THERMOCHEMISTRY

The content in this topic is the basis for mastering Learning Objectives 5.1 to 5.8 as found in the Curriculum Framework.

When you finish reviewing this topic, be sure you are able to:

- Explain how and why potential energy varies with distance between atoms in covalent bonds and intermolecular forces (see also Section 9.7)
- Explain how temperature relates to molecular motion using particle views (see also Section 10.7)
- Use molecular collisions to explain or predict the transfer of heat between systems
- Use the law of conservation of energy to explain energy transfer, including heat and work between systems
- Explain the quantity of energy change that occurs when two substances of different temperatures interact
- Calculate or estimate enthalpy changes associated with chemical reactions
- Calculate or estimate energy changes associated with temperature changes using heat capacity
- Calculate or estimate energy changes associated with physical changes including phase changes using heats of fusion or vaporization
- Use results of a calorimetry experiment to determine change in enthalpy of a chemical or physical process
- Use bond energies to calculate or estimate enthalpies of reaction (see also Section 8.8)

The Nature of Energy　　Section 5.1

Thermodynamics is the study of energy and its transformations.

Thermochemistry is the study of the relationships between energy changes involving heat and chemical reactions.

Energy is the capacity to do work or to transfer heat.

Heat is the energy transferred from one object to another because of a difference in temperature.

A **calorie** is an informal but still used unit for heat energy. One calorie is the amount of energy required to raise the temperature of one gram of water by one degree Celsius. The large Calorie (spelled with a capital C) is used to measure food energy. 1 Cal = 1000 cal.

A **joule** is the SI unit of energy. One calorie is equal to 4.184 joules. 1 cal = 4.184 J.

Common misconception: Commonly. the energy values of various foods are expressed as follows: for fats, 9 Cal/g; for carbohydrates. 4 Cal/g; for protein, 4 Cal/g. These caloric values are large calories and each refers to 1000 cal or 1 kcal.

Energy changes involve the transfer of heat between the **system**, that portion of the universe we single out for study, and the **surroundings**, everything else.

Section 5.2   The First Law of Thermodynamics

The **first law of thermodynamics**, also called the **law of conservation of energy**, states that energy is conserved. The energy of the universe is constant. Energy can be neither created nor destroyed, but it can be changed to other forms.

An **exothermic** process is a process that releases heat to the surroundings. Heat flows out of the system and into the surroundings. The temperature of the surroundings increases.

Common misconception: An exothermic process releases heat. but this does not mean that the system cools off. The word "release" essentially means that potential energy of the system is converted to heat energy so the surroundings increase in temperature during an exothermic process.

An **endothermic** process absorbs heat from the surroundings. Heat flows into the system from the surroundings. The temperature of the surroundings decreases.

Common misconception: An endothermic process absorbs heat, but this does not mean that the temperature of the system increases. The word "absorb" essentially means that heat energy from the surroundings is changed to potential energy of the system, and the temperature of the surroundings decreases.

Your Turn 5.1

Imagine an ice cube melting in your hand. Is the melting of ice endothermic or exothermic? Explain using the terms system and surroundings. Write your answer in the space provided.

All chemical and physical changes involve some form of energy change. Because atoms are composed of electrical particles, electrostatic forces between atoms and molecules form the basis of those energy changes. Figure 5.1 illustrates the forces that exist between charged particles. Opposite charges attract releasing energy (a). Like charges repel and absorb energy when they do so (b).

(a)

(b)
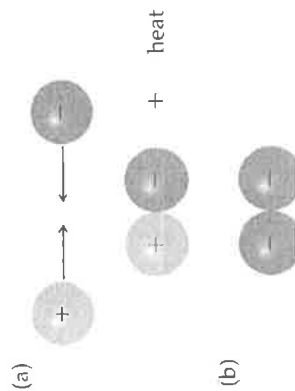
Coulomb's law says that the force acting between two charged particles is related to their charges and the distance between them: $F = kQ_1Q_2/d^2$.

Because energy is force times distance, multiplying the right side by d (distance) gives a similar relationship for energy: $E = kQ_1Q_2/d$.

When two opposite charges attract as in Figure 5.1a, the process is exothermic. The difference in energy is the heat released by the system. Attractive interactions are always exothermic while the separation of opposite charges is always endothermic.

When two like charges repel as in Figure 5.1b, the process is also exothermic. The difference in energy is the heat released by the system. Repulsive interactions are always exothermic, whereas it requires energy to move like charges together.

Your Turn 5.2

Imagine warming your hands near a campfire. Is a campfire an endothermic or exothermic process? Explain. Write your answer in the space provided.

Temperature in Kelvin is proportional to the average kinetic energy of the particles in a sample. Figure 5.2 illustrates two samples of gas particles at two different temperatures. Each arrow indicates the relative kinetic energy of each particle.
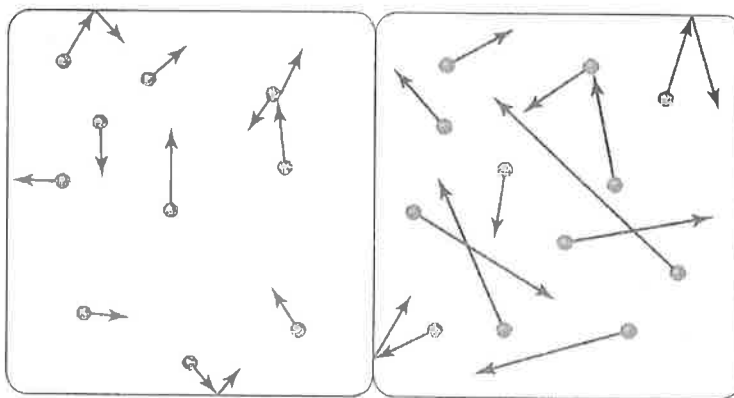

Figure 5.2 Gas particles at two different temperatures.

Which gas has the higher temperature? Justify your answer.

Enthalpy   Section 5.3

Pressure-volume work (P-V work) is the work involved in the expansion or compression of gases and constant pressure. Figure 5.3 shows how a chemical reaction can both release heat *and* do work on its surroundings. Because the reaction produces a gas, the piston moves and pushes back on the atmosphere.
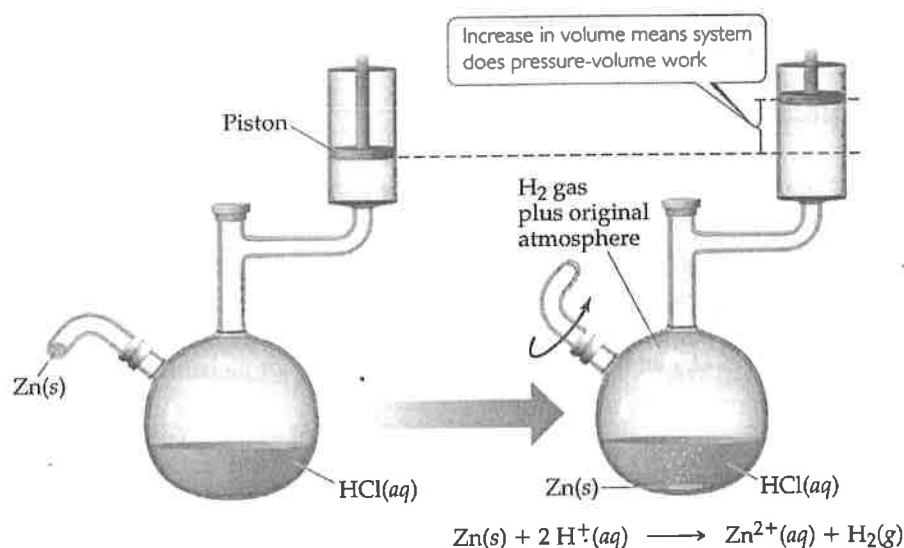

Figure 5.3 A system that does work on its surroundings.

P-V work done by the system is given by the equation: $w = -P\Delta V$, where w is work, P is constant pressure, and ΔV is the change in volume of the system. The negative sign shows the direction of the work. That is, the work is done by the system.

The **internal energy**, ΔE, of the system is the sum of the heat changed, q, and the work, w, done by the system:

$$\Delta E = q + w$$

Enthalpy is the property of a system that accounts for heat flow between the system and the surroundings at constant pressure.

Enthalpy is a **state function**, a property of a system that depends only on the present state of the system, not on the path the system took to reach that state. A state is determined by specifying the system's temperature, pressure, location, and other conditions that are characteristic of the system.

Enthalpy change, ΔH, is the heat absorbed during a physical or chemical process.

ΔH is positive for an endothermic process, one that absorbs heat.

ΔH is negative for an exothermic process, one that releases heat.

Common misconception: The total change in internal energy for all systems is the change in enthalpy plus the work done by the system at constant pressure: $\Delta E = \Delta H - P\Delta V$. However, for most reactions, $P\Delta V$ is very small so it is satisfactory to use ΔH as a measure of energy change during most chemical processes: $\Delta E = \Delta H$.

Section 5.4   Enthalpies of Reaction

Enthalpy changes are usually expressed in kJ or kJ/mol. For endothermic changes, the heat absorbed is always a positive number because endothermic changes absorb heat. For an exothermic reaction, ΔH is negative because exothermic changes liberate (the opposite of absorb) heat.

Enthalpy change, ΔH, can be applied to either a physical or a chemical change.

Common misconception: It is important to understand that the concept of enthalpy change, ΔH, is the same idea for a wide variety of processes. To distinguish specific types of change, ΔH takes on various subscripts.

Table 5.1 lists examples of various types of enthalpy changes. Each subscript for ΔH denotes a specific kind of process.
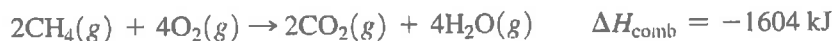
Table 5.1 Enthalpy changes for various types of processes with examples.

Symbol	Type of Process	Definition of Process with Example
ΔH_{rxn} $AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$	Heat of reaction	Enthalpy change for any chemical reaction $\Delta H_{rxn} = -68$ kJ
ΔH_{comb} $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$	Heat of combustion	Enthalpy change for a combustion reaction $\Delta H_{comb} = -802$ kJ
ΔH_{fus} $H_2O(s) \rightarrow H_2O(l)$	Heat of fusion	Heat change when a solid melts $\Delta H_{fus} = -6.0$ kJ
ΔH_{vap} $H_2O(l) \rightarrow H_2O(g)$	Heat of vaporization	Heat change when a liquid vaporizes $\Delta H_{vap} = +44$ kJ

Table 5.1 *(Continued)*

ΔH_{BDE} $H_2(g) \rightarrow H(g) + H(g)$	Bond dissociation energy	Heat required to break a chemical bond $\Delta H_{BDE} = +436 \text{ kJ}$
ΔH_f $H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l)$	Heat of formation	Heat change when one mole of a substance is formed from its elements $\Delta H_f = -285.83 \text{ kJ}$
ΔH_{soln} $LiCl(s) \rightarrow Li^+(aq) + Cl^-(aq)$	Heat of solution	Heat change when solute dissolves in a solvent $\Delta H_{soln} = -37.4 \text{ kJ}$

The magnitude of the enthalpy change, ΔH, for any chemical or physical change is directly proportional to the amount of reactants and products involved in the change. For example, if one mole of methane burns in air to produce -802 kJ of energy, then two moles of methane will produce twice the energy.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H_{comb} = -802 \text{ kJ}$$

$$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g) \qquad \Delta H_{comb} = -1604 \text{ kJ}$$

Because it is directly proportional to the number of moles in a balanced equation, enthalpy change, ΔH, for any amount of reactant or product can be calculated using the mole road.
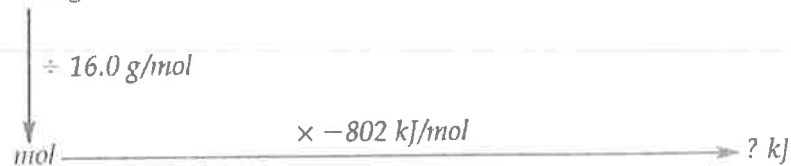
Example:

*How many kJ of heat are absorbed when 25.0 g of methane burn in air?*

Solution:

$$x \text{ kJ} = (25.0 \text{ g } CH_4)/(16.0 \text{ g/mol}) \times (-802 \text{ kJ/mol}) = -1250 \text{ kJ}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H_{comb} = -802 \text{ kJ/mol}$$

25.0 g

$\downarrow$ $\div$ 16.0 g/mol

mol $\xrightarrow{\quad \times -802 \text{ kJ/mol} \quad}$? kJ

The sign of ΔH depends on the direction of the reaction. The magnitude of the enthalpy change for a forward reaction is equal to, but opposite in sign, for a reverse reaction. For example, if it takes $+6$ kJ to melt a mole of solid water, then one mole of liquid water releases -6 kJ of energy upon freezing.

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = +6.0 \text{ kJ}$$

$$H_2O(l) \rightarrow H_2O(s) \qquad \Delta H = -6.0 \text{ kJ}$$
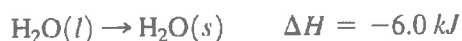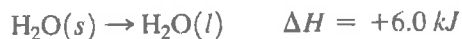
Common misconception: The sign of ΔH indicates the direction of energy flow, not a positive or negative value for energy. A positive sign indicates that heat is absorbed by the system. A negative sign means that heat is released by the system. Often the absolute value of ΔH is used in the context of sentences and its sign is implied. For example, when heat is said to be "absorbed," the sign of ΔH is positive. When heat is "liberated," the sign is negative.

Your Turn 5.3

What scientific law requires that the magnitude of the heat change for forward and reverse processes be the same with opposite signs? Explain. Write your answer in the space provided.

Phase transitions from solid to liquid and from liquid to gas always absorb heat. They are endothermic. Phase transitions from gas to liquid and from liquid to solid always liberate heat. They are exothermic.

$$H_2O(l) \rightarrow H_2O(g) \quad \Delta H_{vap} = +44 \text{ kJ}$$
$$H_2O(g) \rightarrow H_2O(l) \quad \Delta H_{vap} = -44 \text{ kJ}$$
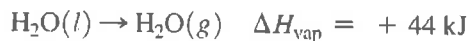
Your Turn 5.4

Why are phase changes from solid to liquid and from liquid to gas always endothermic? Is the process of sublimation (changing directly from a solid to a gas) endothermic or exothermic? Explain. Write your answer in the space provided.

Calorimetry   Section 5.5

Calorimetry is the measurement of heat flow. A calorimeter is an apparatus that measures heat flow.

Heat capacity, C, is the heat required to raise the temperature of an object by 1K. The units for heat capacity are J/K (or J/°C).

> **Common misconception:** Remember that 1 K is the same size as 1 °C (even though they are 273 degrees apart on their respective scales). Kelvin and degrees Celsius are often used interchangeably in various units.

Molar heat capacity, C_{molar} is the amount of heat absorbed by one mole of a substance when it experiences a one-degree temperature change. The units of C_{molar} are J/mol K (or J/mol °C).

Specific heat capacity, c, is the heat capacity of one gram of a substance. The units are J/g K (or J/g°C). Table 5.2 shows the specific heats of some common substances.

Table 5.2   Specific heat capacities of various substances.

Substance	Specific Heat, J/g °C	Substance	Specific Heat, J/g °C
aluminum	0.90	liquid water	4.184
iron	0.46	ice	2.1
silver	0.24	steam	1.9
mercury	0.14	ethanol	2.4

The specific heat of water is worth remembering: 1 cal/g K = 4.184 J/g K.

➜ *Your Turn 5.5*

Explain why the value of the specific heat of water is 1 cal/g K or 4.184 J/g K. Write your answer in the space provided.

Heat capacities, temperature, energy, moles, and grams are related by an analogy to the mole road as shown in Figure 5.4.
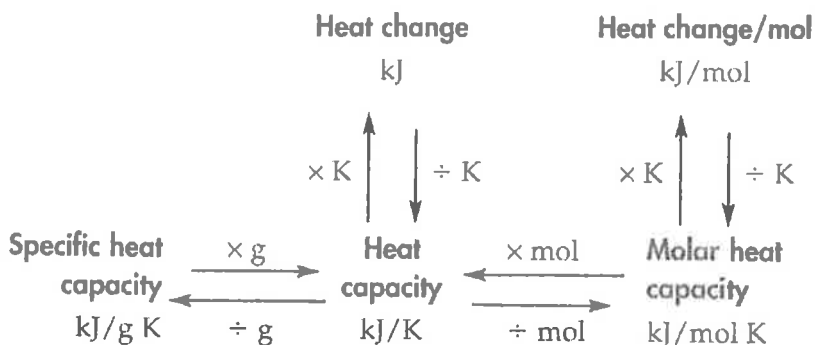

Figure 5.4 Mole road analogy for heat capacity calculations.

Calorimetry is often used to measure enthalpy changes in chemical reactions. For example, the heat of combustion of ethanol, CH_3CH_2OH, can be measured by placing a measured quantity of ethanol and excess oxygen in a bomb calorimeter having a known heat capacity. The ethanol is ignited, the temperature change of the calorimeter is observed, and the heat released by the combustion reaction is calculated from the heat capacity of the calorimeter.

Your Turn 5.6

A student performs an experiment to determine the heat of fusion of ice. In a coffee cup calorimeter, the student adds an ice chip to 4.735 g of water at 44.0 °C. Upon mixing, the temperature of the system drops to 16.0 °C at the point where all the ice has melted. The total mass of the water is 6.097 g.

a. *Calculate the amount of heat lost by the water.*
b. *Calculate the mass of the ice.*
c. *How much heat did the ice gain?*
d. *Assume all the ice was liquid water at 0.0 °C. How much heat did this liquid water gain?*
e. *Use this data to calculate the heat of fusion of ice in kJ/mol.*
f. *If the accepted value is 6.02 kJ/mol, calculate the percentage error of the experiment.*

Hess's Law   Section 5.6

Hess's law states that if a reaction is carried out in a series of steps, ΔH of the overall reaction is equal to the sum of the ΔH's for each individual step. Hess's law is useful in calculating enthalpies of reactions that are difficult or impossible to measure directly. The formation of sulfur trioxide by the reaction of sulfur with oxygen, for example, does not proceed directly under normal conditions, but the heat of the reaction can be calculated from the heats of the individual steps that lead to the reaction.

Example:

Calculate ΔH for the following reaction,

$$2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$$
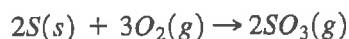
from the enthalpies of these related reactions.

Reaction	ΔH_{rxn}
$S(s) + O_2(g) \rightarrow SO_2(g)$	$-296.9\ kJ$
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	$-196.6\ kJ$

Solution:

The given reactions can be manipulated like algebraic quantities to yield the reaction in question. Their enthalpy values are mathematically manipulated in the same way.

Reaction	ΔH_{rxn}
$2[S(s) + O_2(g) \rightarrow SO_2(g)]$	$2(-296.9\ kJ)$
$+\ 2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	$-\ 196.6\ kJ$
$2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$	$-\ 790.4\ kJ$

Hess's law says that the enthalpy of the reaction is calculated by manipulating the enthalpy quantities in the same way as we manipulated the corresponding reactions.

Common misconception: Be sure to manipulate the ΔH values in the same way you manipulate the reactions. That is, if you multiply a reaction by 2, you must multiply its ΔH value by 2. If you reverse a reaction, you must change the *sign of its ΔH* value. Always be careful of signs.

Figure 5.5 shows an enthalpy diagram illustrating Hess's law for the combustion of methane.

$$CH_4(g) + 2 O_2(g)$$

-890 kJ

-802 kJ

$$CO_2(g) + 2 H_2O(g)$$

-88 kJ
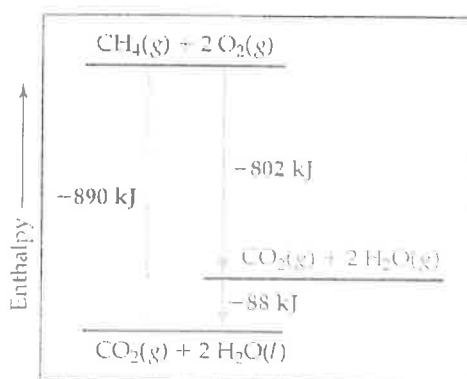
$$CO_2(g) + 2 H_2O(l)$$

Enthalpy

Figure 5.5   An enthalpy diagram illustrating Hess's law. The quantity of heat generated in any chemical reaction is independent of the pathway of the reaction.

Section 5.7   Enthalpies of Formation

A **formation reaction** is a reaction that produces one mole of a substance from its elements in their most stable thermodynamic state. For example, the formation reaction for gaseous hydrogen iodide. HI, includes only one mole of HI as the sole product, and the elements hydrogen and iodine in their most stable forms as the only reactants:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(s) \rightarrow HI(g) \quad \Delta H = +25.94 \text{ kJ}$$
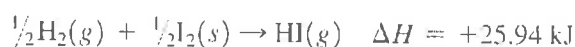
Gaseous diatomic hydrogen and solid diatomic iodine are the most stable thermodynamic states of those elements at 25°C.

The **standard heat of formation,** ΔH_f°, is the heat absorbed when one mole of a substance is formed from its elements in their standard states at 25°C and 1 atmosphere pressure. A heat of formation is ΔH for a formation reaction. For example, the standard enthalpy of formation, ΔH_f°, of HI is the enthalpy of the formation reaction for HI. Its value is +25.94 kJ. Table 5.3 gives the standard heats of formation of some selected substances. Appendix C of *Chemistry: The Central Science* provides a comprehensive table of ΔH_f° values. Keep in mind that each substance listed is the sole product of a formation reaction and that the corresponding ΔH_f° value listed is the enthalpy of that formation reaction under standard conditions.

Table 5.3 Standard enthalpies of formation, ΔH_f° for selected substances.

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
$AlCl_3(s)$	−705.6	$MnO_4^-(aq)$	−541.4
$Br_2(g)$	+30.71	$NH_3(aq)$	−80.29
$Br_2(l)$	0	$NH_3(g)$	−46.19
$Ca(g)$	+179.3	$O(g)$	+247.5
$Ca(s)$	0	$O_2(g)$	0
$C(s, diamond)$	+1.88	$O_3(g)$	+142.3
$C(s, graphite)$	0	$H_2O(g)$	−241.82
$H(g)$	+217.97	$H_2O(l)$	−285.83
$H_2(g)$	0		

Your Turn 5.7

Write the thermochemical equation associated with the standard heat of formation of $AlCl_3(s)$ listed in Table 5.3. Write your answer in the space provided.

Notice that the substances in Table 5.3 include elements, compounds, and ions. Notice also that the heat of formation of any element in its most stable thermodynamic state is zero. For example, the ΔH_f° values for solid monatomic calcium, liquid diatomic bromine, and gaseous diatomic oxygen are all zero because these are the most stable forms of these elements at 25°C and 1 atmosphere pressure.

Your Turn 5.8

Considering the definition of a formation reaction, explain why the standard heat of formation of an element in its most stable thermodynamic state is zero. Write a chemical equation to illustrate your answer. Write your answer in the space provided.

Hess's law allows us to use a relatively small number of measurements to calculate ΔH for a vast number of reactions. Using data from Table 5.3 or from Appendix C of *Chemistry: The Central Science*, the standard enthalpy of many reactions can be calculated from the enthalpies of the reactants and products.

The standard enthalpy of any reaction, ΔH^r_{rxn}, is equal to the sum of the standard enthalpies of formation of products minus the sum of standard enthalpies of formation of reactants. The values for n and m in the following equation represent the coefficients of the balanced equation.
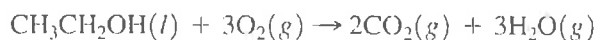
$$\Delta H^\circ_{rxn} = \sum n\, \Delta H^\circ_{f\,products} - \sum m\, \Delta H^\circ_{f\,reactants}$$

Example:

Calculate the standard enthalpy change for the combustion of one mole of liquid ethanol.

Solution:

Write and balance the equation. Use Appendix C in Chemistry: The Central Science *to determine the standard enthalpies of formation for reactants and products. Apply the summation equation. Be sure to multiply each ΔH°_f value by the corresponding coefficient that balances the equation.*

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

From Appendix C: $\Delta H^\circ_f = -238.6\ kJ \quad 0\ kJ \qquad -393.5\ kJ \quad -241.82\ kJ$

$\Delta H^\circ_{rxn} = \sum n\, \Delta H^\circ_{f\,products} - \sum m\, \Delta H^\circ_{f\,reactants}$

$\Delta H^\circ_{rxn} = 2(-393.5\ kJ) + 3(-241.82\ kJ) - (-238.6\ kJ) - 3(0\ kJ)$

$\Delta H^\circ_{rxn} = -1273.9\ kJ$

Common misconception: The hardest part of this type of problem is the arithmetic. Especially be careful to manipulate the $+$ and $-$ signs correctly.

Reexamine Table 5.3. Notice that there is a difference between the ΔH°_f values for liquid water and gaseous water. The difference represents the molar heat of vaporization of water. The equation is:

$$H_2O(l) \longrightarrow H_2O(g)$$

$\Delta H^\circ_f = -285.83\ kJ \qquad -241.82\ kJ$

$\Delta H^\circ_{rxn} = \Delta H^\circ_{vap} = \Delta H^\circ_f[H_2O(g)] - \Delta H^\circ_f[H_2O(l)]$

$\Delta H^\circ_{vap} = -241.82\ kJ - (-285.83\ kJ) = 44.01\ kJ$

Your Turn 5.9

Calculate (a) the enthalpy of sublimation of solid calcium? (b) The heat of solution gaseous ammonia (c) The bond dissociation energy of hydrogen gas (d) The heat change when gaseous bromine condenses to a liquid. Where can you find the data needed to solve these problems? Write chemical equations to illustrate your answers. Write your answers in the space provided.

Multiple Choice Questions

1. The standard enthalpy of formation (ΔH_f°) for potassium chloride is the enthalpy change for the reaction

   A) $K(g) + \frac{1}{2}Cl_2(g) \rightarrow KCl(g)$

   B) $K^+(s) + Cl^-(g) \rightarrow KCl(s)$

   C) $2K(s) + Cl_2(g) \rightarrow 2KCl(s)$

   D) $K(s) + \frac{1}{2}Cl_2(g) \rightarrow KCl(s)$

   E) $K^+(g) + Cl^-(g) \rightarrow KCl(s)$

2. For which of these processes is the value of ΔH expected to be negative?

   I.   The temperature increases when calcium chloride dissolves in water.

   II. Steam condenses to liquid water.

   III. Water freezes.

   IV. Dry ice sublimes.

   A) IV only

   B) I, II, and III

   C) I only

   D) II and III only

   E) I and II only

3. Which is expected to not have a ΔH_f° value of zero?

   A) $F_2(g)$

   B) $Br_2(g)$

   C) $I_2(s)$

   D) $C(s, graphite)$

   E) $N_2(g)$

4. For which of the following equations is the change in enthalpy at 25°C and 1 atmosphere pressure equal to ΔH_f° of $CH_3OH(l)$?

   A) $CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

   B) $CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

   C) $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

   D) $CH_3OH(l) \rightarrow C(s) + 2H_2O(l)$

   E) $C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$

5. Which change will result in an increase in enthalpy of the system?

A) burning a candle

B) freezing water

C) evaporating alcohol

D) dropping a ball

E) condensing steam

6. The standard enthalpy of formation of $Cl(g)$ is $+242 \ kJ/mol$. What is the dissociation energy of a $Cl—Cl$ bond?

A) $+242 \ kJ/mol$

B) $-242 \ kJ/mol$

C) $+484 \ kJ/mol$

D) $+121 \ kJ/mol$

E) $-121 \ kJ/mol$

7. For which process is the sign of ΔH negative?

A) Photosynthesis

B) $CO_2(g) \rightarrow C(s) + O_2(g)$

C) $N_2(g) \rightarrow 2N(g)$

D) $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq) + heat$

E) $H_2O + electricity \rightarrow \frac{1}{2}H_2(g) + O_2(g)$

8. Given the following data, what is the heat of formation of methane gas?

I. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -803 \ kJ$

II. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\Delta H = -242 \ kJ$

III. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -394 \ kJ$

IV. $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H = -111 \ kJ$

A) $-803 \ kJ/mol$

B) $-75 \ kJ/mol$

C) $+167 \ kJ/mol$

9. The standard heat of formation of gaseous sulfur trioxide is $-396 \, kJ/mol$. What is the enthalpy of reaction represented by the following balanced equation?

$$2SO_3(g) \rightarrow 2S(s) + 3O_2(g)$$
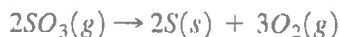
A) $-396 \, kJ$

B) $+396 \, kJ$

C) $+792 \, kJ$

D) $-792 \, kJ$

E) $+198 \, kJ$

10. Given only the following data, what can be said about the following reaction?

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g) \qquad \Delta H = -92 \, kJ$$

A) The enthalpy of products is greater than the enthalpy of reactants.

B) The total bond energies of products are greater than the total bond energies of reactants.

C) The reaction is very fast.

D) Nitrogen and hydrogen have very stable bonds compared to the bonds of ammonia.

E) The reaction is endothermic.

Free Response Questions

1. The heat of combustion of gaseous butane is $-2658 \, kJ/mol$ and the heat of combustion of liquid butane is $-2635 \, kJ/mol$, when, in both cases, all products are gases.

   a. Write a balanced chemical equation for the combustion of gaseous butane.

   b. How many grams of gaseous butane combust when 1550 kJ of heat are produced?

   c. What is the magnitude and sign of the molar heat of vaporization of butane? Explain your reasoning using Hess's law. Is your sign for the heat of vaporization realistic? Explain.

2. When 15.00 g of propane are burned in air to produce all gaseous products, 730.0 kJ of heat are produced.

   a. Calculate the molar heat of combustion of propane.

   b. When 15.00 g of propane are combusted in air to produce gaseous carbon dioxide and liquid water, 790.0 kJ of heat are produced. Explain why the amount of heat available from the combustion of propane depends on the phase of the products.

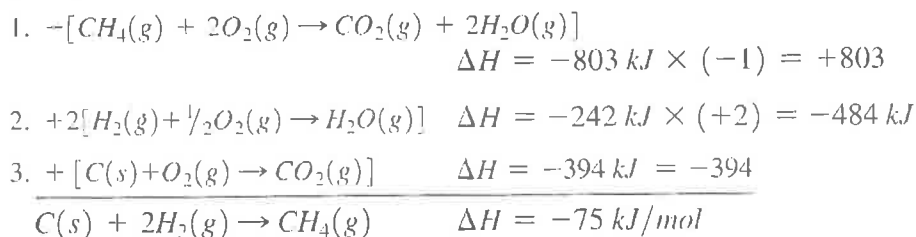   c. Calculate the heat of vaporization of water in units of kJ/g.

Multiple Choice Answers and Explanations

1. D. The enthalpy of formation of a substance is the enthalpy change for the formation of one mole of that substance from its elements in their most stable thermodynamic forms at 25°C and 1 atmosphere pressure. Solid potassium and gaseous diatomic chlorine are the most stable forms of those elements.

2. B. A negative ΔH value is characteristic of an exothermic process, one that releases heat to its surroundings. Exothermic processes increase the temperature of their surroundings. Phase changes from gas to liquid and from liquid to solid are all exothermic processes. The opposite processes are endothermic. Sublimation is the process by which a solid changes directly into a gas, also an endothermic process.

3. B. By definition, the standard heats of formation of elements in their most stable thermodynamic state at 25°C and 1 atmosphere pressure is zero. Bromine is a liquid at 25°C and 1 atmosphere pressure. Solid graphite is the most stable form of carbon.

4. E. Although the direct formation of methanol from its elements is improbable, the heat of formation of methanol is defined as the enthalpy change for this reaction. Answers A, B, and C are all combustion reactions of methanol and Answer D is a decomposition reaction.

5. C. An increase in enthalpy is associated with an endothermic process, one that absorbs energy from its surroundings. Phase changes from solid to liquid or gas and from liquid to gas are always endothermic. Combustion reactions are always exothermic as are phase changes from gas to liquid and from liquid to solid.

6. C. The bond dissociation of chlorine gas is the enthalpy change for this reaction: $Cl_2(g) \rightarrow 2Cl(g)$. Bond dissociation energies always have positive values because bond breaking is always endothermic, so the sign of the heat change is always positive. The formation reaction for $Cl(g)$ is $^1/_2Cl_2(g) \rightarrow Cl(g)$. Notice that the formation equation is exactly half the reaction in question. So the bond dissociation energy is twice the enthalpy of formation.

7. D. ΔH is negative for exothermic processes and positive for endothermic processes. Exothermic processes release heat to their surroundings. Photosynthesis involves absorbing energy from sunlight and is endothermic. Combustion reactions are always exothermic and Answer B is the reverse of a combustion

combustion reaction. (Equation 4 is extraneous.) Apply the corresponding heats to the summation equation and solve for the unknown quantity, the heat of formation of methane.

$$\Delta H^\circ_{rxn} = \sum n \, \Delta H^\circ_{f\,products} - \sum m \, \Delta H^\circ_{f\,reactants}$$

$$\Delta H^\circ_{comb} = 2\Delta H^\circ_f[H_2O] + \Delta H^\circ_f[CO_2] - \Delta H^\circ_f[O_2] - \Delta H^\circ_f[CH_4]$$

$$-803 = 2(-242)+(-394) - 0 - \Delta H^\circ_f CH_4$$

$$\Delta H^\circ_f[CH_4] = -75 \, kJ/mol$$

Another approach is to use Hess's law and mathematically manipulate the given equations to yield the formation reaction for methane. Apply the same mathematical manipulations to the given heats to find the heat of the formation reaction. (This approach is the essence of the summation equation used in the first approach.)

1. $-[CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)]$

$$\Delta H = -803 \, kJ \times (-1) = +803$$

2. $+2[H_2(g)+\frac{1}{2}O_2(g) \rightarrow H_2O(g)]$ $\Delta H = -242 \, kJ \times (+2) = -484 \, kJ$

3. $+ [C(s)+O_2(g) \rightarrow CO_2(g)]$ $\Delta H = -394 \, kJ = -394$

$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$

$C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H = -75 \, kJ/mol$

9. C. The standard heat of formation of gaseous sulfur trioxide is heat change for the formation reaction: $S(s) + 3/2 \, O_2(g) \rightarrow SO_3(g)$. Recognize that the reaction in question is double the formation reaction and the reverse of it. The heat change for the reaction in question is:

$-2(-396) = +792 \, kJ$

10. B. Bond making is always exothermic and bond breaking is always endothermic. The reaction is exothermic, one that releases energy to its surroundings, because the sign of the heat change is negative. The bonds formed by the products are more stable than those broken in the reactants leaving a net energy released to the surroundings.

Free Response Answers

1. a. Butane is the alkane hydrocarbon containing four carbon atoms. Alkanes have all single carbon–carbon bonds and have the general formula, C_nH_{2n-2}. Water and carbon dioxide are the products of the combustion of hydrocarbons.

   $C_4H_{10}(g)+ \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$
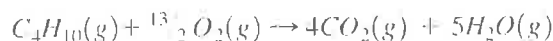
   (Double coefficients are acceptable.)

   b. The amount of heat in a thermochemical equation is proportional to the amount of reactants and products. Use the mole road to convert 1550 kJ to grams.
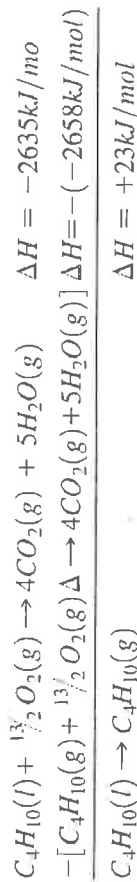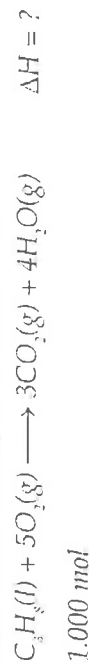
$$C_2H_{10}(g) + 13/2\ O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g) + 1550\ kJ$$

? g

↓ × 58.0 g/mol

÷ 2658 kJ/mol $C_4H_{10}(g)$

mol   1550 kJ

$x\ g = (1550\ kJ)(58.0\ g/mol)/(2658\ kJ/mol\ C_4H_{10}(g))$

$= 33.8\ g\ C_4H_{10}(g)$

c. *The molar heat of vaporization of butane is the difference between the heats of combustion of liquid and gaseous butane. Subtracting the equation for the combustion of gaseous butane from the equation for the combustion of liquid butane yields the equation for the vaporization of butane. Subtracting the corresponding heats yields the heat of vaporization of butane. Vaporization processes are always positive.*

$$C_4H_{10}(l) + {}^{13}/_2\,O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) \qquad \Delta H = -2635kJ/mo$$
$$-[C_4H_{10}(g) + {}^{13}/_2\,O_2(g)\Delta \rightarrow 4CO_2(g) + 5H_2O(g)]\ \Delta H = -(-2658kJ/mol)$$

$$\overline{C_4H_{10}(l) \rightarrow C_4H_{10}(g)} \qquad\qquad \Delta H = +23kJ/mol$$

2. a. *Use the mole road and the balanced chemical equation to calculate the number of kJ burned in one mole of propane. Propane is the alkane hydrocarbon having three carbon atoms.*
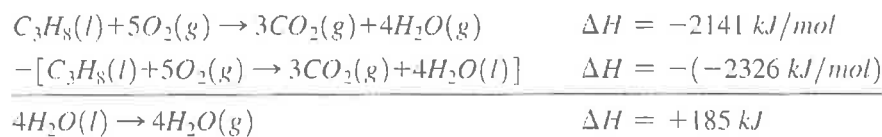
$$C_3H_8(l) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g) \qquad \Delta H = ?$$

1.000 mol

↓ × 44.00 g/mol

g   × −730.0 kJ/15.00 g

↓   kJ

$x\ kJ = 1.000\ mol(44.0\ g/mol)(-730\ kJ/15.0\ g) = -2141\ kJ$

b. *Upon combustion of the same amount of butane, more heat is liberated when liquid water forms than when gaseous water forms because heat is released*

moles of water. Divide by four and by the molar mass of water to obtain the heat of vaporization of water in kJ/g.

$$x\ kJ/g = 1.000\ mol(44.0\ g/mol)(-792.9\ kJ/15.0\ g) = -2326\ kJ/mol$$

$$C_3H_8(l)+5O_2(g) \rightarrow 3CO_2(g)+4H_2O(g) \qquad \Delta H = -2141\ kJ/mol$$
$$-[C_3H_8(l)+5O_2(g) \rightarrow 3CO_2(g)+4H_2O(l)] \qquad \Delta H = -(-2326\ kJ/mol)$$
$$\overline{\hspace{3cm}}$$
$$4H_2O(l) \rightarrow 4H_2O(g) \qquad\qquad\qquad \Delta H = +185\ kJ$$

$$\Delta H = +185\ kJ/4\ mol = 46.25\ kJ/mol$$

$$x\ kJ/g = (46.25\ kJ/mol)/(18.0\ g/mol) = 2.57\ kJ/g$$

Your Turn Answers

5.1. *Melting of ice (the system) is endothermic as evidenced by the cooling of your hand (the surroundings) as the ice melts. Endothermic processes cool the surroundings by taking heat away from the surroundings, and converting it to potential energy of the system.*

5.2. *A campfire (the system) is an exothermic process. It releases heat to your hands (the surroundings). Potential energy of the system is converted to heat energy, and your hands feel the heat coming from the campfire.*

5.3. *The law of conservation of energy says that the energy of the universe is constant. Energy is neither created nor destroyed so the amount of energy that flows into a forward process will be the same as that flowing out of a reverse process. The value for ΔH will be the same for both processes but will have opposite signs. The sign of ΔH indicates the direction of heat flow.*

5.4. *It requires energy to melt a solid or to vaporize a liquid to overcome the strong forces of attraction between particles that exist in solids and liquids. This energy is released when gases change to liquids, and liquids change to solids. Sublimation is always an endothermic process because it requires energy to overcome strong forces of attraction in solids and liquids.*

5.5. *The value of the specific heat of water derives from the original and modern definitions of a calorie. One calorie is the amount of heat necessary to change one gram of water by one degree Celsius (or Kelvin). One calorie is 4.184 J.*

5.6. a. *Heat gained = mass × specific heat × temperature change*

$$q = m \times c \times \Delta T = 4.735\ g \times 4.184\ J/g\ ^\circ C \times (16.0\ ^\circ C - 44.0\ ^\circ C) = -555\ J$$

The negative sign denotes the direction of heat flow, away from the hot water.

b. *Mass of ice = total mass − mass of hot water*
   = 6.097 g−4.735 g = 1.362 g

c. *Heat gained by ice = −heat lost by hot water = +555 J*

d. $q = m \times c \times \Delta T = 1.362\ g \times 4.184\ J/g\ ^\circ C \times (16.0\ ^\circ C - 0\ ^\circ C)$
   $= +91.2\ J$

e. *The heat of fusion of ice is calculated by subtracting the heat required to melt the ice from the total heat change of the system.*

$555\ J - 91.2\ J = 463.8\ J$

$x\ kJ/mol = 463.8\ J\ (1\ kJ/1000\ J)(18.0\ g/mol)/(1.362\ g) = 6.13\ J/mol$

f. *% error = (accepted value − experimental value)/(accepted value) × 100 =*

$(6.13 - 6.02)/6.02 \times 100 = 1.83\%\ \text{error}$

5.7. $Al(s) + 3/2\ Cl_2(g) \rightarrow AlCl_3(s)$

5.8. *The formation of a stable form of an element from that element represents no net change so there is no heat change.*

$Ca(s) \rightarrow Ca(s)\quad \Delta H_{rxn} = 0$

5.9. a. $Ca(s) \rightarrow Ca(g)\quad \Delta H°_f = +179.3\ kJ - 0\ kJ = +179.3\ kJ/mol$

b. $NH_3(g) \rightarrow NH_3(aq)\ \Delta H°_{soln} = -80.29\ kJ - (-46.19\ kJ)$
$= -34.10\ kJ/mol$

c. $H_2(g) \rightarrow 2H(g)\quad \Delta H°_{BDE} = 2(+217.97\ kJ) - 0\ kJ = +435.94\ kJ/mol$

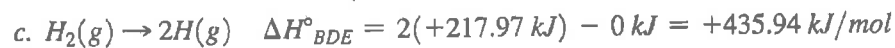d. $Br_2(g) \rightarrow Br_2(l)\quad \Delta H°_{cond} = 0\ kJ - (+30.70\ kJ) = -30.70\ kJ/mol$
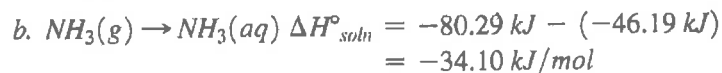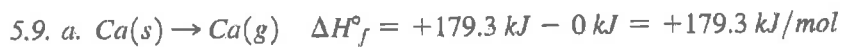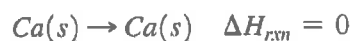
Table 5.3 or Appendix C in Chemistry: The Central Science *has the thermodynamic data to calculate the enthalpies of hundreds of processes.*