

Chapter 16

Preview

- Objectives
- Thermochemistry
- Heat and Temperature
- Specific Heat
- Enthalpy of Reaction
- Enthalpy of Formation
- Stability and Enthalpy of Formation
- Enthalpy of Combustion
- Calculating Enthalpies of Reaction
- Determining Enthalpy of Formation

< Back

Next >

Preview 

Main 

Objectives

- **Define** *temperature* and state the units in which it is measured. ▼
- **Define** *heat* and state its units. ▼
- **Perform** specific-heat calculations. ▼
- **Explain** enthalpy change, enthalpy of reaction, enthalpy of formation, and enthalpy of combustion. ▼
- **Solve** problems involving enthalpies of reaction, enthalpies of formation, and enthalpies of combustion.



Thermochemistry ▼

- Virtually every chemical reaction is accompanied by a change in energy. ▼
- Chemical reactions usually either absorb or release energy as heat. ▼
- **Thermochemistry** is the study of the transfers of energy as heat that accompany chemical reactions and physical changes.



Heat and Temperature ▼

- The energy absorbed or released as heat in a chemical or physical change is measured in a **calorimeter**. ▼
- In one kind of calorimeter, known quantities of reactants are sealed in a reaction chamber that is immersed in a known quantity of water. ▼
 - Energy given off by the reaction is absorbed by the water, and the temperature change of the water is measured. ▼
 - From the temperature change of the water, it is possible to calculate the energy as heat given off by the reaction.



Heat and Temperature, *continued* ▼

- **Temperature** is a measure of the average kinetic energy of the particles in a sample of matter. ▼
 - The greater the kinetic energy of the particles in a sample, the hotter it feels. ▼
- For calculations in thermochemistry, the Celsius and Kelvin temperature scales are used. Celsius and Kelvin temperatures are related by the following equation. ▼

$$K = 273.15 + ^\circ C$$



Heat and Temperature, *continued* ▼

- The amount of energy transferred as heat is usually measured in joules. ▼
- A **joule** is the SI unit of heat as well as all other forms of energy. ▼
- **Heat** can be thought of as the energy transferred between samples of matter because of a difference in their temperatures. ▼
- Energy transferred as heat always moves spontaneously from matter at a higher temperature to matter at a lower temperature.



Specific Heat ▼

- The amount of energy transferred as heat during a temperature change depends on the nature of the material changing temperature, and on its mass. ▼
- The specific heat of a substance is the amount of energy required to raise the temperature of one gram by one Celsius degree (1°C) or one kelvin (1 K). ▼
 - The temperature difference as measured in either Celsius degrees or kelvins is the same.



Specific Heat, *continued* ▾

- Values of specific heat are usually given in units of joules per gram per Celsius degree, $\text{J}/(\text{g}\cdot^{\circ}\text{C})$, or joules per gram per kelvin, $\text{J}/(\text{g}\cdot\text{K})$.



Molar Heat Capacities of Elements and Compounds

Element	C (J/K•mol)	Compound	C (J/K•mol)
Aluminum, Al(<i>s</i>)	24.2	Aluminum chloride, AlCl ₃ (<i>s</i>)	92.0
Argon, Ar(<i>g</i>)	20.8	Barium chloride, BaCl ₂ (<i>s</i>)	75.1
Helium, He(<i>g</i>)	20.8	Cesium iodide, CsI(<i>s</i>)	51.8
Iron, Fe(<i>s</i>)	25.1	Octane, C ₈ H ₁₈ (<i>l</i>)	254.0
Mercury, Hg(<i>l</i>)	27.8	Sodium chloride, NaCl(<i>s</i>)	50.5
Nitrogen, N ₂ (<i>g</i>)	29.1	Water, H ₂ O(<i>g</i>)	36.8
Silver, Ag(<i>s</i>)	25.3	Water, H ₂ O(<i>l</i>)	75.3
Tungsten W(<i>s</i>)	24.2	Water, H ₂ O(<i>s</i>)	37.4

Specific Heat, *continued* ▼

- Specific heat is calculated according to the equation given below. ▼

$$c_p = \frac{q}{m \times \Delta T} \quad \blacktriangledown$$

- c_p is the specific heat at a given pressure, q is the energy lost or gained, m is the mass of the sample, and ΔT is the difference between the initial and final temperatures. ▼
- The above equation can be rearranged to give an equation that can be used to find the quantity of energy gained or lost with a change of temperature. ▼

$$q = c_p \times m \times \Delta T$$



Equation for Specific Heat

Click below to watch the Visual Concept.

[Visual Concept](#)

Specific Heat, *continued*

Sample Problem A ▼

A 4.0 g sample of glass was heated from 274 K to 314 K, a temperature increase of 40. K, and was found to have absorbed 32 J of energy as heat. ▼

- What is the specific heat of this type of glass? ▼
- How much energy will the same glass sample gain when it is heated from 314 K to 344 K?



Specific Heat, *continued*

Sample Problem A Solution ▾

Given: $m = 4.0 \text{ g}$ ▾

$$\Delta T = 40. \text{ K} \quad \nabla$$

$$q = 32 \text{ J} \quad \nabla$$

Unknown: a. c_p in $\text{J}/(\text{g}\cdot\text{K})$ ▾

b. q for ΔT of $314 \text{ K} \rightarrow 344 \text{ K}$ ▾

Solution: ▾

$$\text{a.} \quad c_p = \frac{q}{m \times \Delta T} = \frac{32 \text{ J}}{(4.0 \text{ g})(40. \text{ K})} = 0.20 \text{ J}/(\text{g}\cdot\text{K})$$



Specific Heat, *continued*

Sample Problem A Solution, *continued* ▼

Solution: ▼

b. $q = c_p \times m \times \Delta T$ ▼

$$q = \frac{0.20 \text{ J}}{(\text{g} \cdot \text{K})} (4.0 \text{ g})(344 \text{ K} - 314 \text{ K})$$
 ▼

$$q = \frac{0.20 \text{ J}}{(\text{g} \cdot \text{K})} (4.0 \text{ g})(30 \text{ K}) = 24 \text{ J}$$



Enthalpy of Reaction ▼

- The energy absorbed as heat during a chemical reaction at constant pressure is represented by ΔH . H is the symbol for a quantity called *enthalpy*. ▼
- Only *changes* in enthalpy can be measured. ΔH is read as “change in enthalpy.” ▼
- An **enthalpy change** is the amount of energy absorbed by a system as heat during a process at constant pressure.



Enthalpy of Reaction, *continued* ▼

- Enthalpy change is always the difference between the enthalpies of products and reactants. ▼

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

- A chemical reaction that releases energy is *exothermic*, and the energy of the products is less than the energy of the reactants. ▼

- *example:* ▼



Enthalpy of Reaction, *continued* ▾



- The expression above is an example of a **thermochemical equation**, an equation that includes the quantity of energy released or absorbed as heat during the reaction as written. ▾
- Chemical coefficients in a thermochemical equation should be interpreted as numbers of moles and never as numbers of molecules.



Enthalpy of Reaction, *continued* ▼

- The quantity of energy released is proportional to the quantity of the reactions formed. ▼
 - Producing twice as much water in the equation shown on the previous slide would require twice as many moles of reactants and would release 2×483.6 kJ of energy as heat.



Enthalpy of Reaction, *continued* ▼

- In an *endothermic* reaction, the products have a higher energy than the reactants, and the reaction absorbs energy. ▼

- *example:* ▼



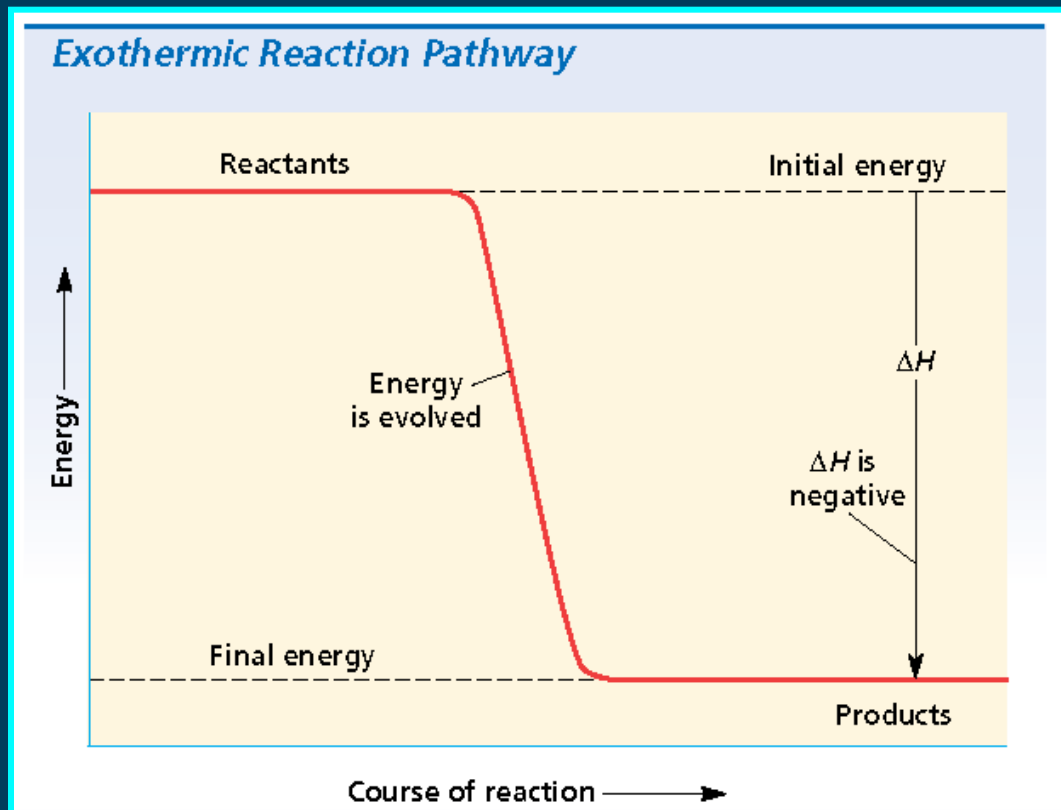
- The physical states of reactants and products must always be included in thermochemical equations, because the states of reactants and products influence the overall amount of energy exchanged.



Enthalpy of Reaction, *continued* ▼

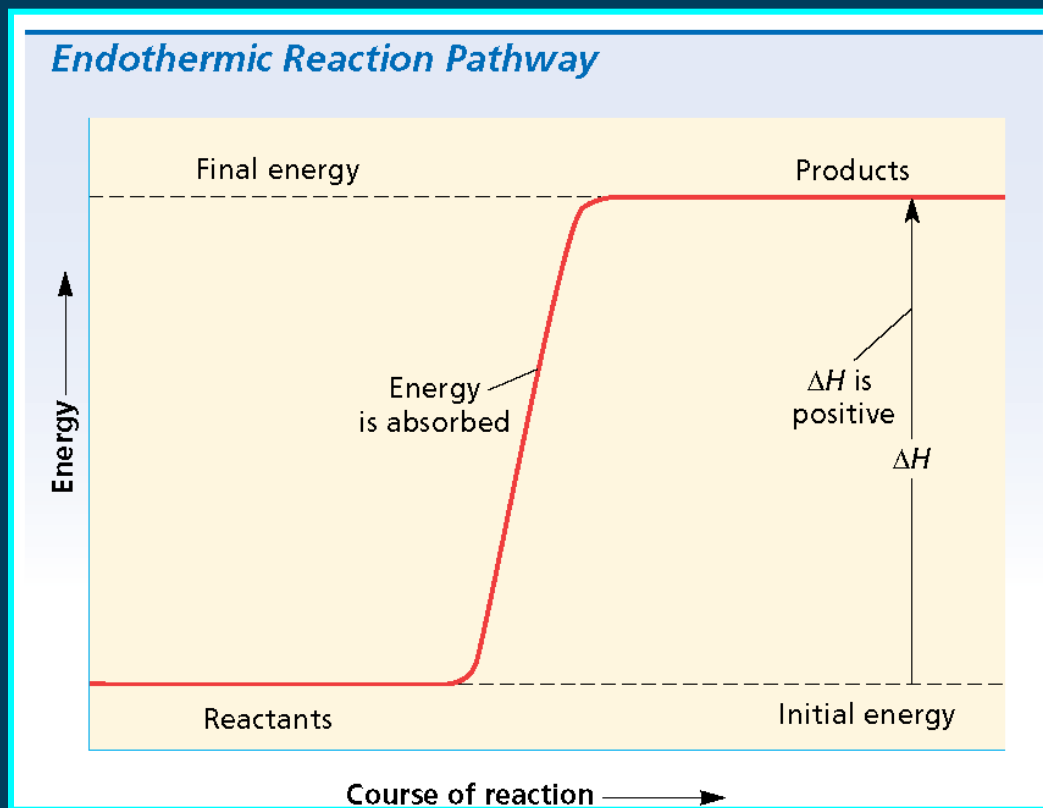
- Thermochemical equations are usually written by designating a ΔH value rather than writing the energy as a reactant or product. ▼
- For an exothermic reaction, ΔH is negative because the system loses energy. ▼
 - The thermochemical equation for the exothermic reaction previously discussed will look like the following: ▼



Enthalpy of Reaction, *continued* ▾

- In an exothermic reaction, energy is evolved, or given off, during the reaction; ΔH is negative.



Enthalpy of Reaction, *continued* ▾

- In an endothermic reaction, energy is absorbed; in this case, ΔH is designated as positive.



Enthalpy of Formation ▼

- The **molar enthalpy of formation** is the enthalpy change that occurs when one mole of a compound is formed from its elements in their standard state at 25°C and 1 atm. ▼
 - Enthalpies of formation are given for a standard temperature and pressure so that comparisons between compounds are meaningful. ▼
- To signify standard states, a ⁰ sign is added to the enthalpy symbol, and the subscript *f* indicates a standard enthalpy of formation: ΔH_f^0



Enthalpy of Formation, *continued* ▼

- Some standard enthalpies of formation are given in the appendix of your book. ▼
- Each entry in the table is the enthalpy of formation for the synthesis of *one mole* of the compound from its elements in their standard states. ▼
- The thermochemical equation to accompany an enthalpy of formation shows the formation of one mole of the compound from its elements in their standard states.



Stability and Enthalpy of Formation ▼

- Compounds with a large negative enthalpy of formation are very stable. ▼
 - **example:** the ΔH_f^0 of carbon dioxide is -393.5 kJ per mol of gas produced. ▼
 - Elements in their standard states are defined as having $\Delta H_f^0 = 0$. ▼
 - This indicates that carbon dioxide is more stable than the elements from which it was formed.



Stability and Enthalpy of Formation, *continued* ▼

- Compounds with positive values of enthalpies of formation are typically unstable. ▼
 - **example:** hydrogen iodide, HI, has a ΔH_f^0 of +26.5 kJ/mol. ▼
 - It decomposes at room temperature into violet iodine vapor, I₂, and hydrogen, H₂.



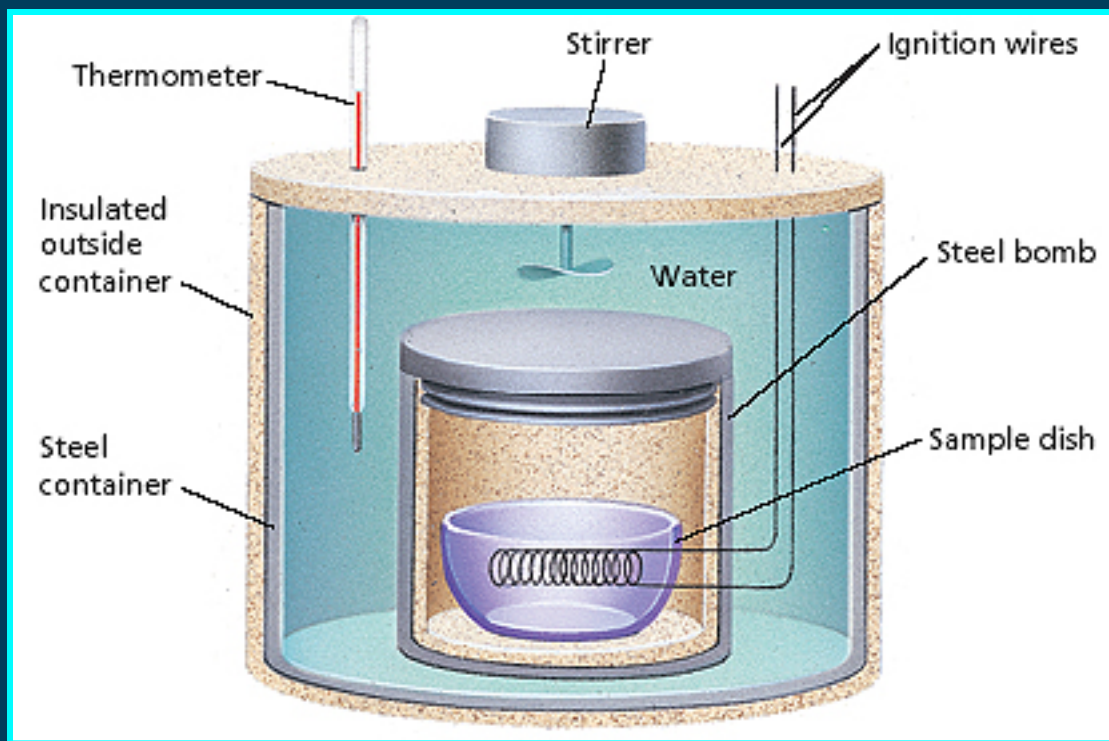
Enthalpy of Combustion ▼

- The enthalpy change that occurs during the complete combustion of one mole of a substance is called the **enthalpy of combustion** of the substance. ▼
- Enthalpy of combustion is defined in terms of *one mole of reactant*, whereas the enthalpy of formation is defined in terms of *one mole of product*. ▼
- ΔH with a subscripted *c*, ΔH_c , refers specifically to enthalpy of combustion.



Enthalpy of Combustion, *continued* ▾

- A combustion calorimeter, shown below, is a common instrument used to determine enthalpies of combustion.



End
Of
Slide

< Back

Next >

Preview 

Main 

Calculating Enthalpies of Reaction ▼

- The basis for calculating enthalpies of reaction is known as **Hess' s law**: the overall enthalpy change in a reaction is equal to the sum of enthalpy changes for the individual steps in the process. ▼
- This means that the energy difference between reactants and products is independent of the route taken to get from one to the other.



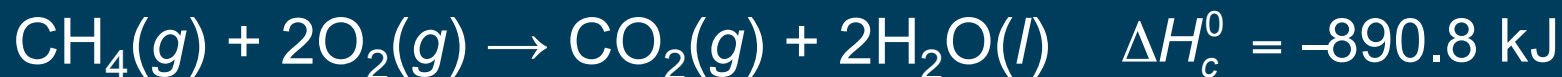
Calculating Enthalpies of Reaction, *continued* ▼

- If you know the reaction enthalpies of individual steps in an overall reaction, you can calculate the overall enthalpy without having to measure it experimentally. ▼
- To demonstrate how to apply Hess's law, we will work through the calculation of the enthalpy of formation for the formation of methane gas, CH₄, from its elements, hydrogen gas and solid carbon: ▼



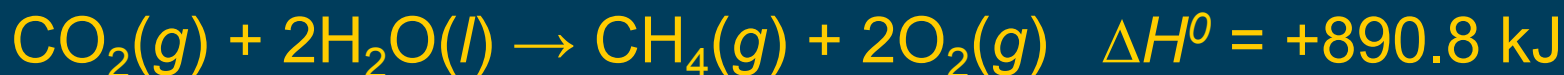
Calculating Enthalpies of Reaction, *continued* ▼

- The component reactions in this case are the combustion reactions of carbon, hydrogen, and methane: ▼



Calculating Enthalpies of Reaction, *continued* ▼

- The overall reaction involves the formation rather than the combustion of methane, so the combustion equation for methane is reversed, and its enthalpy changed from negative to positive: ▼



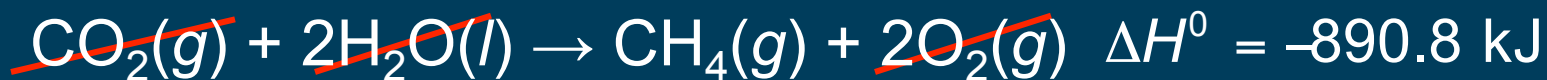
Calculating Enthalpies of Reaction, *continued* ▼

- Because 2 moles of water are used as a reactant in the above reaction, 2 moles of water will be needed as a product. ▼
- Therefore, the coefficients for the formation of water reaction, as well as its enthalpy, need to be multiplied by 2: ▼



Calculating Enthalpies of Reaction, *continued*

- We are now ready to add the three equations together using Hess' s law to give the enthalpy of formation for methane and the balanced equation.



$$\Delta H_f^0 = -74.3 \text{ kJ}$$



Calculating Enthalpies of Reaction, *continued* ▼

- Using Hess's law, any enthalpy of reaction may be calculated using enthalpies of formation for all the substances in the reaction of interest, without knowing anything else about how the reaction occurs. ▼
- Mathematically, the overall equation for enthalpy change will be in the form of the following equation: ▼

$$\Delta H^0 = \text{sum of } [(\Delta H_f^0 \text{ of products}) \times (\text{mol of products})] \\ - \text{sum of } [(\Delta H_f^0 \text{ of reactants}) \times (\text{mol of reactants})]$$



Calculating Enthalpies of Reaction, *continued*

Sample Problem B

Calculate the enthalpy of reaction for the combustion of nitrogen monoxide gas, NO, to form nitrogen dioxide gas, NO₂, as given in the following equation. ▼



Use the enthalpy-of-formation data in the appendix. Solve by combining the known thermochemical equations.



Calculating Enthalpies of Reaction, *continued*

Sample Problem B Solution ▾



Solution: ▾

Using Hess's law, combine the given thermochemical equations in such a way as to obtain the unknown equation, and its ΔH° value.



Calculating Enthalpies of Reaction, *continued*

Sample Problem B Solution, *continued* ▼

The desired equation is:



Reversing the first given reaction and its sign yields the following thermochemical equation:



The other equation should have NO_2 as a product, so we can use the second given equation as is:



Calculating Enthalpies of Reaction, *continued*

Sample Problem B Solution, *continued* ▼

We can now add the equations and their ΔH^0 values to obtain the unknown ΔH^0 value. ▼



Determining Enthalpy of Formation ▼

- When carbon is burned in a limited supply of oxygen, carbon monoxide is produced: ▼



- The above overall reaction consists of two reactions: ▼
 - 1) carbon is oxidized to carbon dioxide ▼
 - 2) carbon dioxide is reduced to give carbon monoxide.



Determining Enthalpy of Formation, *continued* ▼

- Because these two reactions occur simultaneously, it is not possible to directly measure the enthalpy of formation of $\text{CO}(g)$ from $\text{C}(s)$ and $\text{O}_2(g)$. ▼
- We do know the enthalpy of formation of carbon dioxide and the enthalpy of combustion of carbon monoxide: ▼



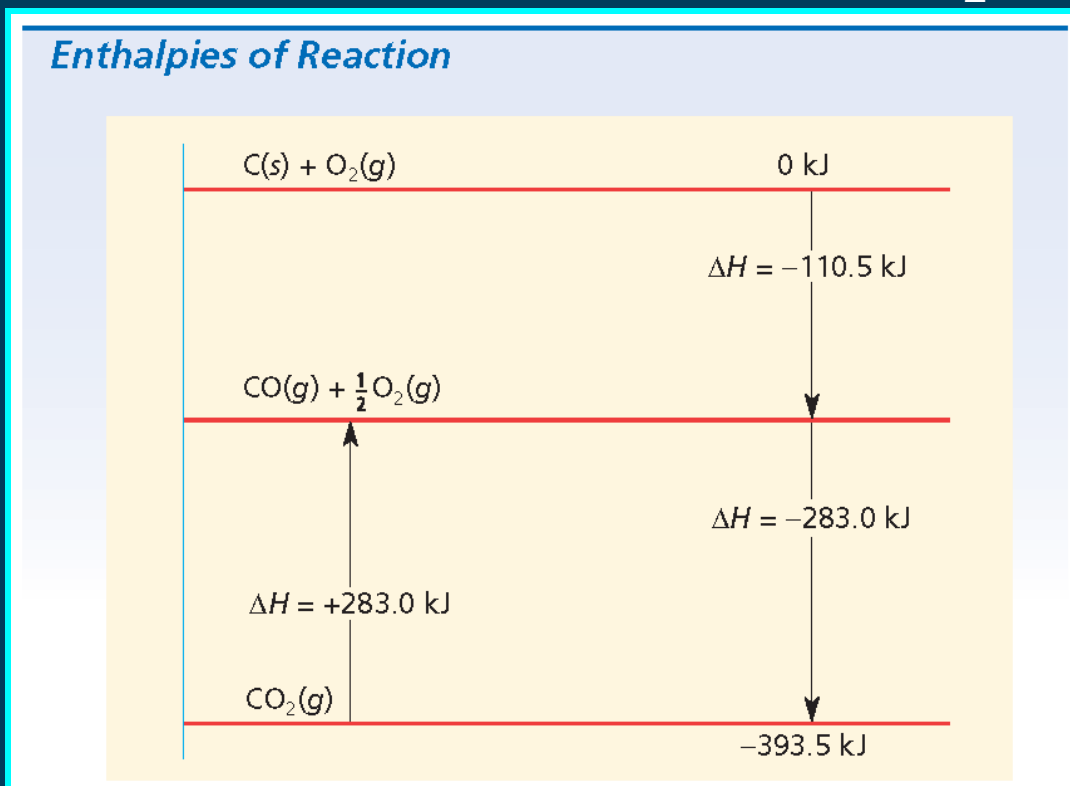
Determining Enthalpy of Formation, *continued*

- We reverse the second equation because we need CO as a product. Adding gives the desired enthalpy of formation of carbon monoxide. ▼



Determining Enthalpy of Formation, *continued*

- The graph below models the process just described. It shows the enthalpies of reaction for CO_2 and CO .



End
Of
Slide

< Back

Next >

Preview

Main

Determining Enthalpy of Formation, *continued*

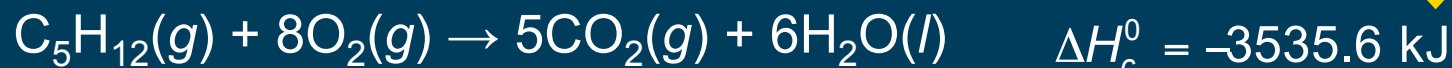
Sample Problem C ▾

Calculate the enthalpy of formation of pentane, C_5H_{12} , using the information on enthalpies of formation and the information on enthalpies of combustion in the appendix. Solve by combining the known thermochemical equations.



Determining Enthalpy of Formation, *continued*

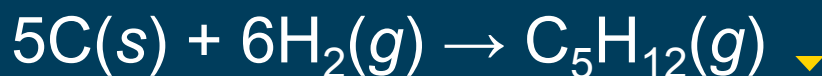
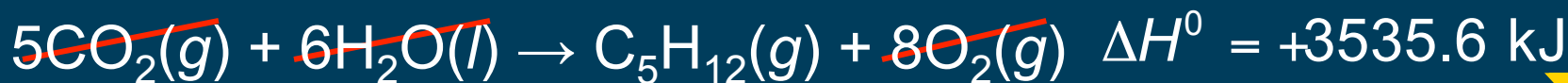
Sample Problem C Solution ▼



Solution: ▼

Combine the given equations according to Hess' s law.



Determining Enthalpy of Formation, *continued*Sample Problem C Solution, *continued* ▼

$$\Delta H_f^0 = -145.7 \text{ kJ}$$



Preview

- Objectives
- Enthalpy and Reaction Tendency
- Free Energy

Chapter 16

Section 2 Driving Force of Reactions

Objectives ▼

- **Explain** the relationship between enthalpy change and the tendency of a reaction to occur. ▼
- **Explain** the relationship between entropy change and the tendency of a reaction to occur. ▼
- **Discuss** the concept of free energy, and explain how the value of this quantity is calculated and interpreted. ▼
- **Describe** the use of free energy change to determine the tendency of a reaction to occur.



< Back

Next >

Preview 

Main 

Enthalpy and Reaction Tendency ▼

- The great majority of chemical reactions in nature are exothermic. ▼
 - The tendency throughout nature is for a reaction to proceed in a direction that leads to a lower energy state. ▼
- Some endothermic reactions *do* occur spontaneously. ▼
- Something other than enthalpy change can help determine whether a reaction will occur.



Entropy and Reaction Tendency ▼

- Melting is one example of a naturally occurring endothermic process. ▼
 - An ice cube melts spontaneously at room temperature as energy is transferred from the warm air to the ice. ▼
- The well-ordered arrangement of water molecules in the ice crystal is lost, and the less-ordered liquid phase of higher energy content is formed. ▼
- A system that can go from one state to another without an enthalpy change does so with an increase in *entropy*.



Entropy and Reaction Tendency, *continued*

- The decomposition of ammonium nitrate:



- On the left side are 2 mol of solid ammonium nitrate.
- The right-hand side of the equation shows 3 mol of gaseous molecules plus 4 mol of a liquid.
- The arrangement of particles on the right-hand side of the equation is more random than the arrangement on the left side and hence is less ordered.



Entropy and Reaction Tendency, *continued* ▼

- There is a tendency in nature to proceed in a direction that increases the randomness of a system. ▼
 - A random system is one that lacks a regular arrangement of its parts. ▼
- This tendency toward randomness is called *entropy*. ▼
- **Entropy**, S , can be defined in a simple qualitative way as a measure of the degree of randomness of the particles, such as molecules, in a system.



Chapter 16

Section 2 Driving Force of Reactions

Standard Entropy Changes for Some Reactions

Reaction	Entropy change, ΔS (J/K)
$\text{CaCO}_3(s) + 2\text{H}_3\text{O}^+(aq) \longrightarrow \text{Ca}^{2+}(aq) + \text{CO}_2(g) + 3\text{H}_2\text{O}(l)$	138
$\text{NaCl}(s) \longrightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$	43
$\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$	25
$\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$	-5
$2\text{Na}(s) + \text{Cl}_2(g) \longrightarrow 2\text{NaCl}(s)$	-181
$2\text{NO}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$	-176

< Back

Next >

Preview 

Main 

Entropy and Reaction Tendency, *continued* ▼

- To understand the concept of entropy, consider the comparison between particles in solids, liquids, and gases. ▼
 - In a solid, the particles are in fixed positions, and we can easily determine the locations of the particles. ▼
 - In a liquid, the particles are very close together, but they can move around. Locating an individual particle is more difficult. The system is more random, and the entropy is higher.



Entropy and Reaction Tendency, *continued* ▾

- In a gas, the particles are moving rapidly and are far apart. Locating an individual particle is much more difficult, and the system is much more random. The entropy is even higher.



Chapter 16

Section 2 Driving Force of Reactions

Entropy

Click below to watch the Visual Concept.

[Visual Concept](#)

[< Back](#)

[Next >](#)

[Preview](#) 

[Main](#) 

Entropy and Reaction Tendency, *continued* ▼

- Absolute entropy, or standard molar entropy, of substances are recorded in tables and reported in units of $\text{kJ}/(\text{mol}\cdot\text{K})$. ▼
- Entropy change, which can also be measured, is defined as the difference between the entropy of the products and the reactants. ▼
- An increase in entropy is represented by a positive value for ΔS , and a decrease in entropy is represented by a negative value for ΔS .



Free Energy ▼

- Processes in nature are driven in two directions: toward least enthalpy and toward largest entropy. ▼
- As a way to predict which factor will dominate for a given system, a function has been defined to relate the enthalpy and entropy factors at a given temperature and pressure. ▼
- This combined enthalpy-entropy function is called the **free energy**, G , of the system; it is also called *Gibbs free energy*.



Free Energy, *continued* ▼

- Only the *change* in free energy can be measured. It can be defined in terms of enthalpy and entropy. ▼
- At a constant pressure and temperature, the free-energy change, ΔG , of a system is defined as the difference between the change in enthalpy, ΔH , and the product of the Kelvin temperature and the entropy change, which is defined as $T\Delta S$: ▼

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$



Chapter 16

Section 2 Driving Force of Reactions

Relating Enthalpy and Entropy to Spontaneity

ΔH	ΔS	ΔG	Is the reaction spontaneous?
Negative	positive	negative	yes, at all temperatures
Negative	negative	either positive or negative	only if $T < \Delta H/\Delta S$
Positive	positive	either positive or negative	only if $T > \Delta H/\Delta S$
Positive	negative	positive	never

< Back

Next >

Preview 

Main 

Chapter 16

Section 2 Driving Force of Reactions

Equation for Free-Energy Change

Click below to watch the Visual Concept.

[Visual Concept](#)

[< Back](#)

[Next >](#)

[Preview](#) 

[Main](#) 

Free Energy, *continued* ▼

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

- The expression for free energy change is for substances in their standard states. ▼
- The product $T\Delta S$ and the quantities ΔG and ΔH have the same units, usually kJ/mol. If $\Delta G < 0$, the reaction is spontaneous. ▼
- ΔH and ΔG can have positive or negative values. This leads to four possible combinations of terms.



Chapter 16

Section 2 Driving Force of Reactions

Relating Enthalpy, Entropy, and Free-Energy Changes

Click below to watch the Visual Concept.

[Visual Concept](#)

[< Back](#)

[Next >](#)

[Preview](#) 

[Main](#) 

Chapter 16

Section 2 Driving Force of Reactions

Comparing Enthalpy and Entropy

Click below to watch the Visual Concept.

[Visual Concept](#)

< Back

Next >

Preview 

Main 

Free Energy, *continued*

Sample Problem D ▾

For the reaction $\text{NH}_4\text{Cl}(s) \rightarrow \text{NH}_3(g) + \text{HCl}(g)$, at 298.15 K, $\Delta H^0 = 176 \text{ kJ/mol}$ and $\Delta S^0 = 0.285 \text{ kJ}/(\text{mol}\cdot\text{K})$. Calculate ΔG^0 , and tell whether this reaction is spontaneous in the forward direction at 298.15 K.



Free Energy, *continued*

Sample Problem D Solution ▾

Given: $\Delta H^0 = 176 \text{ kJ/mol}$ at 298.15 K ▾

$\Delta S^0 = 0.285 \text{ kJ/(mol}\cdot\text{K)}$ at 298.15 K ▾

Unknown: ΔG^0 at 298.15 K ▾

Solution: The value of ΔG^0 can be calculated according to the following equation: ▾

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \nabla$$

$$\Delta G^0 = 176 \text{ kJ/mol} - 298 \text{ K} [0.285 \text{ kJ/(mol}\cdot\text{K)}] \quad \nabla$$

$$\Delta G^0 = 176 \text{ kJ/mol} - 84.9 \text{ kJ/mol} \quad \nabla$$

$$\Delta G^0 = 91 \text{ kJ/mol}$$



End of Chapter 16 Show

< Back

Next >

Preview 

Main 