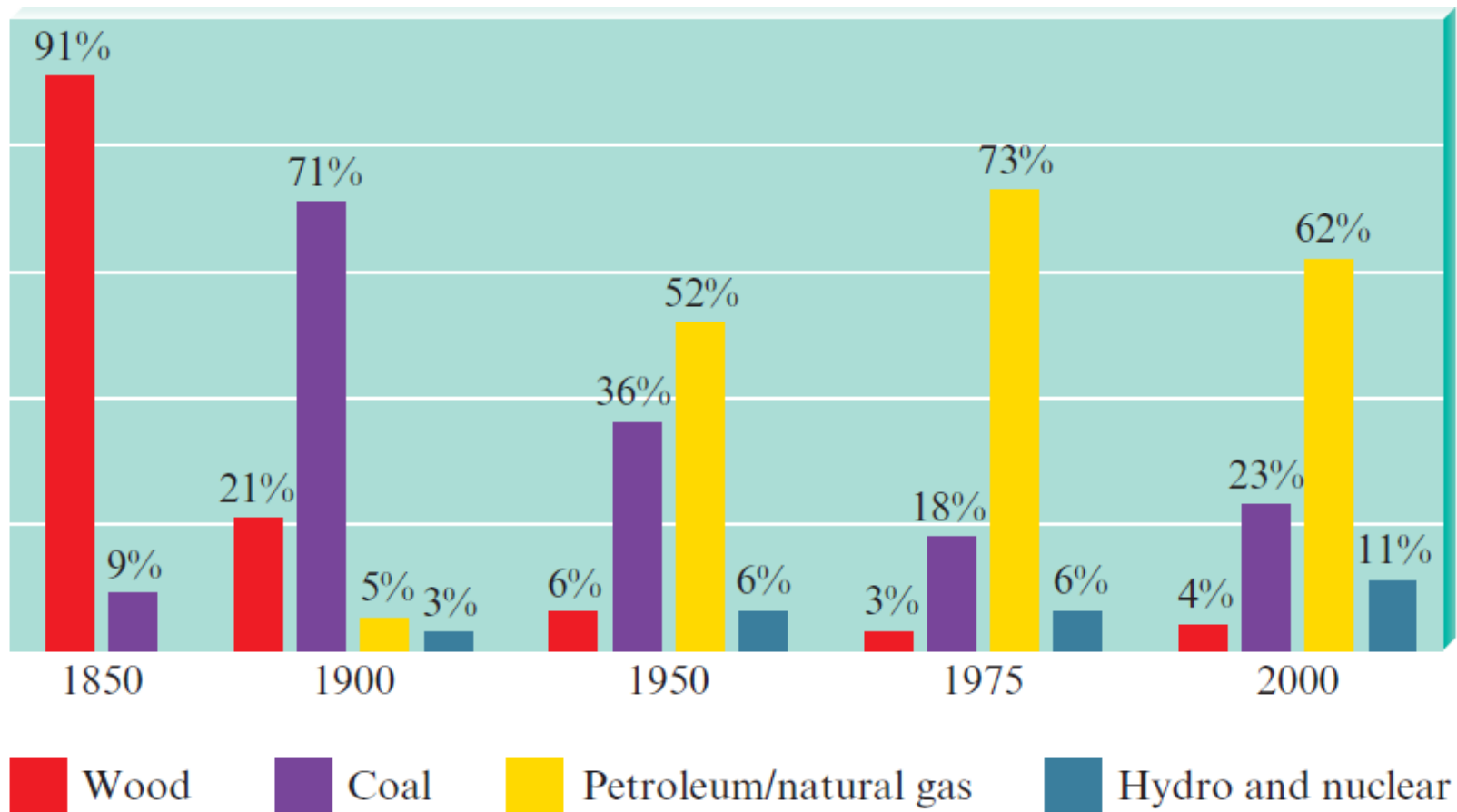
Example 6.11 - Solution (Continued 7)

- The enthalpy of combustion per gram of octane is approximately twice that per gram of methanol
 - Gasoline appears to be superior to methanol for use in a racing car, where weight considerations are usually very important
 - Methanol is used in racing cars since it burns much more smoothly than gasoline in high-performance engines
 - This advantage compensates for its weight disadvantage

Section 6.5

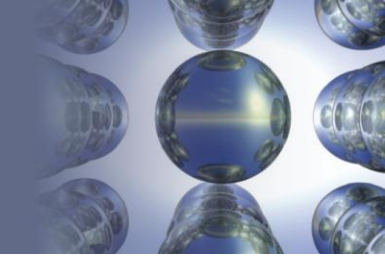
Present Sources of Energy

Figure 6.11 - Energy Sources Used in the United States



Section 6.5

Present Sources of Energy



Petroleum and Natural Gas

- Remains of marine organisms that lived approximately 500 million years ago
 - **Petroleum**: Thick, dark liquid that is mainly composed of hydrocarbons
 - **Natural gas**
 - Mostly consists of methane but also contains significant amounts of ethane, propane, and butane

Section 6.5

Present Sources of Energy

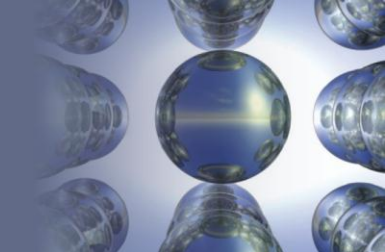
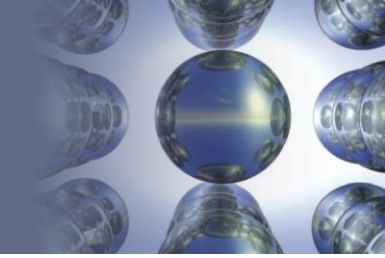


Table 6.3 - Names and Formulas for Some Common Hydrocarbons

Formula	Name
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane

Section 6.5

Present Sources of Energy

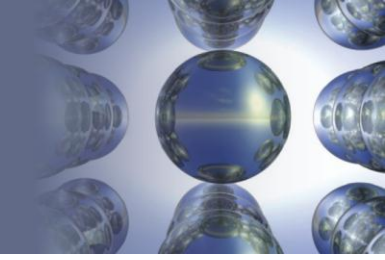


Natural Gas Reserves

- Exist in shale deposits
 - Shale is impermeable, and the gas does not flow out on its own
- Hydraulic fracturing or fracking is used to access shale deposits
 - Involves the injection of a slurry of water, sand, and chemical additives under pressure through a well bore
 - Poses environmental concerns

Section 6.5

Present Sources of Energy



Petroleum

- Mainly consists of hydrocarbons that have chains containing 5 to more than 25 carbons
- For efficient use, petroleum must be separated into fractions by boiling
 - Lighter molecules will boil away, and the heavier molecules will be left behind

Section 6.5

Present Sources of Energy

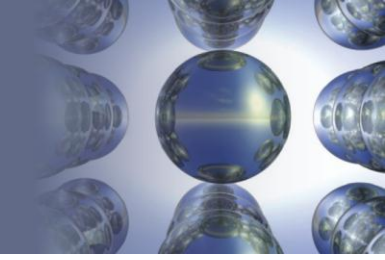


Table 6.4 - Uses of the Various Petroleum Fractions

Petroleum Fraction in Terms of Numbers of Carbon Atoms	Major Uses
C_5-C_{10}	Gasoline
$C_{10}-C_{18}$	Kerosene Jet fuel
$C_{15}-C_{25}$	Diesel fuel Heating oil Lubricating oil
$>C_{25}$	Asphalt

Section 6.5

Present Sources of Energy

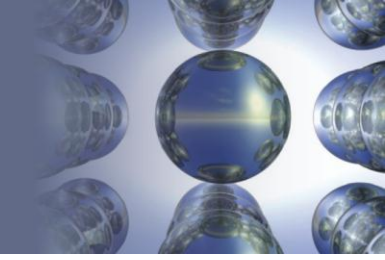


The Petroleum Era

- Industrial Revolution
 - Demand for lamp oil outstripped the traditional sources
 - Edwin Drake drilled the first oil well in 1859 at Titusville, Pennsylvania
 - Used the petroleum to produce kerosene

Section 6.5

Present Sources of Energy

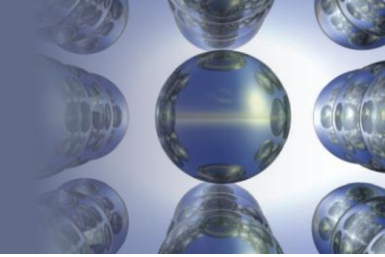


The Petroleum Era (Continued)

- Gasoline age - Marked by the decreased need for kerosene due to the invention of electric lights and the advent of cars
 - William Burton invented pyrolytic cracking
 - Pyrolytic (high-temperature) cracking - Process used to separate gasoline from petroleum
 - Tetraethyl lead was added to gasoline to promote smoother burning
 - Use of lead has been phased out due to environmental concerns

Section 6.5

Present Sources of Energy

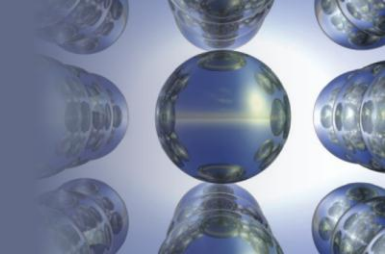


Coal

- Formed from the remains of buried plants that were subject to high pressure and heat over a long period of time
 - Plants contain cellulose (empirical formula CH_2O), a complex molecule with high molar mass (500,000 g/mol)
 - After the plants die, chemical changes decrease the oxygen and hydrogen content of cellulose molecules

Section 6.5

Present Sources of Energy



Coal (Continued)

- Stages of coal maturation
 - Lignite, subbituminous, bituminous, and anthracite
- Each stage has a higher carbon-to-oxygen and carbon-to-hydrogen ratio
 - Composition varies depending on the age and location
 - Available energy from combustion increases as the carbon content of a given mass of coal increases

Section 6.5

Present Sources of Energy

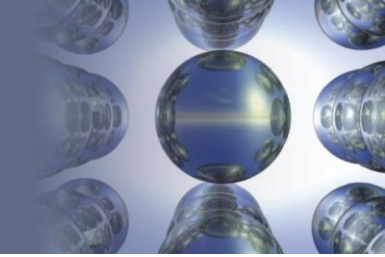
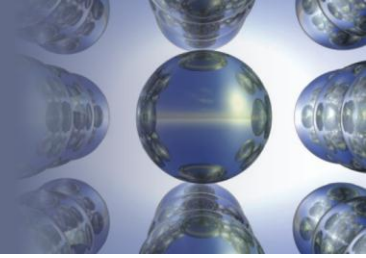


Table 6.5 - Elemental Composition of Various Types of Coal

Type of Coal	Mass Percent of Each Element				
	C	H	O	N	S
Lignite	71	4	23	1	1
Subbituminous	77	5	16	1	1
Bituminous	80	6	8	1	5
Anthracite	92	3	3	1	1

Section 6.5

Present Sources of Energy

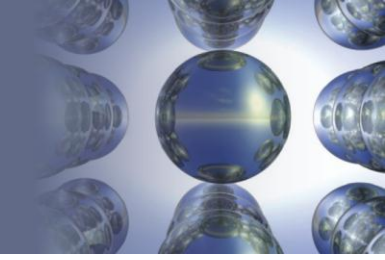


Coal as a Fuel - Disadvantages

- Expensive
- Dangerous to mine underground
- Burning high-sulfur coal leads to air pollution
 - Contributes to acid rain
- Carbon dioxide is produced when coal is burned
 - Significantly affects the earth's climate

Section 6.5

Present Sources of Energy



The Greenhouse Effect

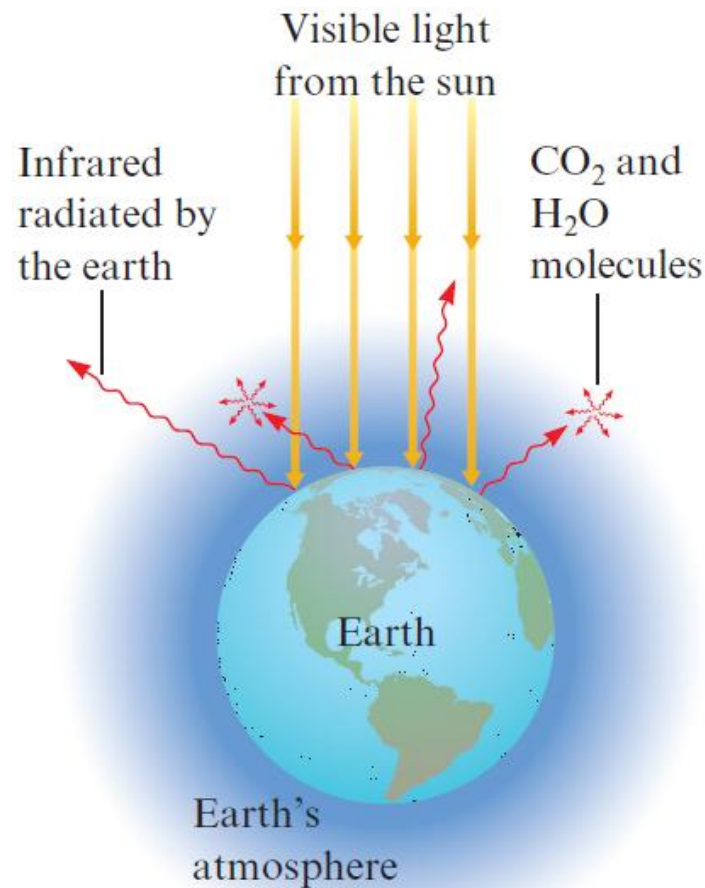
- The earth's atmosphere is transparent to visible light from the sun
 - Does not permit all infrared radiation to pass back into space
 - Molecules such as H_2O and CO_2 strongly absorb this radiation and radiate it back to the earth
 - Earth becomes warmer due to the amount of thermal energy retained by the atmosphere

Section 6.5

Present Sources of Energy

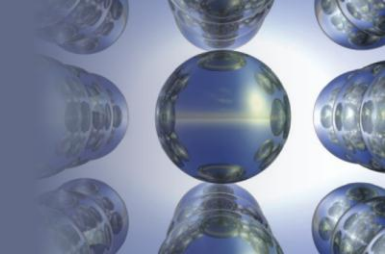


Figure 6.12 - Schematic of the Greenhouse Effect



Section 6.5

Present Sources of Energy

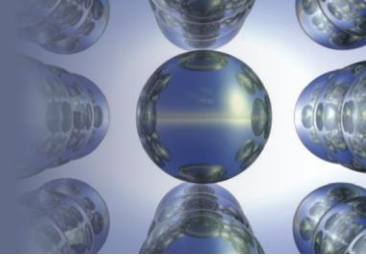


The Earth's Surface

- Temperature is controlled by water content of the atmosphere and greenhouse gases
 - The atmosphere's water content is controlled by the water cycle
- Extensive usage of fossil fuels has increased carbon dioxide concentration in the atmosphere
 - Increases the earth's average temperature
 - Causes dramatic climate changes and affects agriculture

Section 6.6

New Energy Sources



Potential Energy Sources

Sun

Nuclear
processes

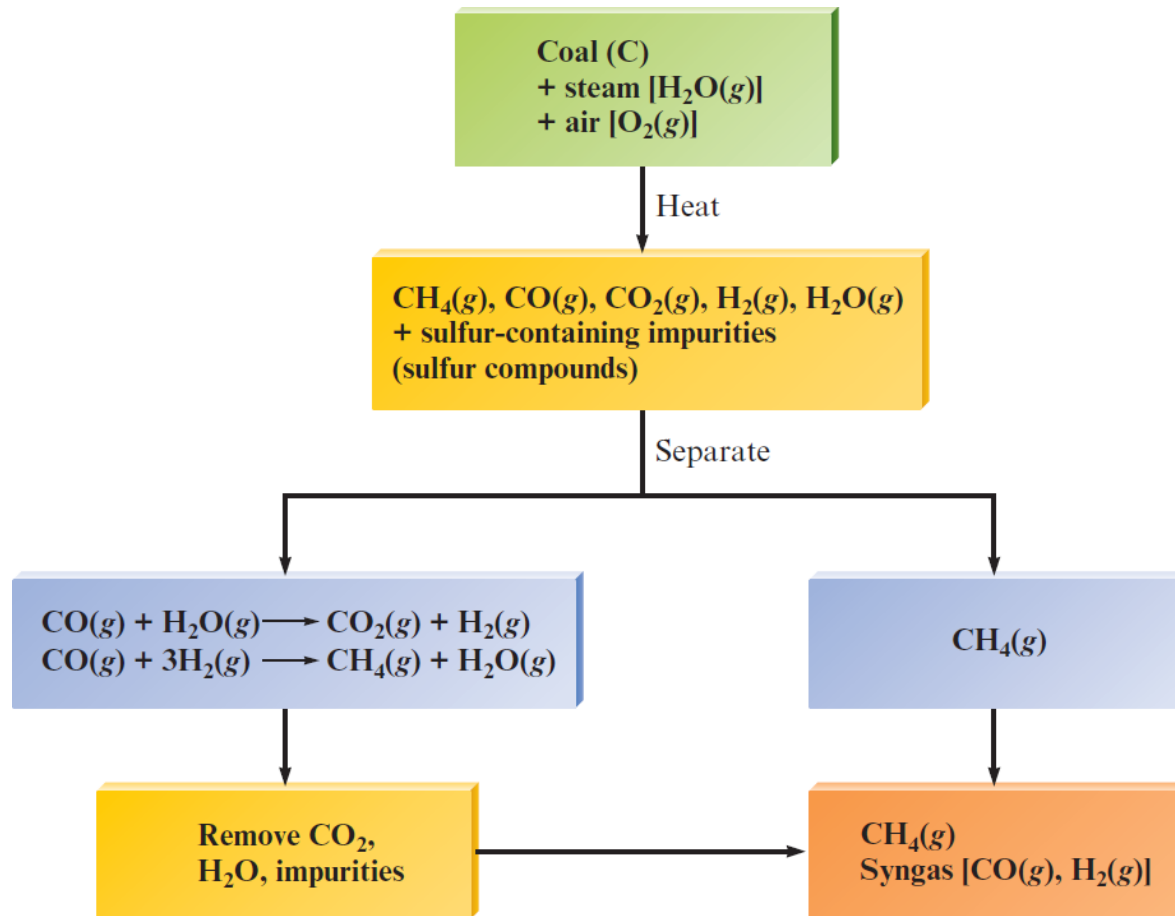
Biomass

Synthetic
fuels

Section 6.6

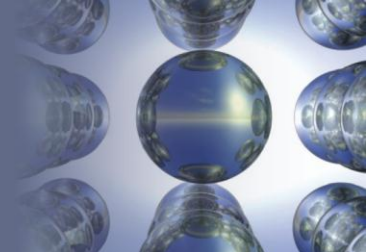
New Energy Sources

Figure 6.14 - Coal Gasification



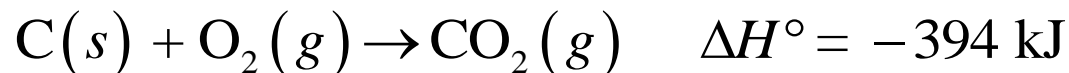
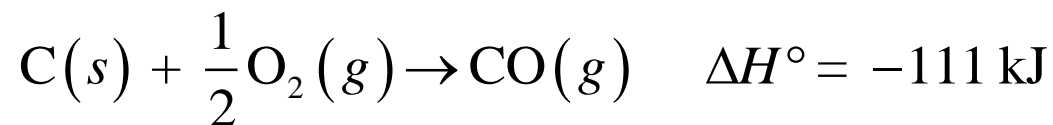
Section 6.6

New Energy Sources

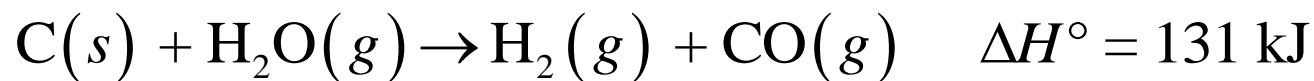


Reactions in Coal Gasification

■ Exothermic reactions

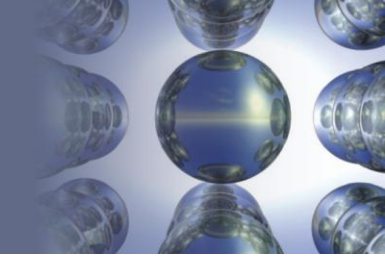


■ Endothermic reaction



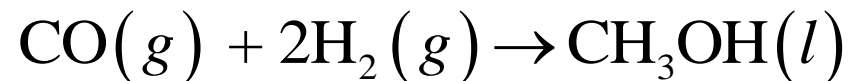
Section 6.6

New Energy Sources



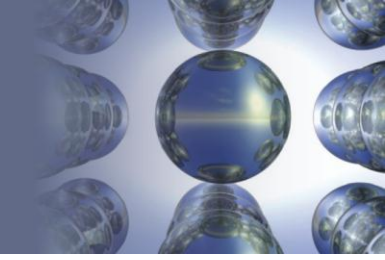
Syngas (Synthesis Gas)

- Mixture of carbon monoxide and hydrogen
- Uses
 - Can be used directly as fuel
 - Essential raw material in the production of other fuels
 - Syngas can be directly converted to methanol



Section 6.6

New Energy Sources

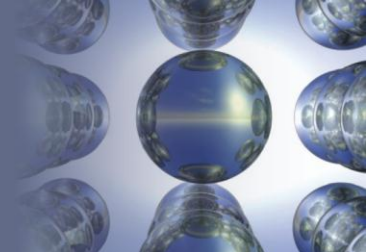


Formation of Coal Slurry

- Suspension of fine particles in a liquid
- Contains a mixture of pulverized coal and water
- Slurry can be handled, stored, and burned in a manner similar to that used for residual oil

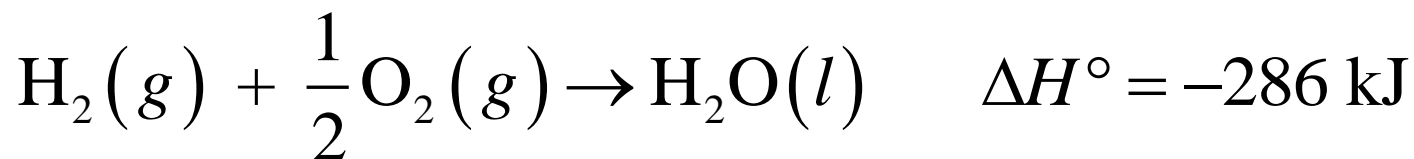
Section 6.6

New Energy Sources



Hydrogen as a Fuel

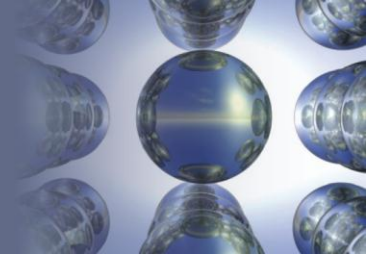
- Combustion reaction that demonstrates hydrogen's potential as a fuel:



- Since the reaction's product is water, hydrogen has an advantage over fossil fuels

Section 6.6

New Energy Sources

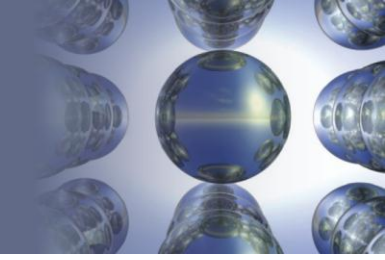


Hydrogen as a Fuel - Major Problem

- Cost of production
 - Main source of hydrogen gas is from the treatment of natural gas with steam
 - The reaction is highly endothermic
$$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow 3\text{H}_2(g) + \text{CO}(g)$$
 - Most methods for producing hydrogen require tremendous amounts of energy, which is not economically feasible

Section 6.6

New Energy Sources

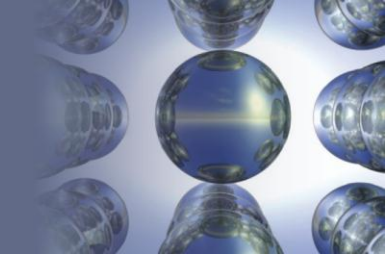


Alternate Sources of Hydrogen

- **Electrolysis of water**
 - Involves passing current through water
 - Not economically feasible due to the current cost of electricity
- **Corn**
 - Starch is fermented to produce alcohol that is decomposed in a reactor at 140° C with a rhodium and cerium oxide catalyst to give hydrogen

Section 6.6

New Energy Sources

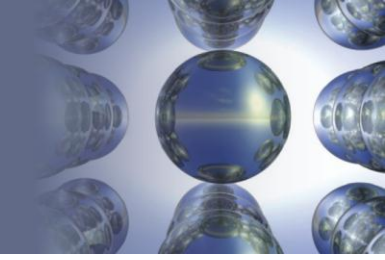


Alternate Sources of Hydrogen (Continued)

- **Thermal decomposition**
 - Involves heating water to several thousand degrees where it decomposes into hydrogen and oxygen
 - Expensive to attain high temperatures required for this process
- **Thermochemical decomposition**
 - Chemical reactions and heat are used to split water into its components

Section 6.6

New Energy Sources

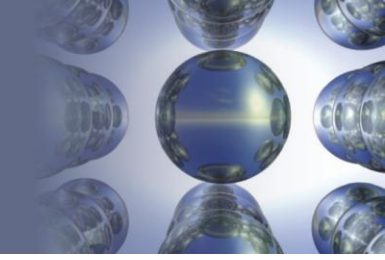


Hydrogen as a Fuel - Problems

- Storage and transportation
 - Hydrogen decomposes to atoms on metal surfaces, which may pose a potential leakage threat
 - Atoms may migrate into the metal and cause structural changes that make the metal brittle
 - Could cause harm to the atmosphere by raising atmospheric hydrogen levels
- Relatively small amount of energy is available per unit volume of hydrogen

Section 6.6

New Energy Sources

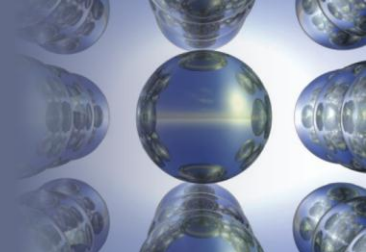


Example 6.12 - Enthalpies of Combustion

- Compare the energy available from the combustion of a given volume of methane and the same volume of hydrogen at the same temperature and pressure

Section 6.6

New Energy Sources

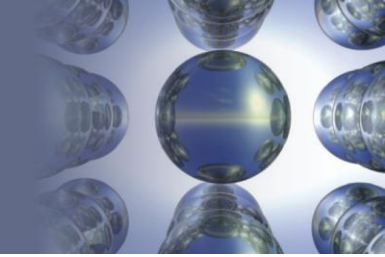


Example 6.12 - Solution

- We know that the heat released for the combustion of methane is 55 kJ/g CH_4 and for and hydrogen is 141 kJ/g H_2
- We also know from our study of gases that 1 mole of $\text{H}_2(g)$ has the same volume as 1 mole of $\text{CH}_4(g)$ at the same temperature and pressure (assuming ideal behavior)

Section 6.6

New Energy Sources



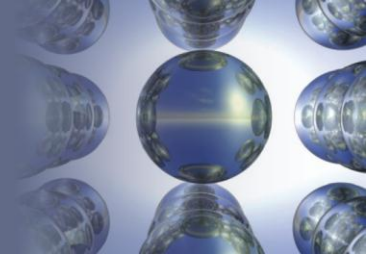
Example 6.12 - Solution (Continued 1)

- For molar volumes of both gases under the same conditions of temperature and pressure,

$$\frac{\text{Enthalpy of combustion of 1 molar volume of H}_2(g)}{\text{Enthalpy of combustion of 1 molar volume of CH}_4(g)}$$
$$= \frac{\text{enthalpy of combustion per mole of H}_2}{\text{enthalpy of combustion per mole of CH}_4}$$
$$= \frac{(-141 \cancel{\text{ kJ/g}})(2.02 \cancel{\text{ g H}_2/\text{mol H}_2})}{(-55 \cancel{\text{ kJ/g}})(16.04 \cancel{\text{ g CH}_4/\text{mol CH}_4})} = \frac{-285}{-882} \approx \frac{1}{3}$$

Section 6.6

New Energy Sources

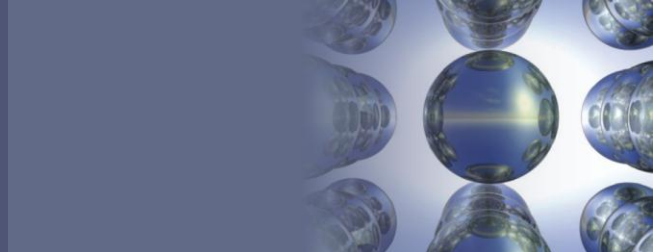


Example 6.12 - Solution (Continued 2)

- About three times the volume of hydrogen gas is needed to furnish the same energy as a given volume of methane

Section 6.6

New Energy Sources

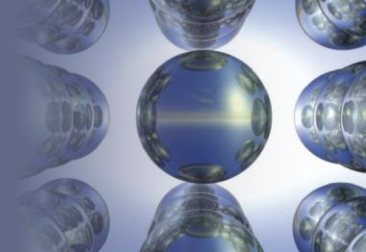


Interactive Example 6.13 - Comparing Enthalpies of Combustion

- Assuming that the combustion of hydrogen gas provides three times as much energy per gram as gasoline, calculate the volume of liquid H_2 (density = 0.0710 g/mL) required to furnish the energy contained in 80.0 L (about 20 gal) of gasoline (density = 0.740 g/mL)
 - Calculate also the volume that this hydrogen would occupy as a gas at 1.00 atm and 25° C

Section 6.6

New Energy Sources

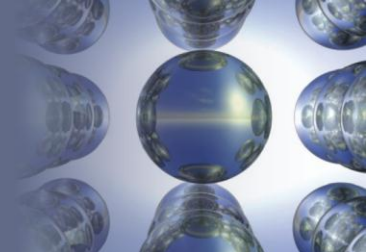


Interactive Example 6.13 - Solution

- Where are we going?
 - To calculate the volume of $\text{H}_2(l)$ required and its volume as a gas at the given conditions
- What do we know?
 - Density for $\text{H}_2(l) = 0.0710 \text{ g/mL}$
 - 80.0 L gasoline
 - Density for gasoline = 0.740 g/mL
 - $\text{H}_2(g) \Rightarrow P = 1.00 \text{ atm}, T = 25^\circ \text{ C} = 298 \text{ K}$

Section 6.6

New Energy Sources



Interactive Example 6.13 - Solution (Continued 1)

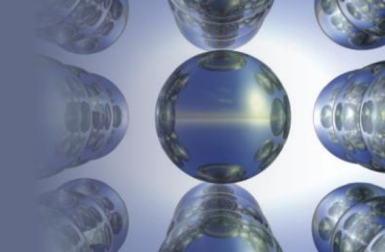
- How do we get there?
 - What is the mass of gasoline?

$$80.0 \cancel{\text{ L}} \times \frac{1000 \cancel{\text{ mL}}}{1 \cancel{\text{ L}}} \times \frac{0.740 \text{ g}}{\cancel{\text{ mL}}} = 59,200 \text{ g}$$

- How much $\text{H}_2(l)$ is needed?
 - Since H_2 furnishes three times as much energy per gram as gasoline, only a third as much liquid hydrogen is needed to furnish the same energy

Section 6.6

New Energy Sources



Interactive Example 6.13 - Solution (Continued 2)

$$\text{Mass of H}_2(l) \text{ needed} = \frac{59,200 \text{ g}}{3} = 19,700 \text{ g}$$

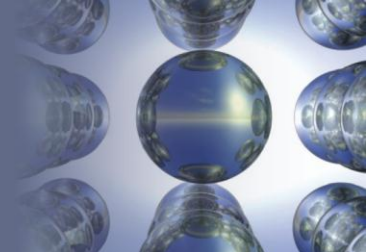
- Since density = mass/volume, then volume = mass/density, and the volume of H₂(l) needed is

$$V = \frac{19,700 \cancel{\text{ g}}}{0.0710 \cancel{\text{ g}}/\text{mL}} = 2.77 \times 10^5 \text{ mL} = 277 \text{ L}$$

- Thus, 277 L of liquid H₂ is needed to furnish the same energy of combustion as 80.0 L of gasoline

Section 6.6

New Energy Sources



Interactive Example 6.13 - Solution (Continued 3)

- What is the volume of the $\text{H}_2(g)$?
 - To calculate the volume that this hydrogen would occupy as a gas at 1.00 atm and 25°C , we use the ideal gas law:

$$PV = nRT$$

- In this case:

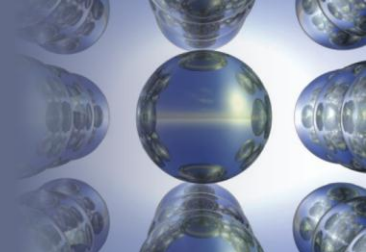
$$P = 1.00 \text{ atm}$$

$$T = 273 + 25^\circ\text{C} = 298 \text{ K}$$

$$R = 0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$$

Section 6.6

New Energy Sources



Interactive Example 6.13 - Solution (Continued 4)

- What are the moles of $\text{H}_2(g)$?

$$n = 19,700 \text{ g } \cancel{\text{H}_2} \times \frac{1 \text{ mol } \text{H}_2}{2.016 \text{ g } \cancel{\text{H}_2}} = 9.77 \times 10^3 \text{ mol } \text{H}_2$$

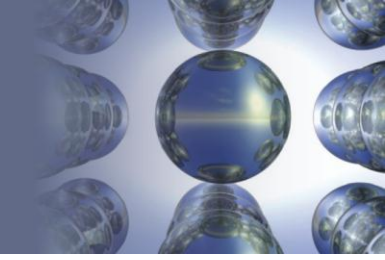
- Thus,

$$V = \frac{nRT}{P} = \frac{(9.77 \times 10^3 \text{ mol}) (0.08206 \text{ L} \cdot \cancel{\text{atm}} / \cancel{\text{K}} \cdot \cancel{\text{mol}}) (298 \cancel{\text{K}})}{1.00 \cancel{\text{atm}}}$$
$$= 2.39 \times 10^5 \text{ L} = 239,000 \text{ L}$$

- At 1 atm and 25°C , the hydrogen gas needed to replace 20 gal of gasoline occupies a volume of 239,000 L

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New Energy Sources

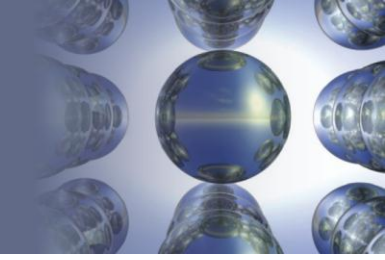


Other Energy Alternatives

- Oil shale deposits
 - Consist of a complex carbon-based material called kerogen
 - Difficult to extract
- Ethanol and methanol
 - Produced through fermentation
 - Alternative fuel for car engines

Section 6.6

New Energy Sources



Other Energy Alternatives (Continued)

- **Seed oil**
 - Oil seeds are processed to produce an oil that is mainly composed of carbon and hydrogen
 - This oil would react with oxygen to produce carbon dioxide, water, and heat
 - **Advantage - Renewability**