GENERAL CHEMISTRY

Principles and Modern Applications

TENTH EDITION

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Thermochemistry

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Thermochemistry

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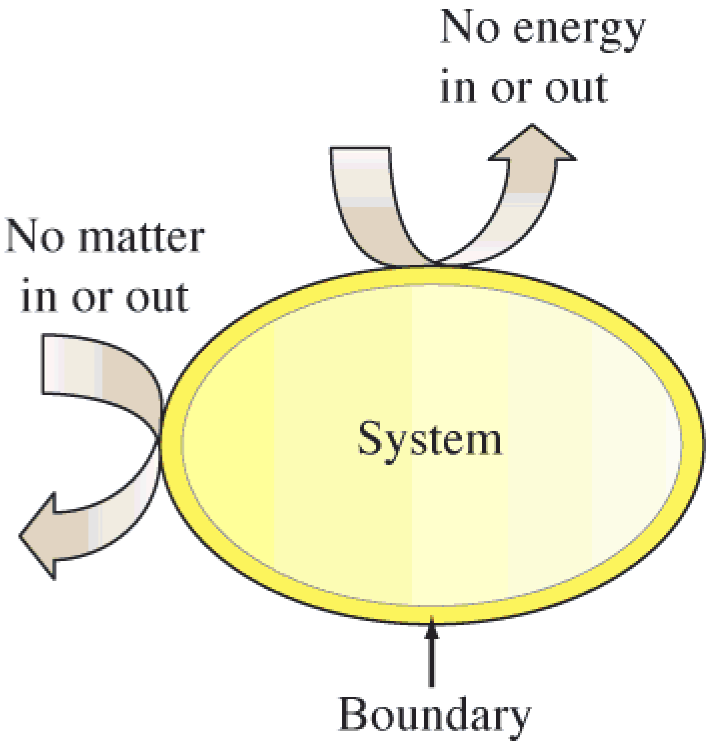
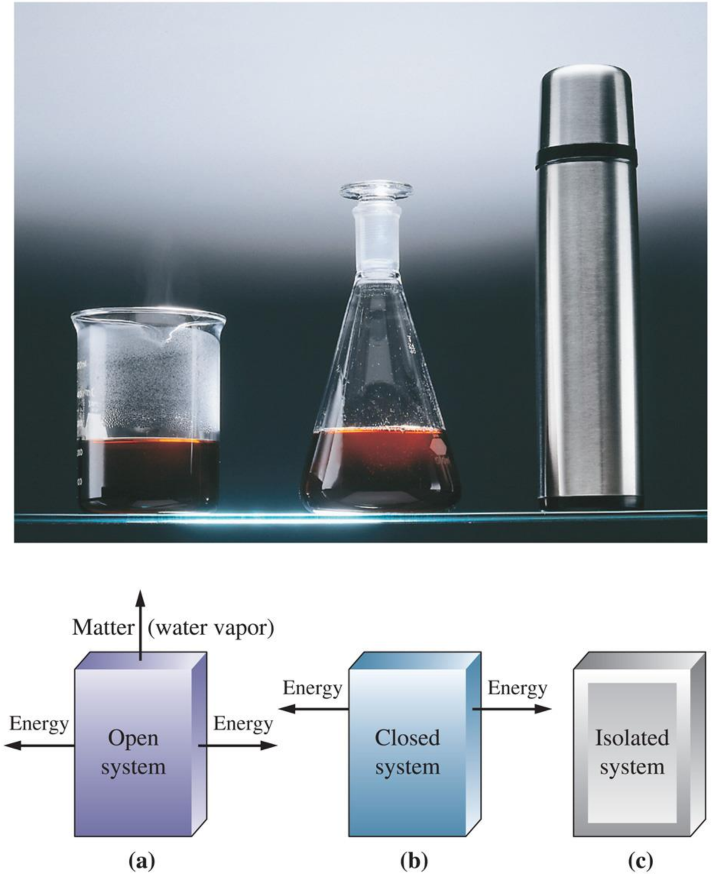
6-1 Getting Started: Some Terminology



▲ **Isolated system**

6-1 Getting Started: Some Terminology



▲ FIGURE 7-1

Systems and their surroundings

Energy, U

The capacity to do work.

Work, w

Force acting through a distance.

Kinetic Energy, e_K

The energy of motion.

Potential Energy, V

The stored energy has potential to do work.

Kinetic Energy

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

Work

$$w = F \times d$$

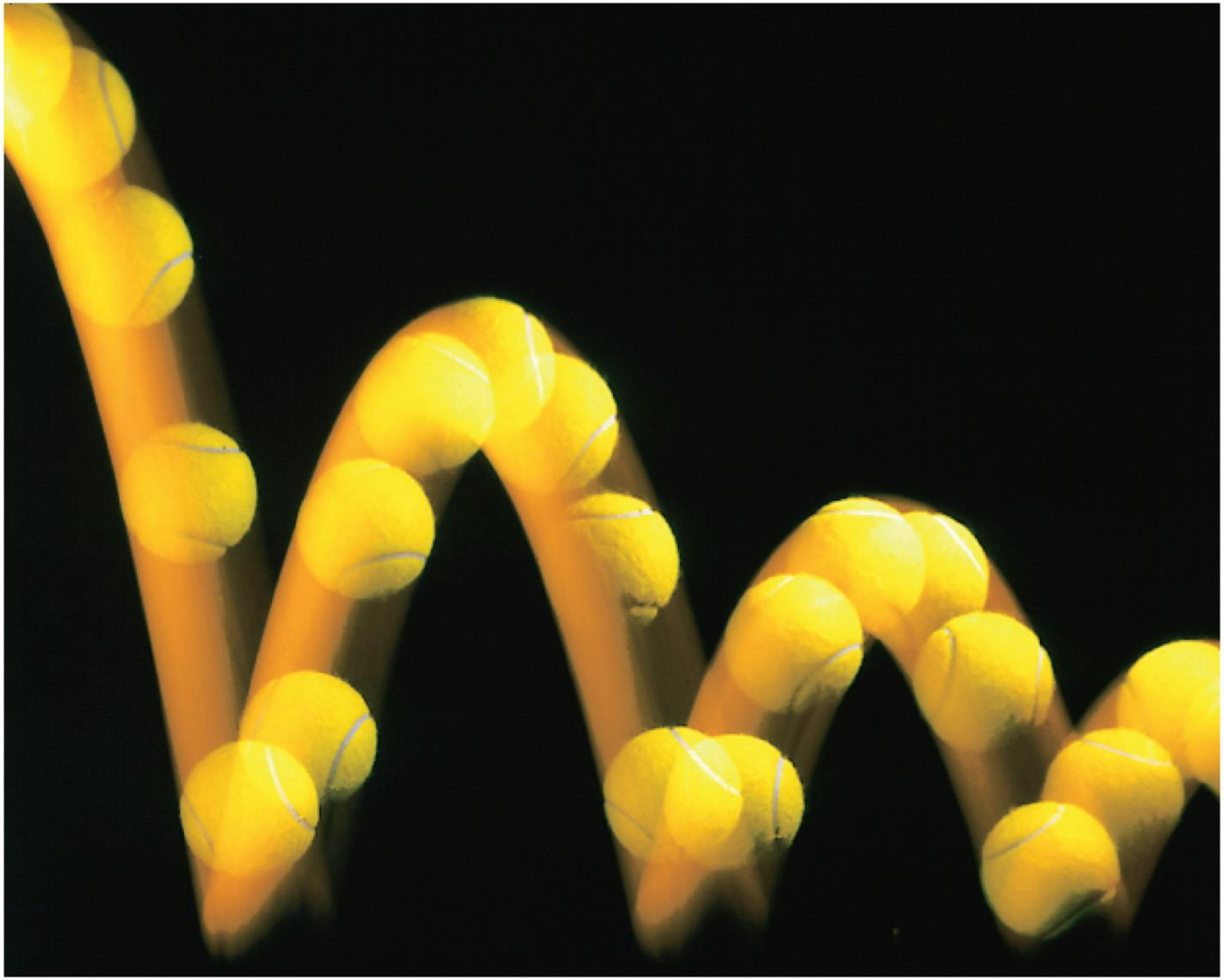
$$= m \times a \times d \qquad [w] = \text{kg}\left(\frac{\text{m}}{\text{s}^2}\right)\text{m} = \text{J}$$

Potential Energy

Energy due to condition, position, or composition.

Associated with forces of attraction or repulsion between objects.

Energy can change from potential to kinetic.



▲ FIGURE 7-2

Potential energy (P.E.) and kinetic energy (K.E.)

7-2 Heat

Thermal Energy

Kinetic energy associated with random molecular motion.

In general proportional to temperature.

Number of particle is also important.

An intensive property.

Heat and Work

q and *w*.

Energy changes.

Heat:

Internal energy is *transferred* between a system and its surroundings as a result of a temperature difference.

Heat *"flows"* from hotter to colder.

  Temperature may change.

  Phase may change (an isothermal process).

  - Thermal energy is used to overcome molecular interactions during phase change. (T const.)
  - İsothermal process

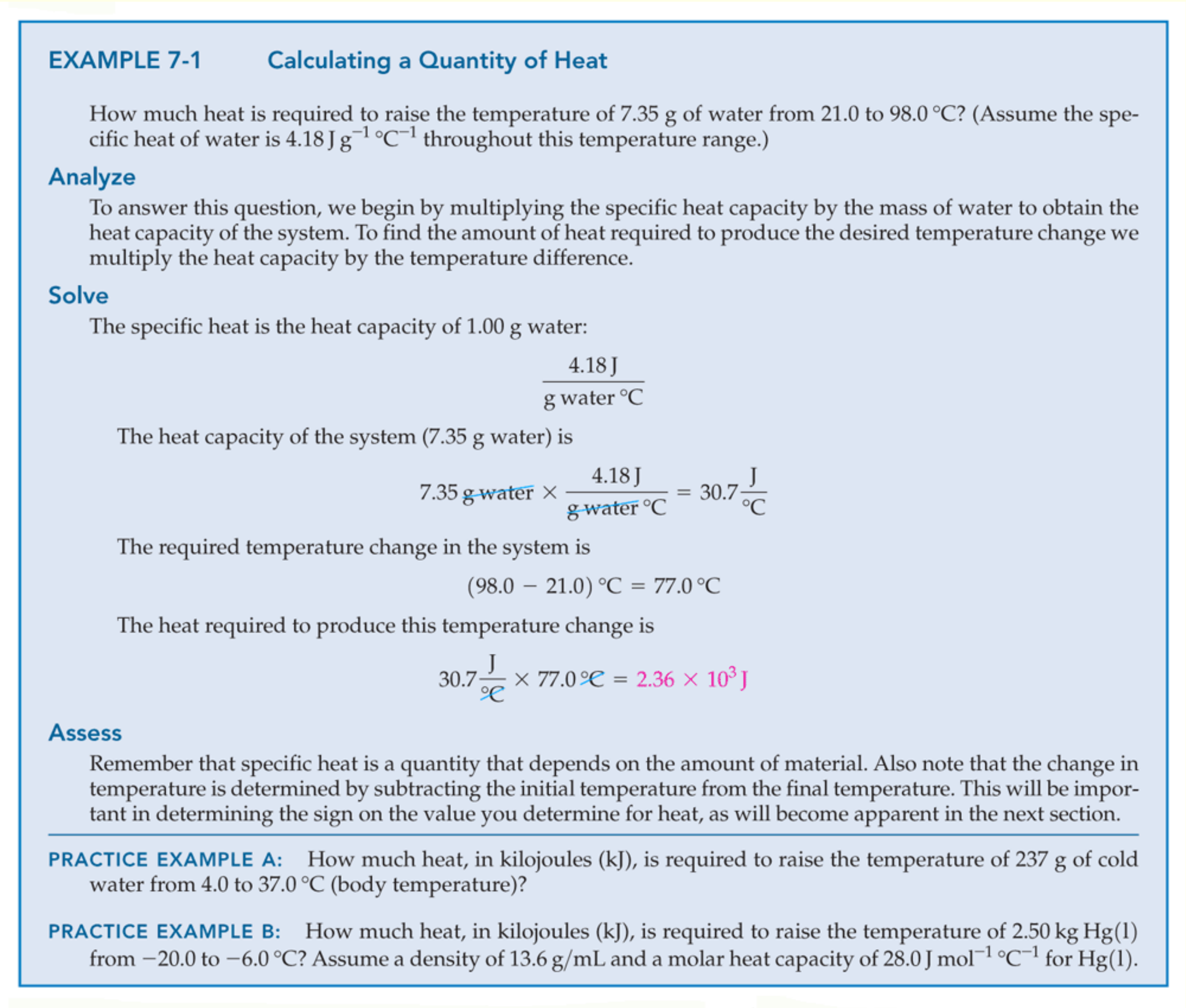
Calorie (cal)

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

Joule (J)

SI unit for heat

1 cal = 4.184 J



EXAMPLE 7-1 Calculating a Quantity of Heat

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

Analyze

To answer this question, we begin by multiplying the specific heat capacity by the mass of water to obtain the heat capacity of the system. To find the amount of heat required to produce the desired temperature change we multiply the heat capacity by the temperature difference.

Solve

The specific heat is the heat capacity of 1.00 g water:

$$\frac{4.18\ \text{J}}{\text{g water}\ ^\circ\text{C}}$$

The heat capacity of the system (7.35 g water) is

$$7.35\ \cancel{\text{g water}} \times \frac{4.18\ \text{J}}{\cancel{\text{g water}}\ ^\circ\text{C}} = 30.7\ \frac{\text{J}}{^\circ\text{C}}$$

The required temperature change in the system is

$$(98.0 - 21.0)\ ^\circ\text{C} = 77.0\ ^\circ\text{C}$$

The heat required to produce this temperature change is

$$30.7\ \frac{\text{J}}{\cancel{^\circ\text{C}}} \times 77.0\ \cancel{^\circ\text{C}} = 2.36 \times 10^3\ \text{J}$$

Assess

Remember that specific heat is a quantity that depends on the amount of material. Also note that the change in temperature is determined by subtracting the initial temperature from the final temperature. This will be important in determining the sign on the value you determine for heat, as will become apparent in the next section.

PRACTICE EXAMPLE A: How much heat, in kilojoules (kJ), is required to raise the temperature of 237 g of cold water from 4.0 to 37.0 °C (body temperature)?

PRACTICE EXAMPLE B: How much heat, in kilojoules (kJ), is required to raise the temperature of 2.50 kg Hg(l) from −20.0 to −6.0 °C? Assume a density of 13.6 g/mL and a molar heat capacity of $28.0\ \text{J mol}^{-1}\ ^\circ\text{C}^{-1}$ for Hg(l).

Heat Capacity

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

Molar heat capacity.

System is one mole of substance.

Specific heat capacity, c.

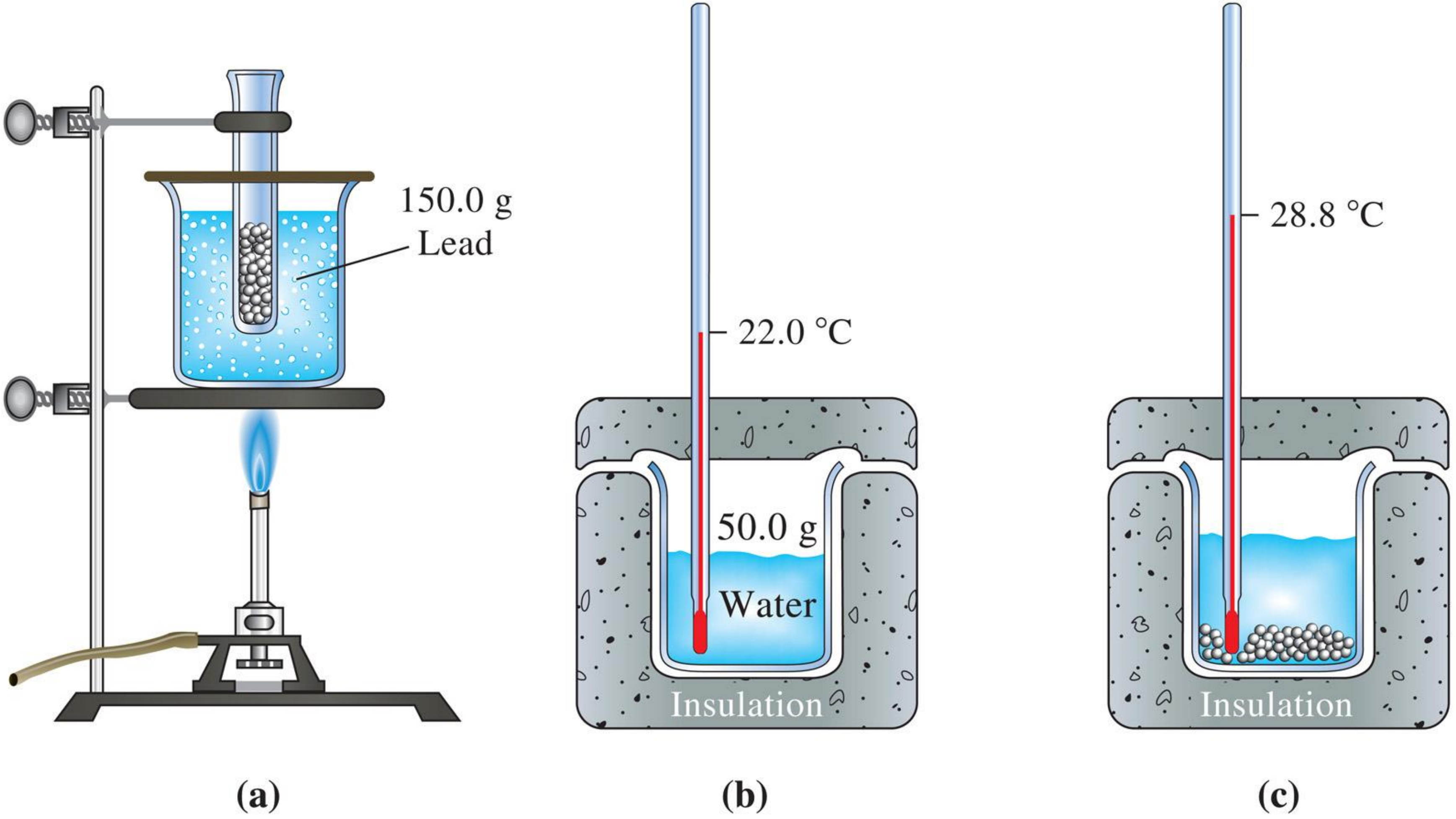
System is one gram of substance

Heat capacity

(Mass of system) x specific heat.

$$q = mc\Delta T$$

$$q = C\Delta T$$



▲ FIGURE 7-3

Determining the specific heat of lead – Example 7-2 illustrated

EXAMPLE 7-2 Determining a Specific Heat from Experimental Data

Use data presented in Figure 7-3 to calculate the specific heat of lead.

Analyze

Keep in mind that if we know any four of the five quantities—q, m, specific heat, T_f, T_i—we can solve equation (7.5) for the remaining one. We know from Figure 7-3 that a known quantity of lead is heated and then dumped into a known amount of water at a known temperature, which is the initial temperature. Once the system comes to equilibrium, the water temperature is the final temperature. In this type of question, we will use equation (7.5).

Solve

First, use equation (7.5) to calculate q_{water}.

$$q_{\text{water}} = 50.0\text{ g water} \times \frac{4.18\text{ J}}{\text{g water }^\circ\text{C}} \times (28.8 - 22.0)\ ^\circ\text{C} = 1.4 \times 10^3\text{ J}$$

From equation (7.8) we can write

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

Now, from equation (7.5) again, we obtain

$$q_{\text{lead}} = 150.0\text{ g lead} \times \text{specific heat of lead} \times (28.8 - 100.0)\ ^\circ\text{C} = -1.4 \times 10^3\text{ J}$$

$$\text{specific heat of lead} = \frac{-1.4 \times 10^3\text{ J}}{150.0\text{ g lead} \times (28.8 - 100.0)\ ^\circ\text{C}} = \frac{-1.4 \times 10^3\text{ J}}{150.0\text{ g lead} \times -71.2\ ^\circ\text{C}} = 0.13\text{ J g}^{-1}\ ^\circ\text{C}^{-1}$$

Assess

The key concept to recognize is that energy, in the form of heat, flowed from the lead, which is our system, to the water, which is part of the surroundings. A quick way to make sure that we have done the problem correctly is to check the sign on the final answer. For specific heat, the sign should always be positive and have the units of $\text{J g}^{-1}\ ^\circ\text{C}^{-1}$.

PRACTICE EXAMPLE A: When 1.00 kg lead (specific heat $= 0.13\text{ J g}^{-1}\ ^\circ\text{C}^{-1}$) at 100.0 °C is added to a quantity of water at 28.5 °C, the final temperature of the lead–water mixture is 35.2 °C. What is the mass of water present?

PRACTICE EXAMPLE B: A 100.0 g copper sample (specific heat $= 0.385\text{ J g}^{-1}\ ^\circ\text{C}^{-1}$) at 100.0 °C is added to 50.0 g water at 26.5 °C. What is the final temperature of the copper–water mixture?

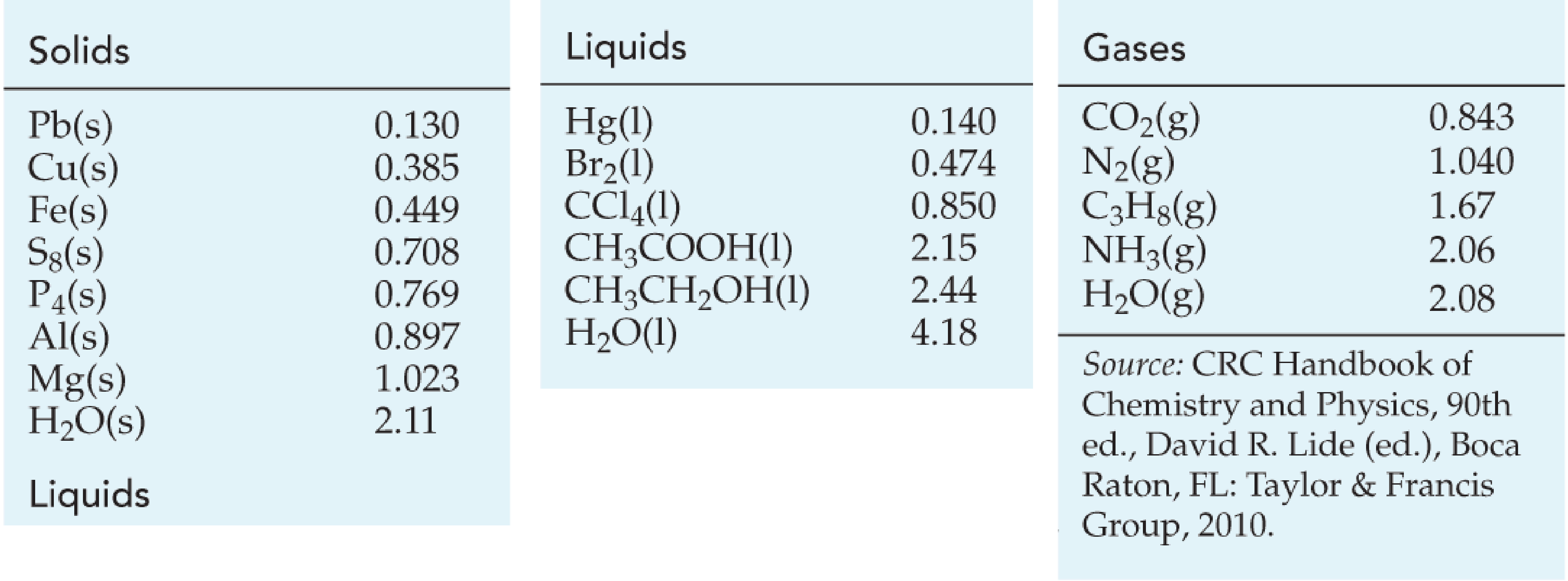
Law of conservation of energy

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

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

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

TABLE 7.1 Some Specific Heat Values, J g^{-1} °C^{-1}



Solids	
$Pb(s)$	0.130
$Cu(s)$	0.385
$Fe(s)$	0.449
$S_8(s)$	0.708
$P_4(s)$	0.769
$Al(s)$	0.897
$Mg(s)$	1.023
$H_2O(s)$	2.11

Liquids

Liquids	
$Hg(l)$	0.140
$Br_2(l)$	0.474
$CCl_4(l)$	0.850
$CH_3COOH(l)$	2.15
$CH_3CH_2OH(l)$	2.44
$H_2O(l)$	4.18

Gases	
$CO_2(g)$	0.843
$N_2(g)$	1.040
$C_3H_8(g)$	1.67
$NH_3(g)$	2.06
$H_2O(g)$	2.08

Source: CRC Handbook of Chemistry and Physics, 90th ed., David R. Lide (ed.), Boca Raton, FL: Taylor & Francis Group, 2010.

7-3 Heats of Reaction and Calorimetry

Chemical energy.

Contributes to the internal energy of a system.

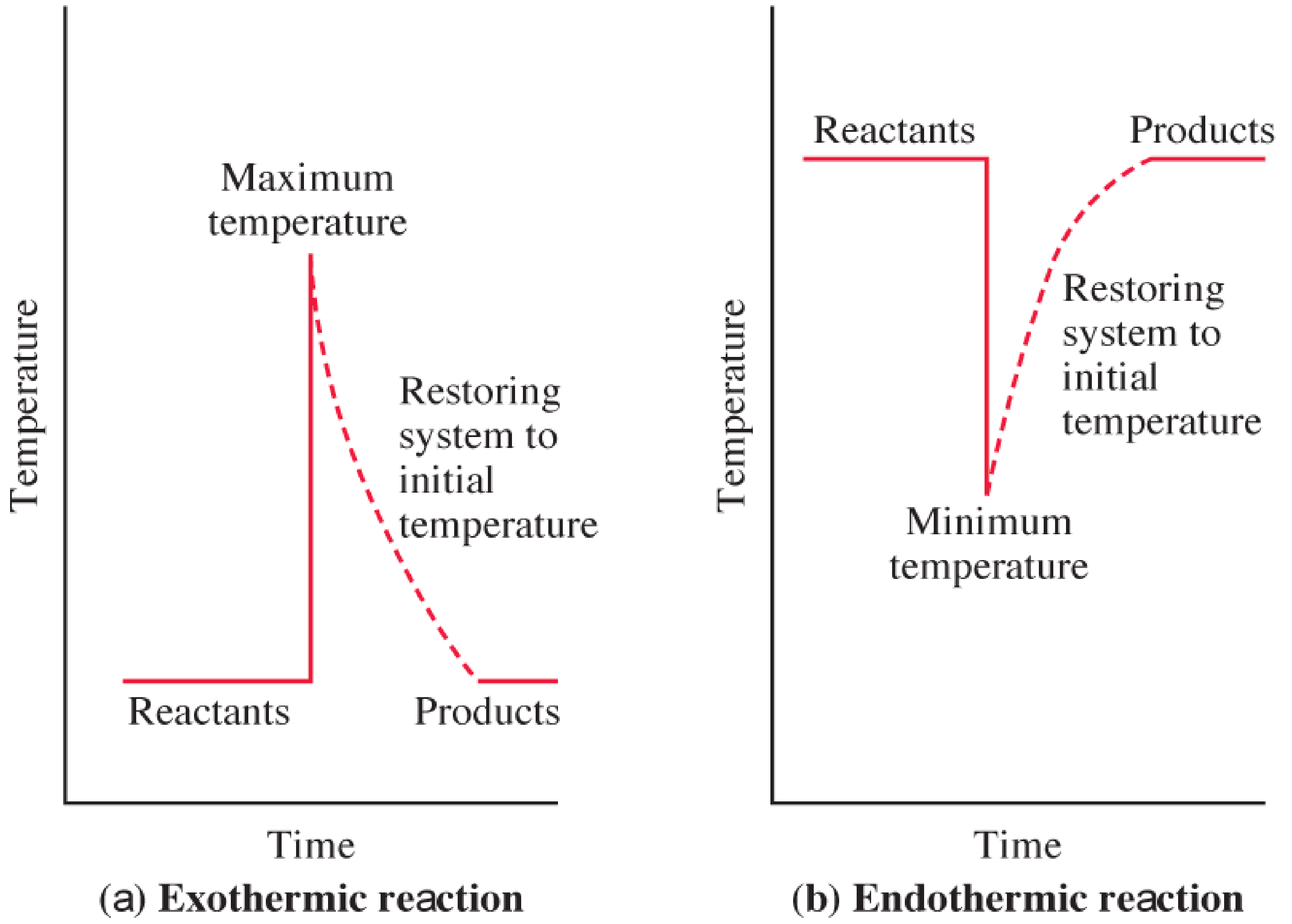
Heat of reaction, $q_{rxn.}$

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

Exothermic and endothermic reactions

KEEP IN MIND

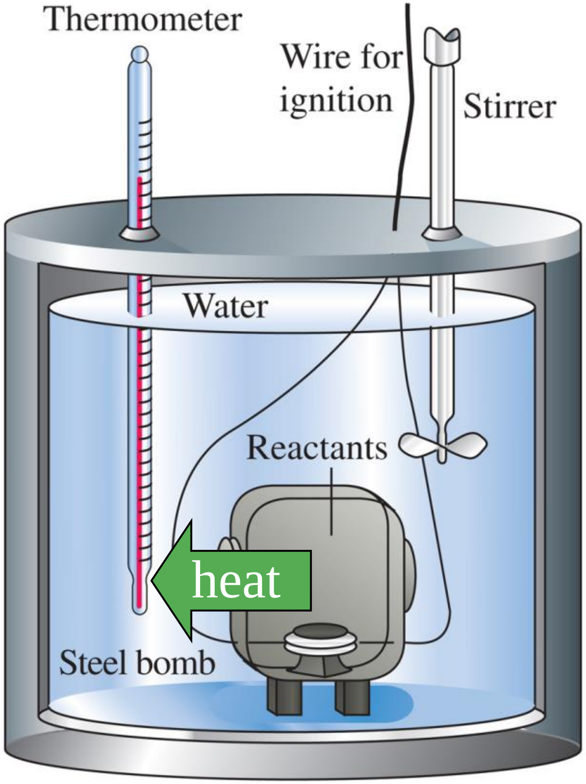
that the temperature of a reaction mixture usually changes during a reaction, so the mixture must be returned to the initial temperature (actually or hypothetically) before we assess how much heat is exchanged with the surroundings.



▲ FIGURE 7-4

Conceptualizing a heat of reaction at constant temperature

Bomb Calorimetry



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

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

Define the heat capacity of the calorimeter:

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

▲ FIGURE 7-5

A bomb calorimeter assembly

EXAMPLE 7-3 Using Bomb Calorimetry Data to Determine a Heat of Reaction

The combustion of 1.010 g sucrose, $C_{12}H_{22}O_{11}$, in a bomb calorimeter causes the temperature to rise from 24.92 to 28.33 °C. The heat capacity of the calorimeter assembly is 4.90 kJ/°C. **(a)** What is the heat of combustion of sucrose expressed in kilojoules per mole of $C_{12}H_{22}O_{11}$? **(b)** Verify the claim of sugar producers that one teaspoon of sugar (about 4.8 g) contains only 19 Calories.

Analyze

We are given a specific heat and two temperatures, the initial and the final, which indicate that we are to use equation (7.5). In these kinds of experiments one obtains the amount of heat generated by the reaction by measuring the temperature change in the surroundings. This means that $q_{\text{rxn}} = -q_{\text{calorim}}$.

Solve

(a) Calculate q_{calorim} with equation (7.10).

$$q_{\text{calorim}} = 4.90\ \text{kJ/°C} \times (28.33 - 24.92)\ \text{°C} = (4.90 \times 3.41)\ \text{kJ} = 16.7\ \text{kJ}$$

Now, using equation (7.9), we get

$$q_{\text{rxn}} = -q_{\text{calorim}} = -16.7\ \text{kJ}$$

This is the heat of combustion of the 1.010 g sample.
Per gram $C_{12}H_{22}O_{11}$:

$$q_{\text{rxn}} = \frac{-16.7\ \text{kJ}}{1.010\ \text{g}\ C_{12}H_{22}O_{11}} = -16.5\ \text{kJ/g}\ C_{12}H_{22}O_{11}$$

Per mole $C_{12}H_{22}O_{11}$:

$$q_{\text{rxn}} = \frac{-16.5\ \text{kJ}}{\text{g}\ C_{12}H_{22}O_{11}} \times \frac{342.3\ \text{g}\ C_{12}H_{22}O_{11}}{1\ \text{mol}\ C_{12}H_{22}O_{11}} = -5.65 \times 10^3\ \text{kJ/mol}\ C_{12}H_{22}O_{11}$$

(b) To determine the caloric content of sucrose, we can use the heat of combustion per gram of sucrose determined in part **(a)**, together with a factor to convert from kilojoules to kilocalories. (Because 1 cal = 4.184 J, 1 kcal = 4.184 kJ.)

$$?\ \text{kcal} = \frac{4.8\ \text{g}\ C_{12}H_{22}O_{11}}{\text{tsp}} \times \frac{-16.5\ \text{kJ}}{\text{g}\ C_{12}H_{22}O_{11}} \times \frac{1\ \text{kcal}}{4.184\ \text{kJ}} = \frac{-19\ \text{kcal}}{\text{tsp}}$$

1 food Calorie (1 Calorie with a capital C) is actually 1000 cal, or 1 kcal. Therefore, 19 kcal = 19 Calories. The claim is justified.

Assess

A combustion reaction is an exothermic reaction, which means that energy flows, in the form of heat, from the reaction system to the surroundings. Therefore, the q for a combustion reaction is negative.

PRACTICE EXAMPLE A: Vanillin is a natural constituent of vanilla. It is also manufactured for use in artificial vanilla flavoring. The combustion of 1.013 g of vanillin, $C_8H_8O_3$, in the same bomb calorimeter as in Example 7-3 causes the temperature to rise from 24.89 to 30.09 °C. What is the heat of combustion of vanillin, expressed in kilojoules per mole?

PRACTICE EXAMPLE B: The heat of combustion of benzoic acid is −26.42 kJ/g. The combustion of a 1.176 g

The “Coffee-Cup” Calorimeter

▲ FIGURE 7-6

A Styrofoam “coffee-cup” calorimeter

A simple calorimeter.

- Well insulated and therefore *isolated*.
- Measure temperature change.

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

EXAMPLE 7-4 Determining a Heat of Reaction from Calorimetric Data

In the neutralization of a strong acid with a strong base, the essential reaction is the combination of $H^+(aq)$ and $OH^-(aq)$ to form water (recall page 165).

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

Two solutions, 25.00 mL of 2.50 M HCl(aq) and 25.00 mL of 2.50 M NaOH(aq), both initially at 21.1 °C, are added to a Styrofoam-cup calorimeter and allowed to react. The temperature rises to 37.8 °C. Determine the heat of the neutralization reaction, expressed per mole of H_2O formed. Is the reaction endothermic or exothermic?

Analyze

In addition to assuming that the calorimeter is an isolated system, assume that all there is in the system to absorb heat is 50.00 mL of water. This assumption ignores the fact that 0.0625 mol each of NaCl and H_2O are formed in the reaction, that the density of the resulting NaCl(aq) is not exactly 1.00 g/mL, and that its specific heat is not exactly $4.18\,\text{J g}^{-1}\,°\text{C}^{-1}$. Also, ignore the small heat capacity of the Styrofoam cup itself.

Because the reaction is a neutralization reaction, let us call the heat of reaction q_{neutr}. Now, according to equation (7.9), $q_{\text{neutr}} = -q_{\text{calorim}}$, and if we make the assumptions described above, we can solve the problem.

Solve

We begin with

$$q_{\text{calorim}} = 50.00\text{ mL} \times \frac{1.00\text{ g}}{\text{mL}} \times \frac{4.18\text{ J}}{\text{g }°\text{C}} \times (37.8 - 21.1)\,°\text{C} = 3.5 \times 10^3\text{ J}$$

$$q_{\text{neutr}} = -q_{\text{calorim}} = -3.5 \times 10^3\text{ J} = -3.5\text{ kJ}$$

In 25.00 mL of 2.50 M HCl, the amount of H^+ is

$$?\text{ mol H}^+ = 25.00\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{2.50\text{ mol}}{1\text{ L}} \times \frac{1\text{ mol H}^+}{1\text{ mol HCl}} = 0.0625\text{ mol H}^+$$

Similarly, in 25.00 mL of 2.50 M NaOH there is 0.0625 mol OH^-. Thus, the H^+ and the OH^- combine to form 0.0625 mol H_2O. (The two reactants are in *stoichiometric* proportions; neither is in excess.)

The amount of heat produced per mole of H_2O is

$$q_{\text{neutr}} = \frac{-3.5\text{ kJ}}{0.0625\text{ mol H}_2\text{O}} = -56\text{ kJ/mol H}_2\text{O}$$

Assess

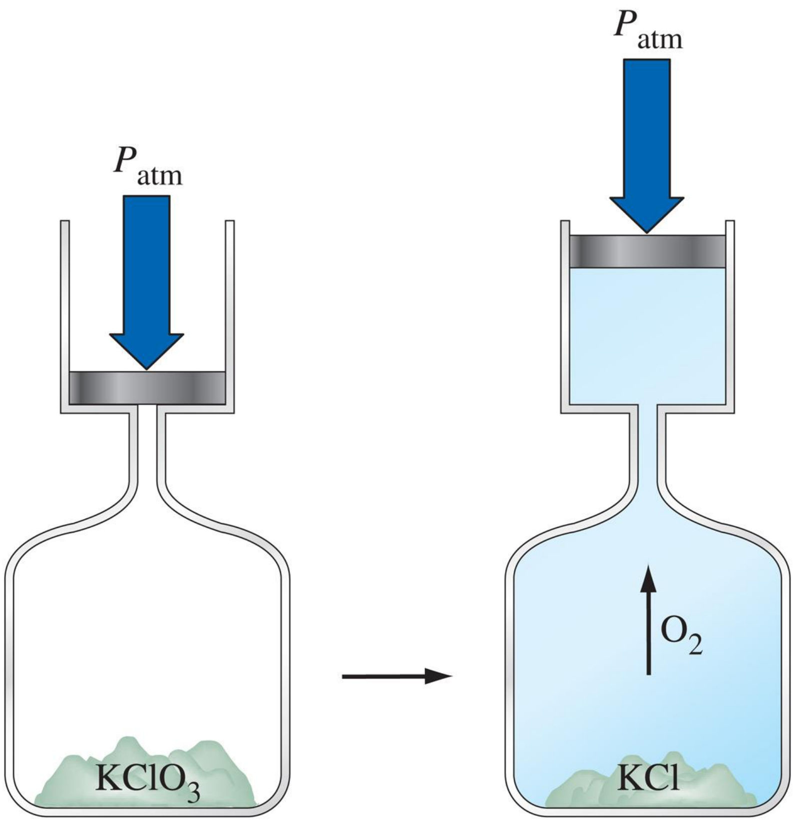
Because q_{neutr} is a *negative* quantity, the neutralization reaction is *exothermic*. Even though, in this example, we considered a specific reaction, the result $q_{\text{neutr}} = -56$ kJ/mol is more general. We will obtain the same value of q_{neutr} by considering any strong acid-strong base reaction because the net ionic equation is the same for all strong acid-strong base reactions.

PRACTICE EXAMPLE A: Two solutions, 100.0 mL of 1.00 M $AgNO_3(aq)$ and 100.0 mL of 1.00 M NaCl(aq), both initially at 22.4 °C, are added to a Styrofoam-cup calorimeter and allowed to react. The temperature rises to 30.2 °C. Determine q_{rxn} per mole of AgCl(s) in the reaction.

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

PRACTICE EXAMPLE B: Two solutions, 100.0 mL of 1.020 M HCl and 50.0 mL of 1.988 M NaOH, both initially at 24.52 °C, are mixed in a Styrofoam-cup calorimeter. What will be the final temperature of the mixture? Make

7-4 Work



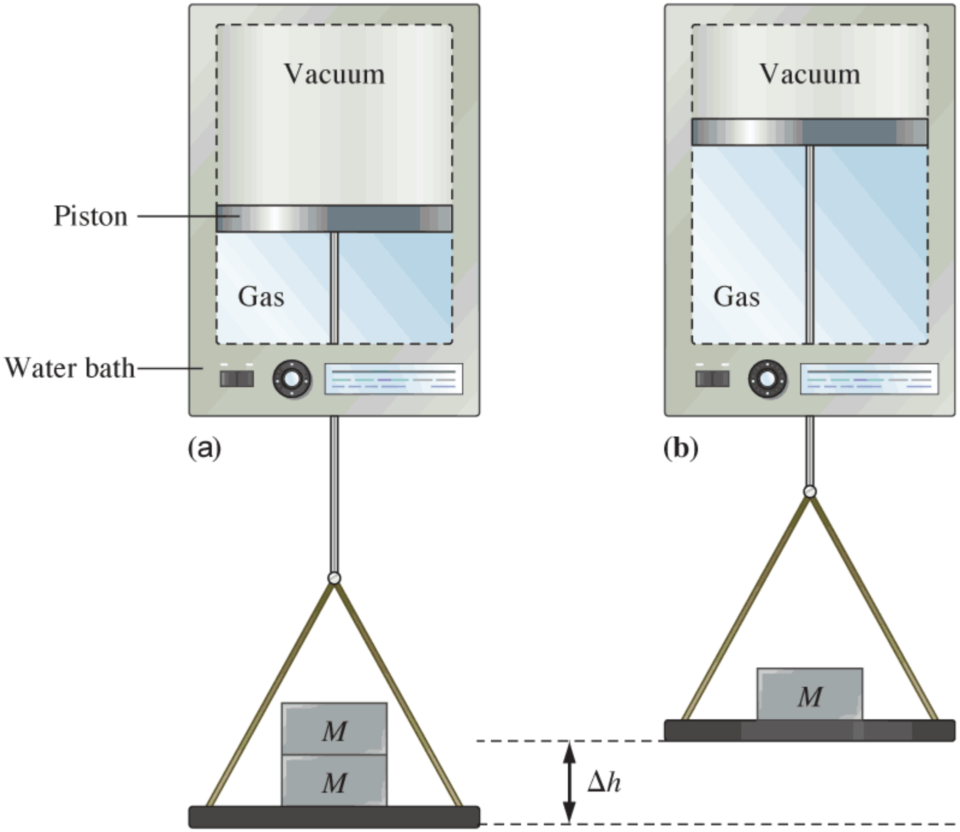
In addition to heat effects chemical reactions may also do *work*.

Gas formed pushes against the atmosphere.

The volume changes.

Pressure-volume work.

▲ FIGURE 7-7 **Illustrating work (expansion) during the chemical reaction**
$2\ KClO_3(s) \longrightarrow 2\ KCl(s) + 3\ O_2(g)$



▲ FIGURE 7-8
Pressure–volume work

$$w = F \times d$$
$$= (m \times g) \times \Delta h$$
$$= \frac{(m \times g)}{A} \times \Delta h \times A$$
$$= P\Delta V$$
$$w = -P_{ext}\Delta V$$

▲
Pressure-volume work

unit of work:

1 bar L=100 J

1 atm L= 101.325 J

Check Ratios of R with units bar and J

$$\frac{8.3145 \text{ J/mol K}}{0.083145 \text{ barL/molK}} = 100 \text{ J/barL}$$

EXAMPLE 7-5 Calculating Pressure–Volume Work

Suppose the gas in Figure 7-8 is 0.100 mol He at 298 K, the two weights correspond to an external pressure of 2.40 atm in Figure 7-8(a), and the single weight in Figure 7-8(b) corresponds to an external pressure of 1.20 atm. How much work, in joules, is associated with the gas expansion at constant temperature?

Analyze

We are given enough data to calculate the initial and final gas volumes (note that the identity of the gas does not enter into the calculations because we are assuming ideal gas behavior). With these volumes, we can obtain ΔV. The external pressure in the pressure–volume work is the *final* pressure: 1.20 atm. The product $-P_{\text{ext}} \times \Delta V$ must be multiplied by a factor to convert work in liter-atmospheres to work in joules.

Solve

First calculate the initial and final volumes.

$$V_{\text{initial}} = \frac{nRT}{P_{\text{i}}} = \frac{0.100\ \text{mol} \times 0.0821\ \text{L atm mol}^{-1}\,\text{K}^{-1} \times 298\ \text{K}}{2.40\ \text{atm}} = 1.02\ \text{L}$$

$$V_{\text{final}} = \frac{nRT}{P_{\text{f}}} = \frac{0.100\ \text{mol} \times 0.0821\ \text{L atm mol}^{-1}\,\text{K}^{-1} \times 298\ \text{K}}{1.20\ \text{atm}} = 2.04\ \text{L}$$

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

$$w = -P_{\text{ext}} \times \Delta V = -1.20\ \text{atm} \times 1.02\ \text{L} \times \frac{101\ \text{J}}{1\ \text{L atm}} = -1.24 \times 10^{2}\ \text{J}$$

Assess

The negative value signifies that the expanding gas (i.e., the system) does work on its surroundings. Keep in mind that the ideal gas equation embodies Boyle's law: The volume of a fixed amount of gas at a fixed temperature is inversely proportional to the pressure. Thus, in Example 7-5 we could simply write that

$$V_{\text{f}} = 1.02\ \text{L} \times \frac{2.40\ \text{atm}}{1.20\ \text{atm}}$$

$$V_{\text{f}} = 2.04\ \text{L}$$

PRACTICE EXAMPLE A: How much work, in joules, is involved when 0.225 mol N_2 at a constant temperature of 23 °C is allowed to expand by 1.50 L in volume against an external pressure of 0.750 atm? [*Hint:* How much of this information is required?]

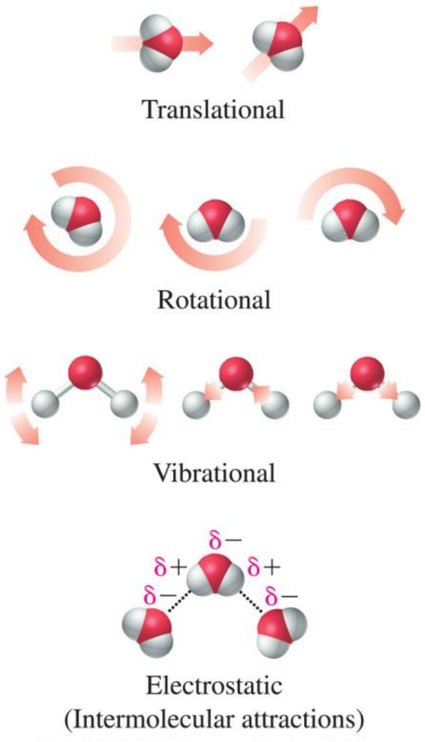
PRACTICE EXAMPLE B: How much work is done, in joules, when an external pressure of 2.50 atm is applied, at a constant temperature of 20.0 °C, to 50.0 g $N_2(g)$ in a 75.0 L cylinder? The cylinder is like that shown in Figure 7-8.

7-5 The First Law of Thermodynamics

Internal Energy, U.

Total energy (potential and kinetic) in a system.

- Translational kinetic energy.
- Molecular rotation.
- Bond vibration.
- Intermolecular attractions.
- Chemical bonds.
- Electrons.



▲ FIGURE 7-9

Some contributions to the internal energy of a system

The First Law of Thermodynamics

A system contains *only* internal energy.

- A system does not contain heat or work.
- These only occur during a *change* in the system.

$$\boxed{\Delta U = q + w}$$

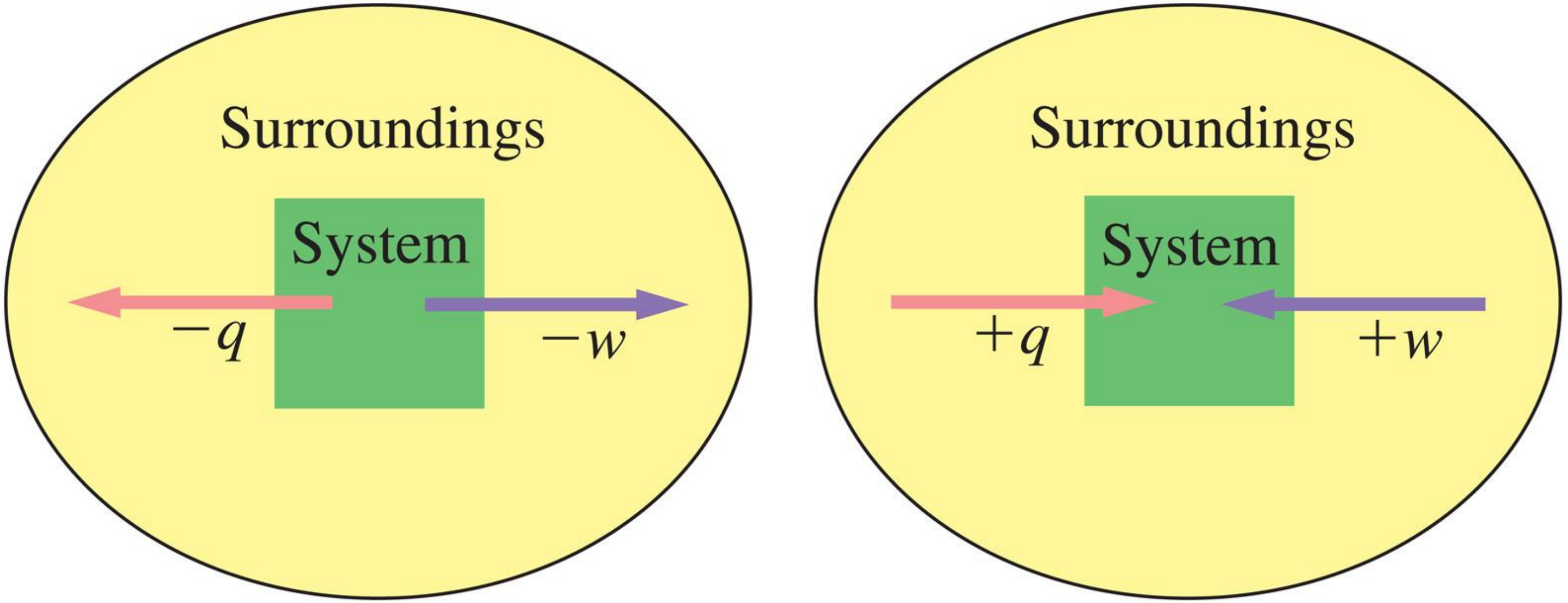
Law of Conservation of Energy

- The energy of an isolated system is constant

The First Law of Thermodynamics

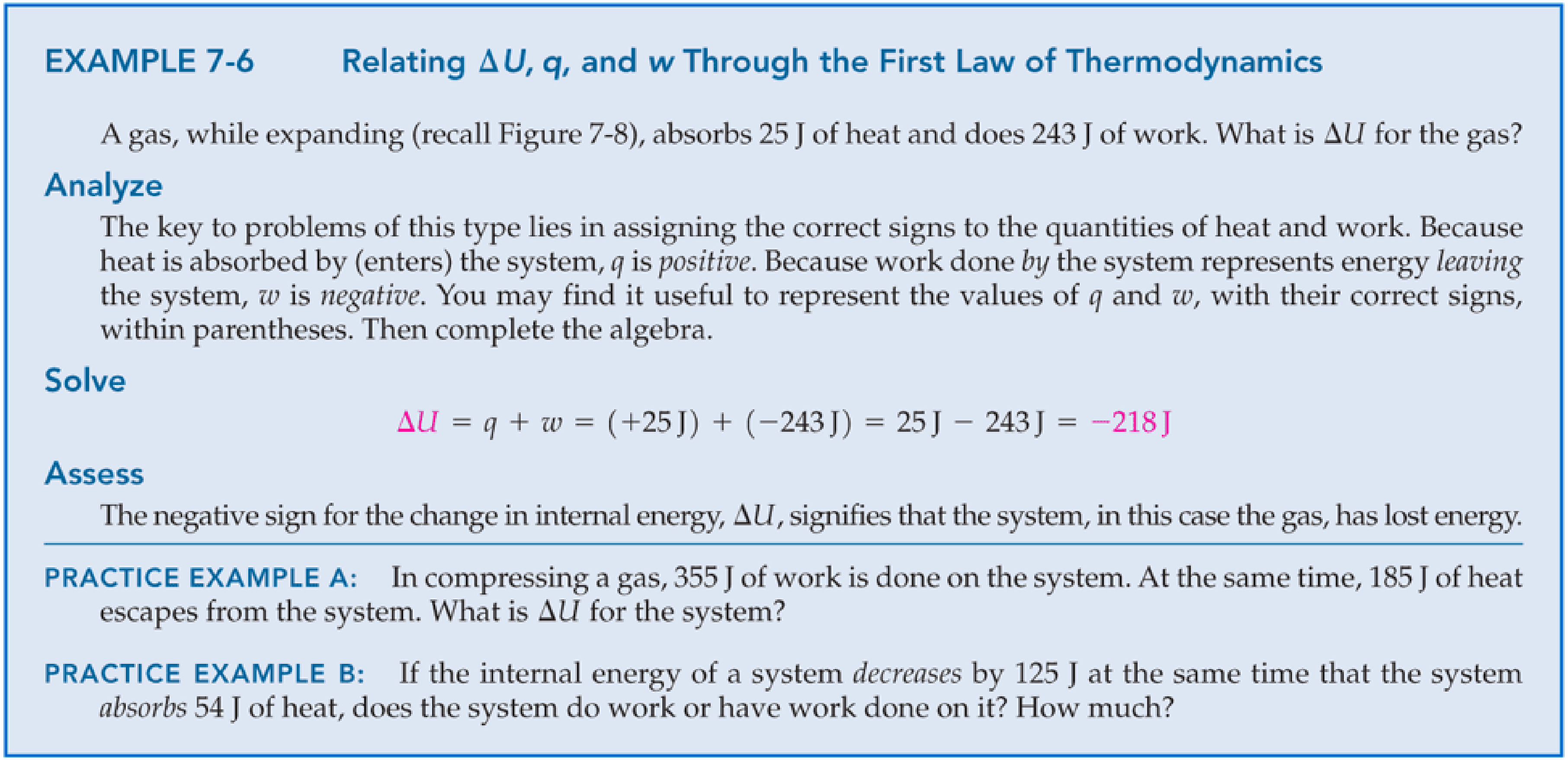
An isolated system is unable to exchange either heat or work with its surroundings, so that $\Delta U_{\text{isolated}}$ system = 0, and we can say:

The energy of an isolated system is constant.



▲ FIGURE 7-10

Illustration of sign conventions used in thermodynamics



EXAMPLE 7-6 Relating ΔU, q, and w Through the First Law of Thermodynamics

A gas, while expanding (recall Figure 7-8), absorbs 25 J of heat and does 243 J of work. What is ΔU for the gas?

Analyze

The key to problems of this type lies in assigning the correct signs to the quantities of heat and work. Because heat is absorbed by (enters) the system, q is *positive*. Because work done *by* the system represents energy *leaving* the system, w is *negative*. You may find it useful to represent the values of q and w, with their correct signs, within parentheses. Then complete the algebra.

Solve

$$\Delta U = q + w = (+25\,\text{J}) + (-243\,\text{J}) = 25\,\text{J} - 243\,\text{J} = -218\,\text{J}$$

Assess

The negative sign for the change in internal energy, ΔU, signifies that the system, in this case the gas, has lost energy.

PRACTICE EXAMPLE A: In compressing a gas, 355 J of work is done on the system. At the same time, 185 J of heat escapes from the system. What is ΔU for the system?

PRACTICE EXAMPLE B: If the internal energy of a system *decreases* by 125 J at the same time that the system *absorbs* 54 J of heat, does the system do work or have work done on it? How much?

Functions of State

Any property that has a unique value for a specified state of a system is said to be a **function of state** or a **state function**.

Water at 293.15 K and 1.00 atm is in a specified state.

d = 0.99820 g/mL

This density is a unique function of the state.

It does not matter *how* the state was established.

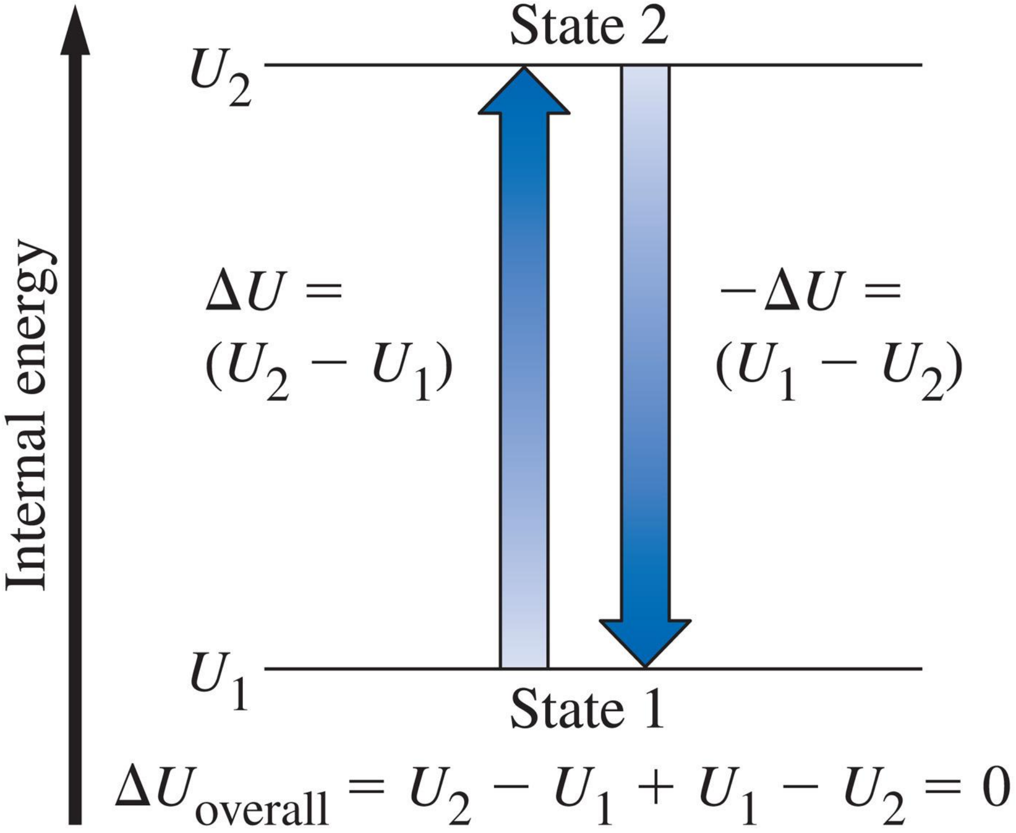
Functions of State

U is a function of state.

Not easily measured.

ΔU has a unique value between two states.

Is easily measured.



Path Dependent Functions

Changes in heat and work are not functions of state.

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

let us consider a two step process from
2.40 atm to 1.80 atm, and finally to 1.20 atm.

Path Dependent Functions

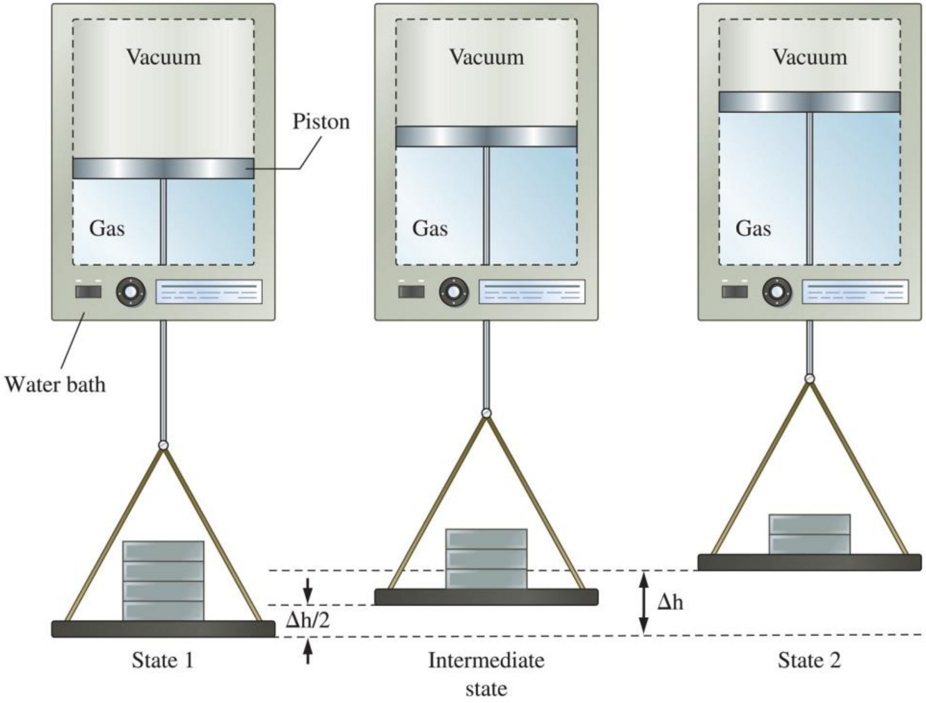
$w = (-1.80\ \text{atm})(1.36-1.02)\text{L} - (1.20\ \text{atm})(2.04-1.36)\text{L}$

$= -0.61\ \text{L atm} - 0.82\ \text{L atm}$

$= -1.43\ \text{L atm}$

$= -1.44 \times 10^2\ \text{J}$

Compared -1.24×10^2 J for the one stage process

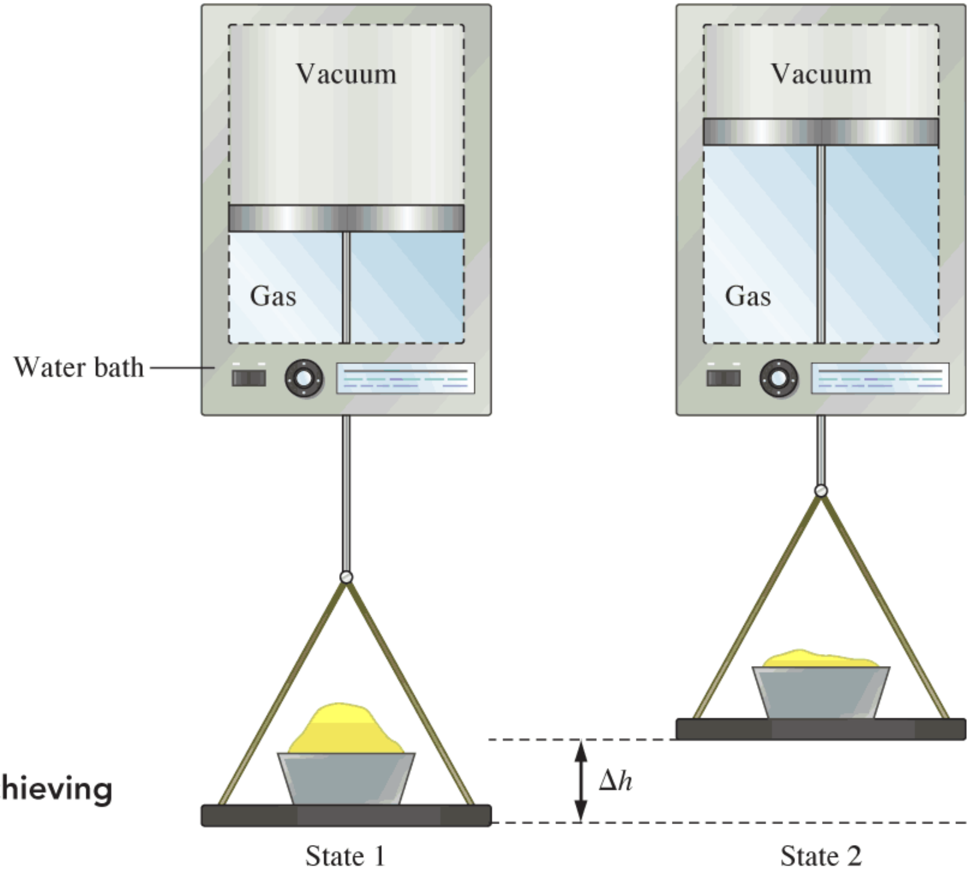


▲ FIGURE 7-11

A two-step expansion for the gas shown in Figure 7-8

Reversible Process:

- İnfinitesimal change, infinite number of intermediate process.
- Very slow change.
- Equilibrium between system and surrounding during the process.
- More work!



▶ FIGURE 7-12
A different method of achieving the expansion of a gas

7-6 Heats of Reaction: ΔU and ΔH

$$\text{Reactants} \rightarrow \text{Products}$$

$$U_i \qquad\qquad U_f$$

$$\Delta U = U_f - U_i$$

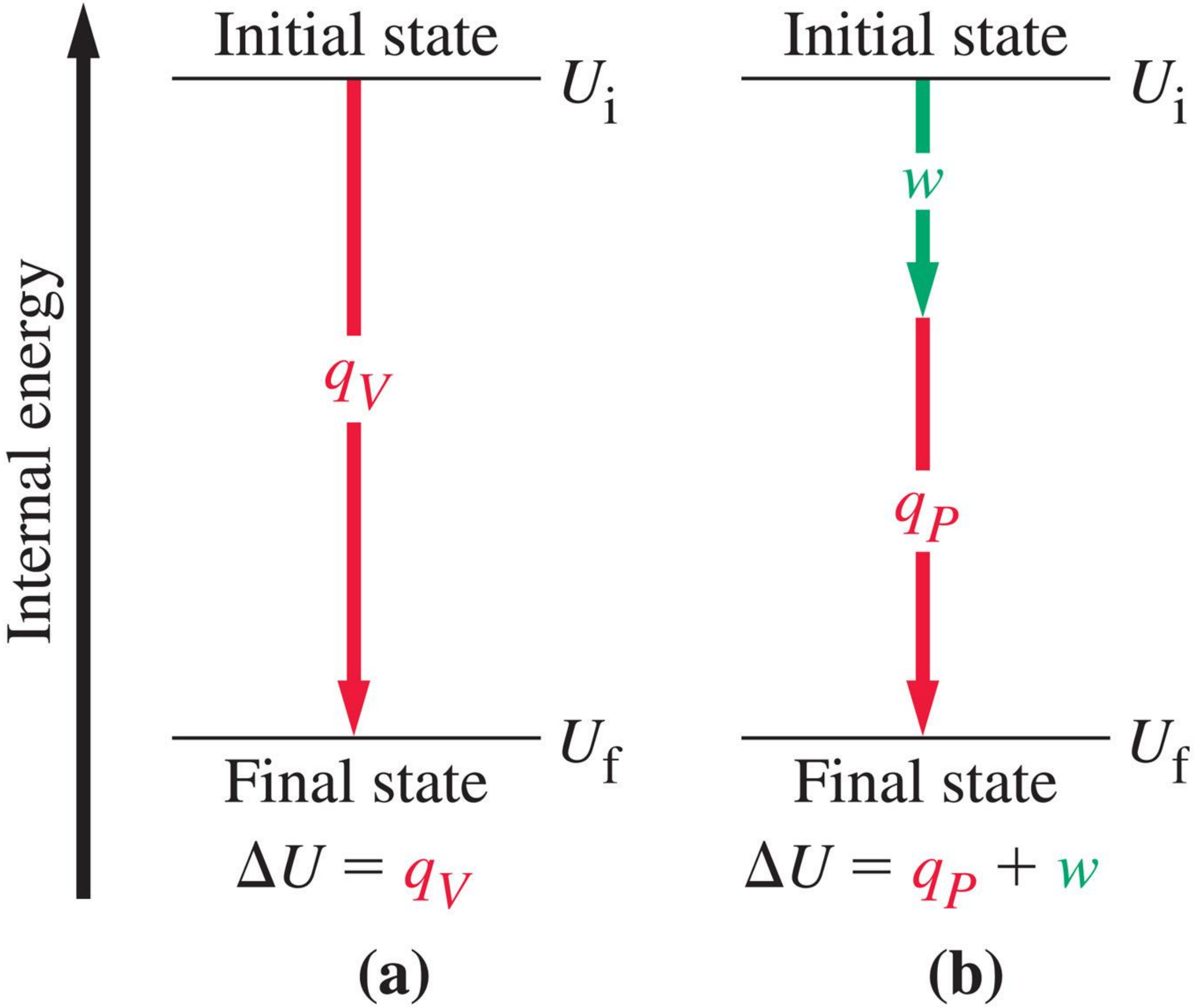
$$\Delta U = q_{rxn} + w$$

Combustıon rex, In a system at constant volume (bomb calorimeter):

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

But we live in a constant pressure world!

How does q_p relate to q_v?



▲ FIGURE 7-13

Two different paths leading to the same internal energy change in a system

Heats of Reaction

$$q_V = q_P + w$$

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

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

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

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

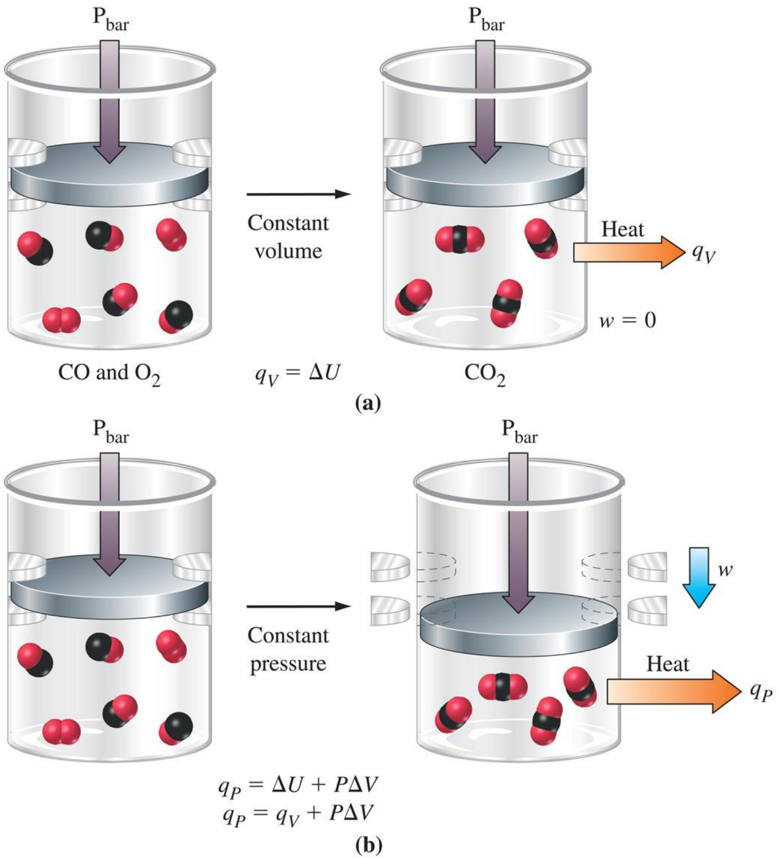
Let **enthalpy** be $H = U + PV$

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

If we work at constant pressure and temperature:

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

Comparing Heats of Reaction



$$q_V = \Delta U = \Delta H - P\Delta V$$

$$= -563.5 \text{ kJ/mol}$$

$$w = P\Delta V = P(V_f - V_i)$$

$$= RT(n_f - n_i)$$

$$= -2.5 \text{ kJ}$$

$$q_P \quad = \Delta H$$

$$= -566 \text{ kJ/mol}$$

▲ FIGURE 7-14

Comparing heats of reaction at constant volume and constant pressure for the reaction 2 CO(g) + 1 O_2(g) $\longrightarrow$ 2 CO_2(g)

EXAMPLE 7-7 Stoichiometric Calculations Involving Quantities of Heat

How much heat is associated with the complete combustion of 1.00 kg of sucrose, $C_{12}H_{22}O_{11}$?

Analyze

Equation (7.16) represents the combustion of 1 mol of sucrose. In that reaction the amount of heat generated is given as $\Delta H = -5.65 \times 10^3$ kJ/mol. The first step is to determine the number of moles in 1.00 kg of sucrose, and then use that value with the change in enthalpy for the reaction.

Solve

Express the quantity of sucrose in moles.

$$? \text{ mol} = 1.00 \text{ kg } C_{12}H_{22}O_{11} \times \frac{1000 \text{ g } C_{12}H_{22}O_{11}}{1 \text{ kg } C_{12}H_{22}O_{11}} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.3 \text{ g } C_{12}H_{22}O_{11}} = 2.92 \text{ mol } C_{12}H_{22}O_{11}$$

Formulate a conversion factor (shown in blue) based on the information in equation (7.16)—that is, -5.65×10^3 kJ of heat is associated with the combustion of 1 mol $C_{12}H_{22}O_{11}$.

$$? \text{ kJ} = 2.92 \text{ mol } C_{12}H_{22}O_{11} \times \frac{-5.65 \times 10^3 \text{ kJ}}{1 \text{ mol } C_{12}H_{22}O_{11}} = -1.65 \times 10^4 \text{ kJ}$$

The negative sign denotes that heat is given off in the combustion.

Assess

As discussed on page 249, the heat produced by a combustion reaction is not immediately transferred to the surroundings. Use data from Table 7.1 to show that the heat released by this reaction is *more* than that required to raise the temperature of the products to 100 °C.

PRACTICE EXAMPLE A: What mass of sucrose must be burned to produce 1.00×10^3 kJ of heat?

PRACTICE EXAMPLE B: A 25.0 mL sample of 0.1045 M HCl(aq) was neutralized by NaOH(aq). Use the result of Example 7-4 to determine the heat evolved in this neutralization.

Enthalpy Change (ΔH) Accompanying a Change in State of Matter

Molar enthalpy of vaporization:

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

Molar enthalpy of fusion:

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

EXAMPLE 7-8 Enthalpy Changes Accompanying Changes in States of Matter

Calculate ΔH for the process in which 50.0 g of water is converted from liquid at 10.0 °C to vapor at 25.0 °C.

Analyze

The key to this calculation is to view the process as proceeding in two steps: first raising the temperature of liquid water from 10.0 to 25.0 °C, and then completely vaporizing the liquid at 25.0 °C. The total enthalpy change is the sum of the changes in the two steps. For a process at constant pressure, $\Delta H = q_P$, so we need to calculate the heat absorbed in each step.

Solve

HEATING WATER FROM 10.0 TO 25.0°C

This heat requirement can be determined by the method shown in Example 7-1; that is, we apply equation (7.5).

$$? \text{ kJ} = 50.0 \text{ g H}_2\text{O} \times \frac{4.18 \text{ J}}{\text{g H}_2\text{O °C}} \times (25.0 - 10.0) \text{ °C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 3.14 \text{ kJ}$$

VAPORIZING WATER AT 25.0°C

For this part of the calculation, the quantity of water must be expressed in moles so that we can then use the molar enthalpy of vaporization at 25 °C: 44.0 kJ/mol.

$$? \text{ kJ} = 50.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{44.0 \text{ kJ}}{1 \text{ mol H}_2\text{O}} = 122 \text{ kJ}$$

TOTAL ENTHALPY CHANGE

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

Assess

Note that the enthalpy change is positive, which reflects that the system (i.e., the water) gains energy. The reverse would be true for condensation of water at 25.0 °C and cooling it to 10.0 °C.

PRACTICE EXAMPLE A: What is the enthalpy change when a cube of ice 2.00 cm on edge is brought from −10.0 °C to a final temperature of 23.2 °C? For ice, use a density of 0.917 g/cm^3, a specific heat of 2.01 J g^{-1} °C^{-1}, and an enthalpy of fusion of 6.01 kJ/mol.

PRACTICE EXAMPLE B: What is the maximum mass of ice at −15.0 °C that can be completely converted to water vapor at 25.0 °C if the available heat for this transition is 5.00 × 10^3 kJ?

Standard States and Standard Enthalpy Changes

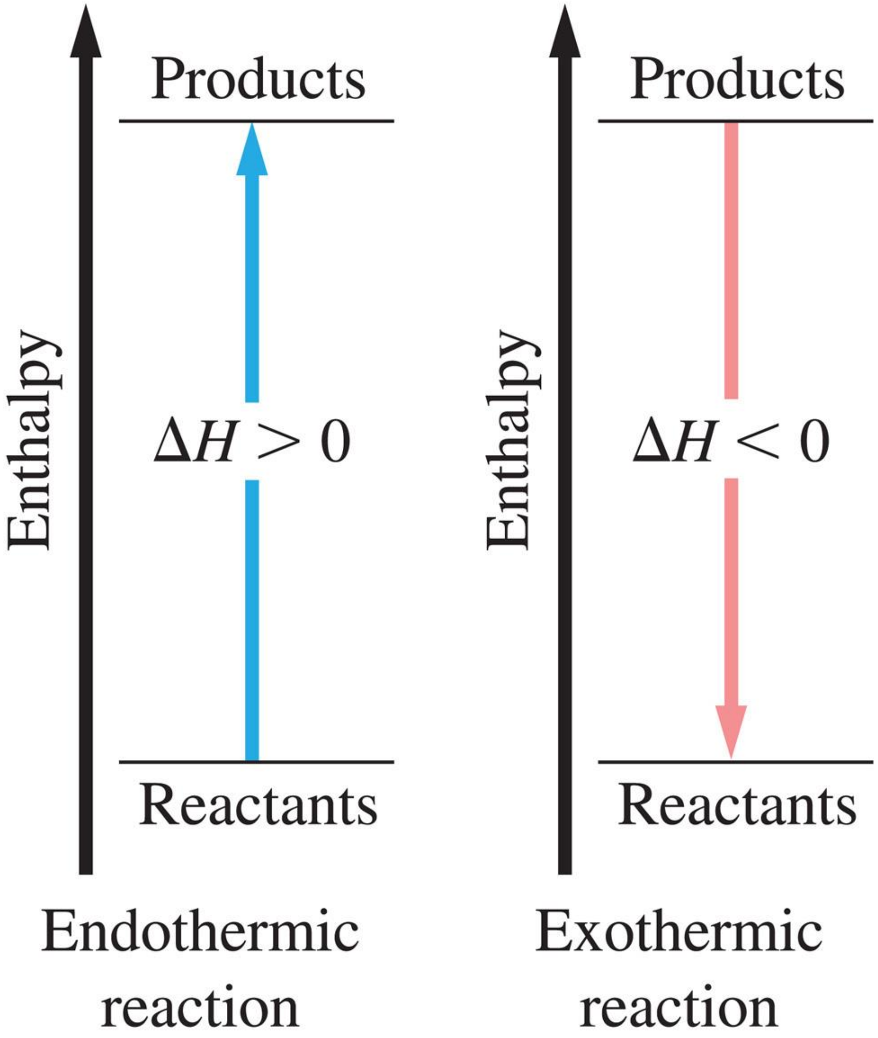
Define a particular state as a standard state.

Standard enthalpy of reaction, ΔH°

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

Standard State

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



▲ FIGURE 7-15

Enthalpy Diagrams

7-7 Indirect Determination of Δ*H*: Hess's Law

- Δ*H* is an extensive property.

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

$N_2(g) + O_2(g) \rightarrow 2\ NO(g) \quad \Delta H^\circ = +180.50\ \text{kJ}$

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g) \quad \Delta H^\circ = +90.25\ \text{kJ}$

- Δ*H* changes sign when a process is reversed

$NO(g) \rightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \quad \Delta H^\circ = -90.25\ \text{kJ}$

- Hess's law of constant heat summation

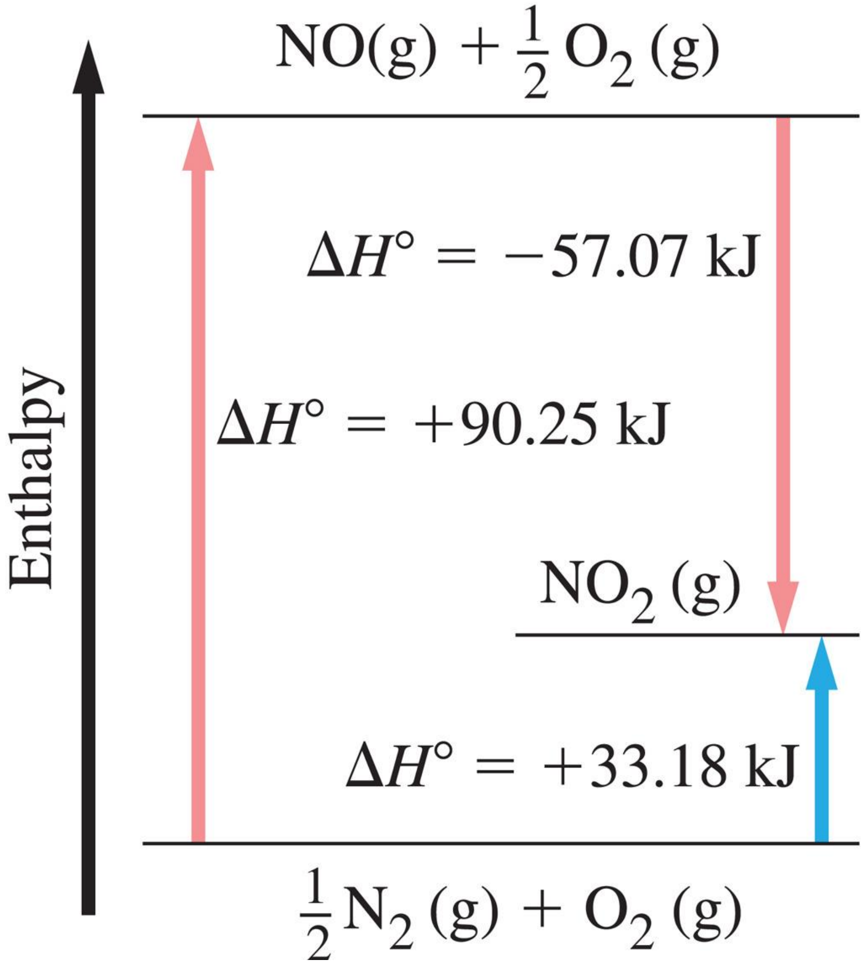
$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow \cancel{NO}(g) + \cancel{\tfrac{1}{2}O_2}\,(g) \qquad \Delta H^\circ = +90.25\text{ kJ}$$

$$\cancel{NO}(g) + \cancel{\tfrac{1}{2}O_2}(g) \rightarrow NO_2(g) \qquad \Delta H^\circ = -57.07\text{ kJ}$$

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H^\circ = +33.18\text{ kJ}$$

If a process occurs in stages or steps (even hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.

Hess's Law Schematically



EXAMPLE 7-9 Applying Hess's Law

Use the heat of combustion data from page 268 to determine ΔH° for reaction (7.18)

$$3\,C(\text{graphite}) + 4\,H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H^\circ = ?$$

Analyze

To determine an enthalpy change with Hess's law, we need to combine the appropriate chemical equations. A good starting point is to write chemical equations for the given combustion reactions based on *one mole* of the indicated reactant. Recall (see page 114) that the products of the combustion of carbon–hydrogen–oxygen compounds are $CO_2(g)$ and $H_2O(l)$.

Solve

Begin by writing the following equations

$$\begin{array}{lll} \textbf{(a)} & C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) & \Delta H^\circ = -2219.9\text{ kJ} \\ \textbf{(b)} & C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) & \Delta H^\circ = -393.5\text{ kJ} \\ \textbf{(c)} & H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) & \Delta H^\circ = -285.8\text{ kJ} \end{array}$$

Because our objective in reaction (7.18) is to *produce* $C_3H_8(g)$, the next step is to find a reaction in which $C_3H_8(g)$ is formed—the *reverse* of reaction **(a)**.

$$-(\text{a}){:}\ 3\,CO_2(g) + 4\,H_2O(l) \longrightarrow C_3H_8(g) + 5\,O_2(g) \qquad \Delta H^\circ = -(-2219.9)\text{ kJ} = +2219.9\text{ kJ}$$

Now, we turn our attention to the reactants, C(graphite) and $H_2(g)$. To get the proper number of moles of each, we must multiply equation **(b)** by three and equation **(c)** by four.

$$\begin{array}{lll} 3 \times (\text{b}){:} & 3\,C(\text{graphite}) + 3\,O_2(g) \longrightarrow 3\,CO_2(g) & \Delta H^\circ = 3(-393.5\text{ kJ}) = -1181\text{ kJ} \\ 4 \times (\text{c}){:} & 4\,H_2(g) + 2\,O_2(g) \longrightarrow 4\,H_2O(l) & \Delta H^\circ = 4(-285.8\text{ kJ}) = -1143\text{ kJ} \end{array}$$

Here is the overall change we have described: 3 mol C(graphite) and 4 mol $H_2(g)$ have been consumed, and 1 mol $C_3H_8(g)$ has been produced. This is exactly what is required in equation (7.18). We can now combine the three modified equations.

$$\begin{array}{lll} -(\text{a}){:} & \cancel{3\,CO_2(g)} + \cancel{4\,H_2O(l)} \longrightarrow C_3H_8(g) + \cancel{5\,O_2(g)} & \Delta H^\circ = +2219.9\text{ kJ} \\ 3 \times (\text{b}){:} & 3\,C(\text{graphite}) + \cancel{3\,O_2(g)} \longrightarrow \cancel{3\,CO_2(g)} & \Delta H^\circ = -1181\text{ kJ} \\ 4 \times (\text{c}){:} & 4\,H_2(g) + \cancel{2\,O_2(g)} \longrightarrow \cancel{4\,H_2O(l)} & \Delta H^\circ = -1143\text{ kJ} \\ \hline & 3\,C(\text{graphite}) + 4\,H_2(g) \longrightarrow C_3H_8(g) & \Delta H^\circ = -104\text{ kJ} \end{array}$$

Assess

Hess's law is a powerful technique to determine the enthalpy of reaction by using a series of unrelated reactions, along with their enthalpies of reaction. In this example, we took three unrelated combustion reactions and were able to determine the enthalpy of reaction of another reaction.

7-8 Standard Enthalpies of Formation ΔH_f°

Enthalpy is a state function. It can not measured directly. Enthalpy change can be measured

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

> The standard enthalpy of formation of a pure element in its reference state is 0.

Lower entalphy, higher stabilty:

Carbon:

C(graphite) $\longrightarrow$ C(diamond) $\Delta H_f^\circ = 1.9$ kJ

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$Br_2(l) \longrightarrow Br_2(g)$ $\Delta H_f^\circ = 30.91$ kJ

▲

Liquid bromine vaporizing

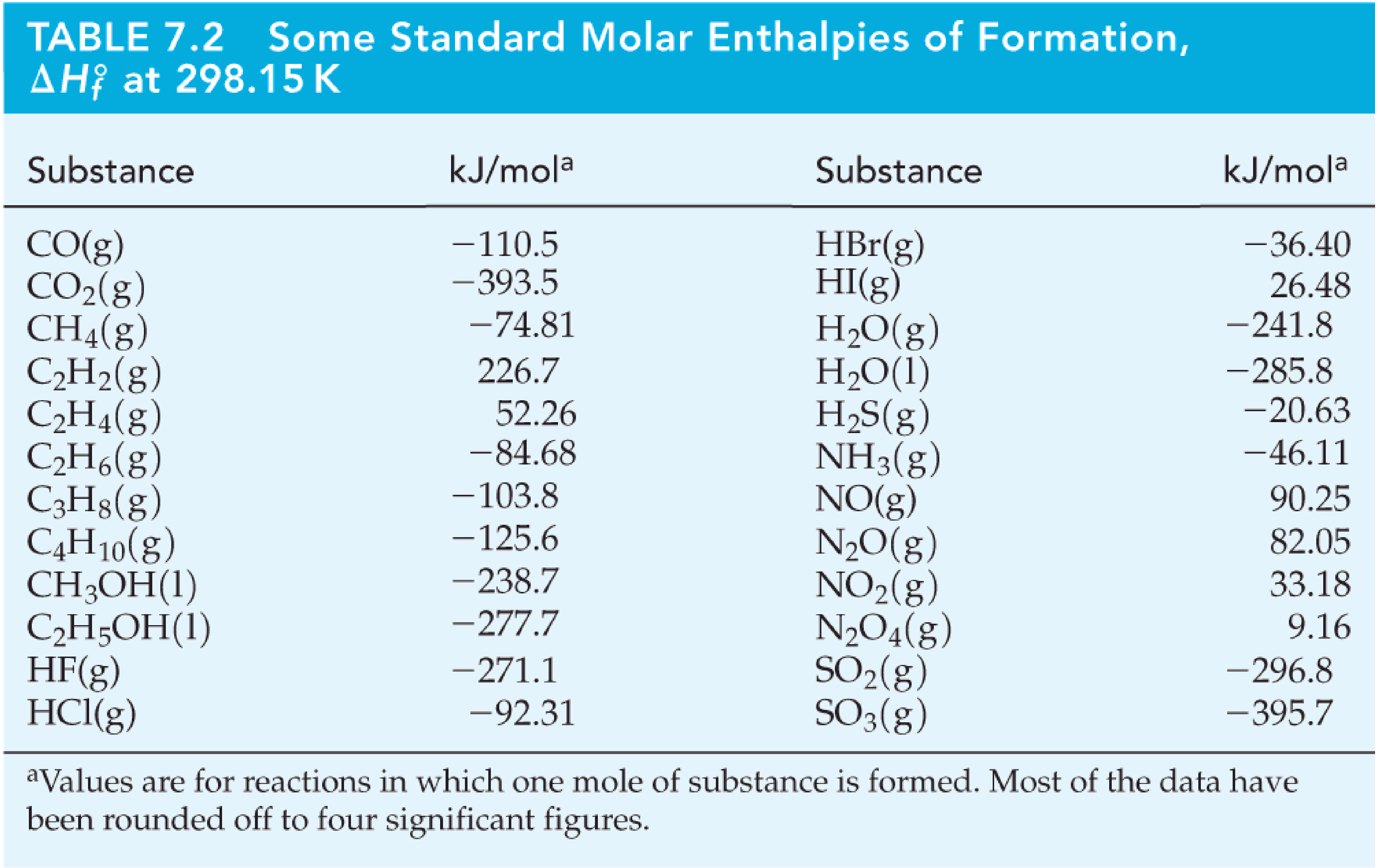
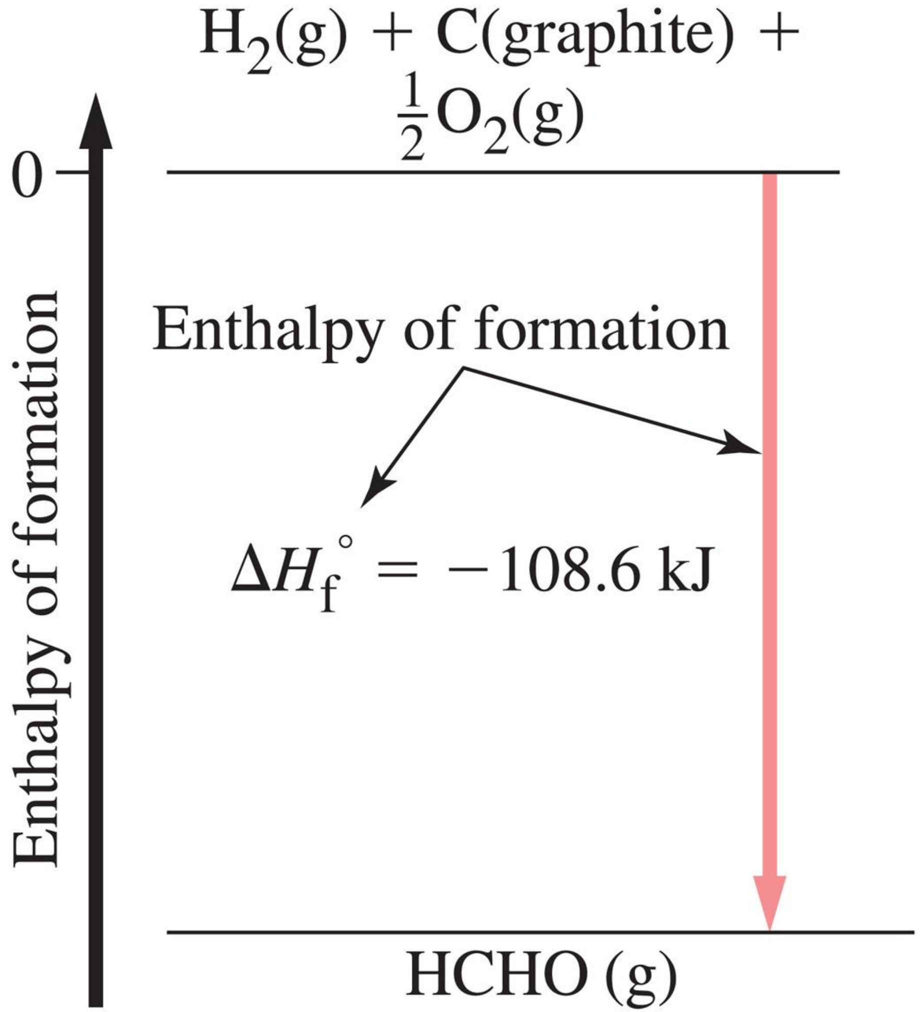


TABLE 7.2 Some Standard Molar Enthalpies of Formation, ΔH_f° at 298.15 K

Substance	kJ/mol[a]	Substance	kJ/mol[a]
$CO(g)$	−110.5	$HBr(g)$	−36.40
$CO_2(g)$	−393.5	$HI(g)$	26.48
$CH_4(g)$	−74.81	$H_2O(g)$	−241.8
$C_2H_2(g)$	226.7	$H_2O(l)$	−285.8
$C_2H_4(g)$	52.26	$H_2S(g)$	−20.63
$C_2H_6(g)$	−84.68	$NH_3(g)$	−46.11
$C_3H_8(g)$	−103.8	$NO(g)$	90.25
$C_4H_{10}(g)$	−125.6	$N_2O(g)$	82.05
$CH_3OH(l)$	−238.7	$NO_2(g)$	33.18
$C_2H_5OH(l)$	−277.7	$N_2O_4(g)$	9.16
$HF(g)$	−271.1	$SO_2(g)$	−296.8
$HCl(g)$	−92.31	$SO_3(g)$	−395.7

[a] Values are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.

Standard Enthalpy of Formation



EXAMPLE 7-10 Relating a Standard Enthalpy of Formation to a Chemical Equation

The enthalpy of formation of formaldehyde is $\Delta H_f^\circ = -108.6$ kJ/mol HCHO(g) at 298 K. Write the chemical equation to which this value applies.

Analyze

The equation must be written for the formation of one mole of gaseous HCHO. The most stable forms of the elements at 298.15 K and 1 bar are gaseous H_2 and O_2 and solid carbon in the form of graphite (Fig. 7-19). Note that we need one fractional coefficient in this equation.

Solve

$$H_2(g) + \frac{1}{2}O_2(g) + C(\text{graphite}) \longrightarrow HCHO(g) \qquad \Delta H_f^\circ = -108.6\ \text{kJ}$$

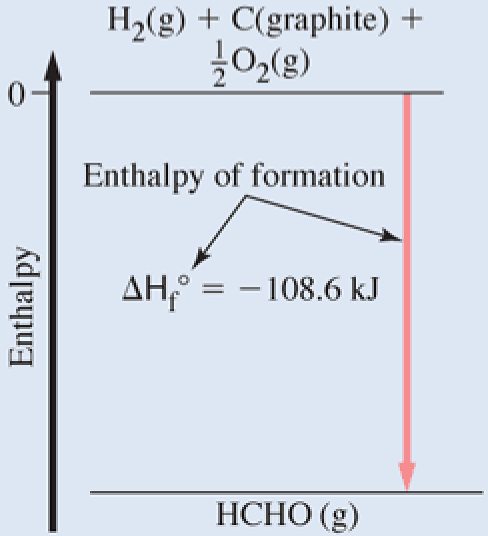
Assess

When answering these types of problems, we must remember to use the elements in their most stable form under the given conditions. In this example, the stated conditions were 298 K and 1 bar.

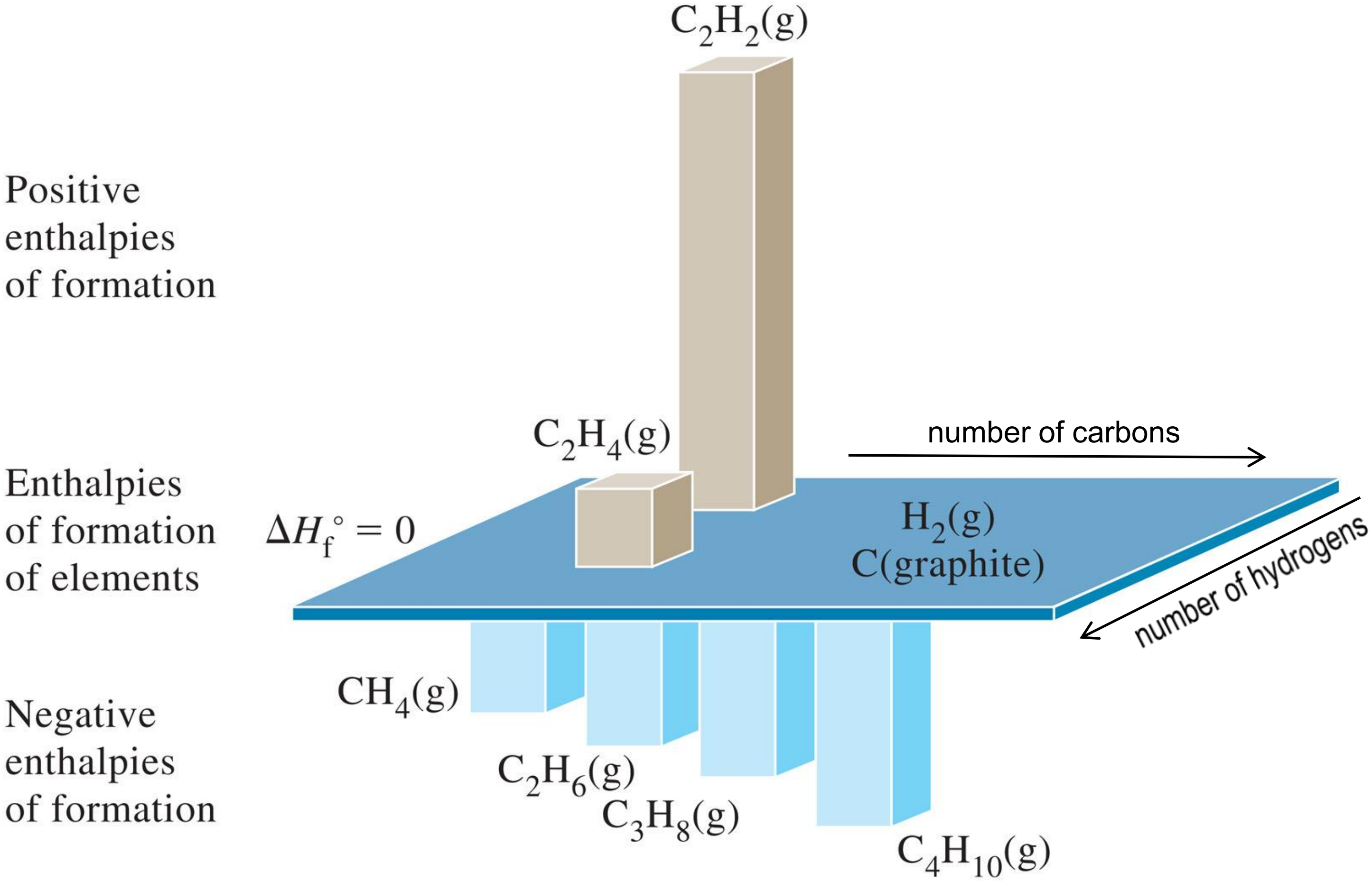
PRACTICE EXAMPLE A: The standard enthalpy of formation for the amino acid leucine is -637.3 kJ/mol $C_6H_{13}O_2N(s)$. Write the chemical equation to which this value applies.

PRACTICE EXAMPLE B: How is ΔH° for the following reaction related to the standard enthalpy of formation of $NH_3(g)$ listed in Table 7.2? What is the value of $\Delta H^\circ = ?$

$$2\,NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g) \qquad \Delta H^\circ = ?$$



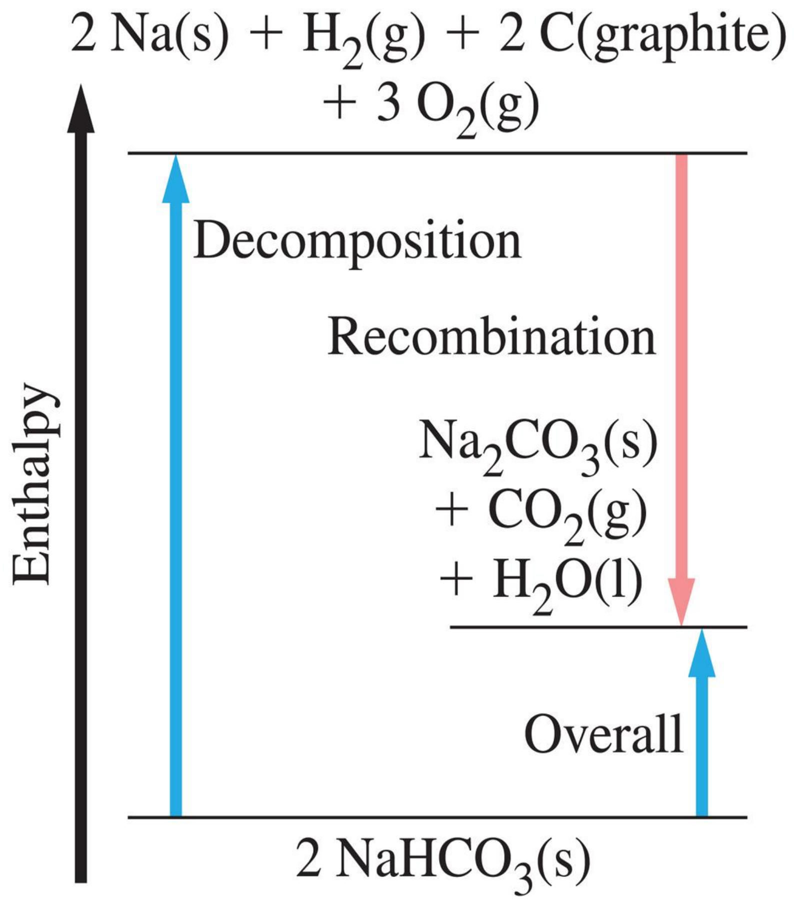
▲ FIGURE 7-19
Standard enthalpy of formation of formaldehyde, HCHO(g)
The formation of HCHO(g) from its elements in their standard states is an exothermic reaction. The heat evolved per mole of HCHO(g) formed is the standard enthalpy (heat) of formation.



▲ FIGURE 7-18

Some standard enthalpies of formation at 298.15 K

Standard Enthalpies of Reaction

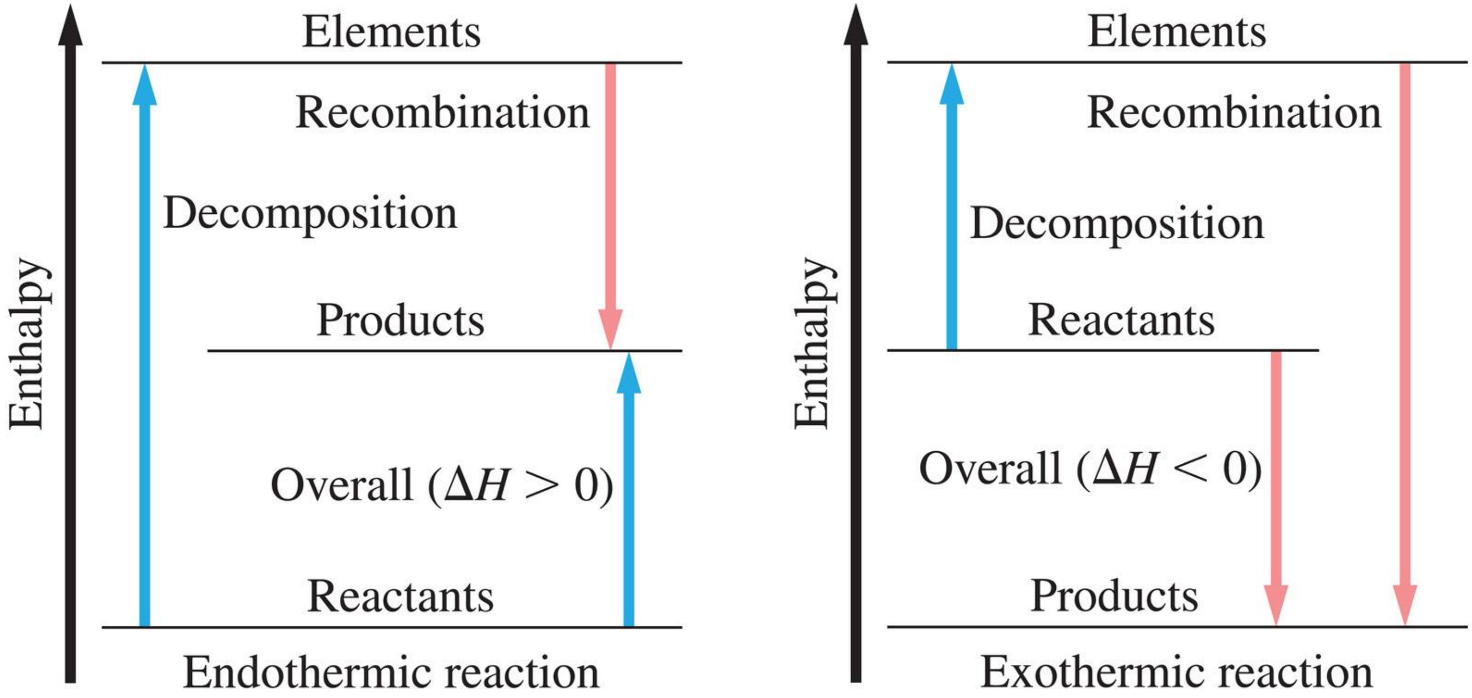


$$\Delta H_{\text{overall}} = -2\Delta H_f^\circ{}_{\text{NaHCO}_3} + \Delta H_f^\circ{}_{\text{Na}_2\text{CO}_3} + \Delta H_f^\circ{}_{\text{CO}_2} + \Delta H_f^\circ{}_{\text{H}_2\text{O}}$$

▲ FIGURE 7-20

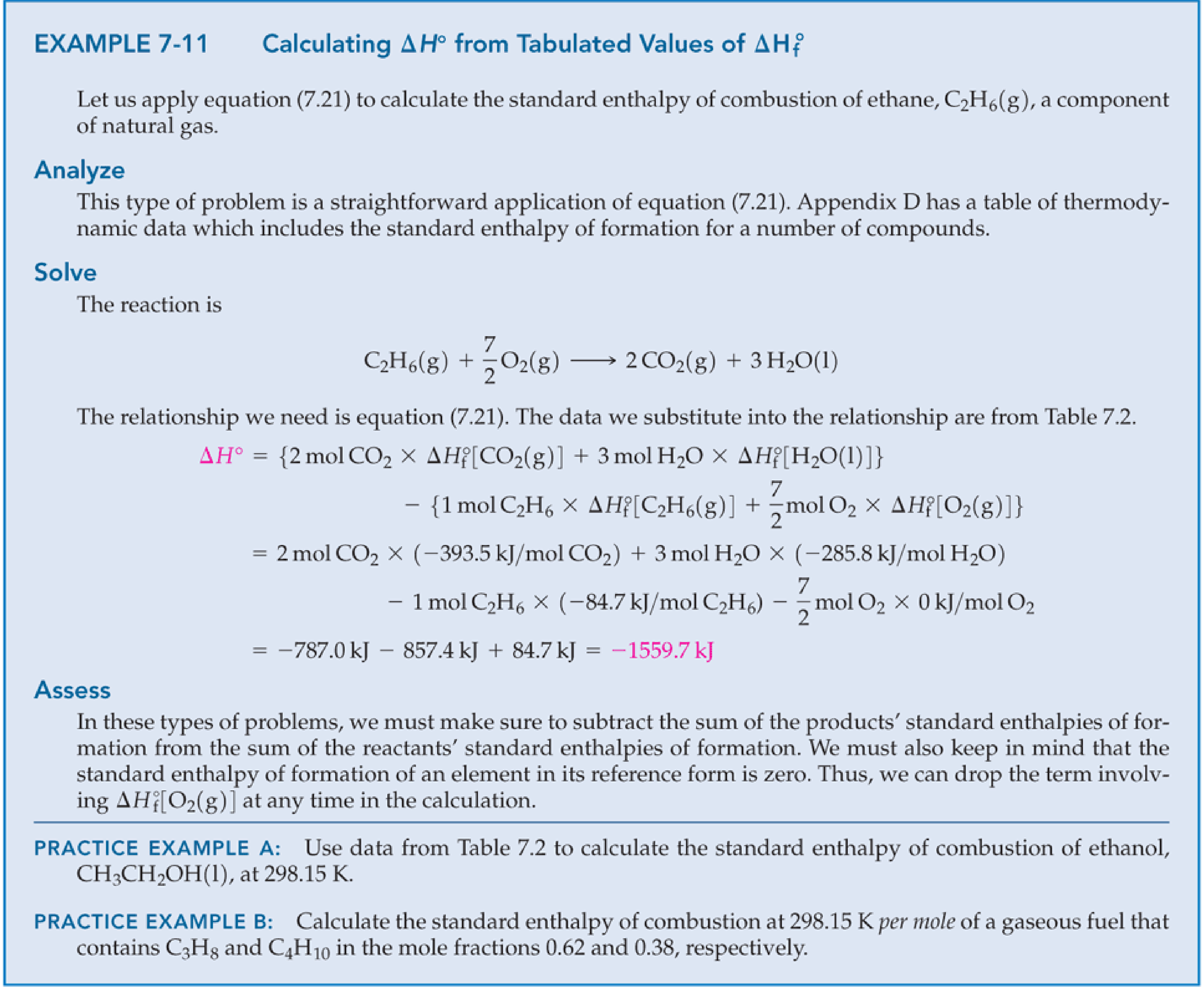
Computing heats of reaction from standard enthalpies of formation

$$\Delta H^\circ = \sum \nu_p \Delta H_f^\circ \text{ (products)} - \sum \nu_r \Delta H_f^\circ \text{ (reactants)} \quad \textbf{(7.21)}$$



▲ FIGURE 7-21

Diagramatic representation of equation (7.21)



EXAMPLE 7-11 Calculating ΔH° from Tabulated Values of ΔH_f°

Let us apply equation (7.21) to calculate the standard enthalpy of combustion of ethane, $C_2H_6(g)$, a component of natural gas.

Analyze

This type of problem is a straightforward application of equation (7.21). Appendix D has a table of thermodynamic data which includes the standard enthalpy of formation for a number of compounds.

Solve

The reaction is

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$$

The relationship we need is equation (7.21). The data we substitute into the relationship are from Table 7.2.

$$\begin{aligned}\Delta H^\circ &= \{2\text{ mol } CO_2 \times \Delta H_f^\circ[CO_2(g)] + 3\text{ mol } H_2O \times \Delta H_f^\circ[H_2O(l)]\}\\ &\qquad - \{1\text{ mol } C_2H_6 \times \Delta H_f^\circ[C_2H_6(g)] + \frac{7}{2}\text{mol } O_2 \times \Delta H_f^\circ[O_2(g)]\}\\ &= 2\text{ mol } CO_2 \times (-393.5\text{ kJ/mol } CO_2) + 3\text{ mol } H_2O \times (-285.8\text{ kJ/mol } H_2O)\\ &\qquad - 1\text{ mol } C_2H_6 \times (-84.7\text{ kJ/mol } C_2H_6) - \frac{7}{2}\text{mol } O_2 \times 0\text{ kJ/mol } O_2\\ &= -787.0\text{ kJ} - 857.4\text{ kJ} + 84.7\text{ kJ} = -1559.7\text{ kJ}\end{aligned}$$

Assess

In these types of problems, we must make sure to subtract the sum of the products' standard enthalpies of formation from the sum of the reactants' standard enthalpies of formation. We must also keep in mind that the standard enthalpy of formation of an element in its reference form is zero. Thus, we can drop the term involving $\Delta H_f^\circ[O_2(g)]$ at any time in the calculation.

PRACTICE EXAMPLE A: Use data from Table 7.2 to calculate the standard enthalpy of combustion of ethanol, $CH_3CH_2OH(l)$, at 298.15 K.

PRACTICE EXAMPLE B: Calculate the standard enthalpy of combustion at 298.15 K *per mole* of a gaseous fuel that contains C_3H_8 and C_4H_{10} in the mole fractions 0.62 and 0.38, respectively.

Ionic Reactions in Solutions

$$\mathrm{H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)} \qquad \Delta H^\circ = -55.8\ \mathrm{kJ} \tag{7.22}$$

$$\begin{aligned}\Delta H^\circ = 1\ \mathrm{mol\ H_2O} \times \Delta H_f^\circ[\mathrm{H_2O(l)}] - \{1\ \mathrm{mol\ H^+} \times \Delta H_f^\circ[\mathrm{H^+(aq)}] \\ + 1\ \mathrm{mol\ OH^-} \times \Delta H_f^\circ[\mathrm{OH^-(aq)}]\} = -55.8\ \mathrm{kJ}\end{aligned}$$

$$\Delta H_f^\circ[\mathrm{OH^-(aq)}] = \frac{55.8\ \mathrm{kJ} + (1\ \mathrm{mol\ H_2O} \times \Delta H_f^\circ[\mathrm{H_2O(l)}]) - (1\ \mathrm{mol\ H^+} \times \Delta H_f^\circ[\mathrm{H^+(aq)}])}{1\ \mathrm{mol\ OH^-}}$$

$$\Delta H_f^\circ[\mathrm{OH^-(aq)}] = \frac{55.8\ \mathrm{kJ} - 285.8\ \mathrm{kJ} - 0\ \mathrm{kJ}}{1\ \mathrm{mol\ OH^-}} = -230.0\ \mathrm{kJ/mol\ OH^-}$$

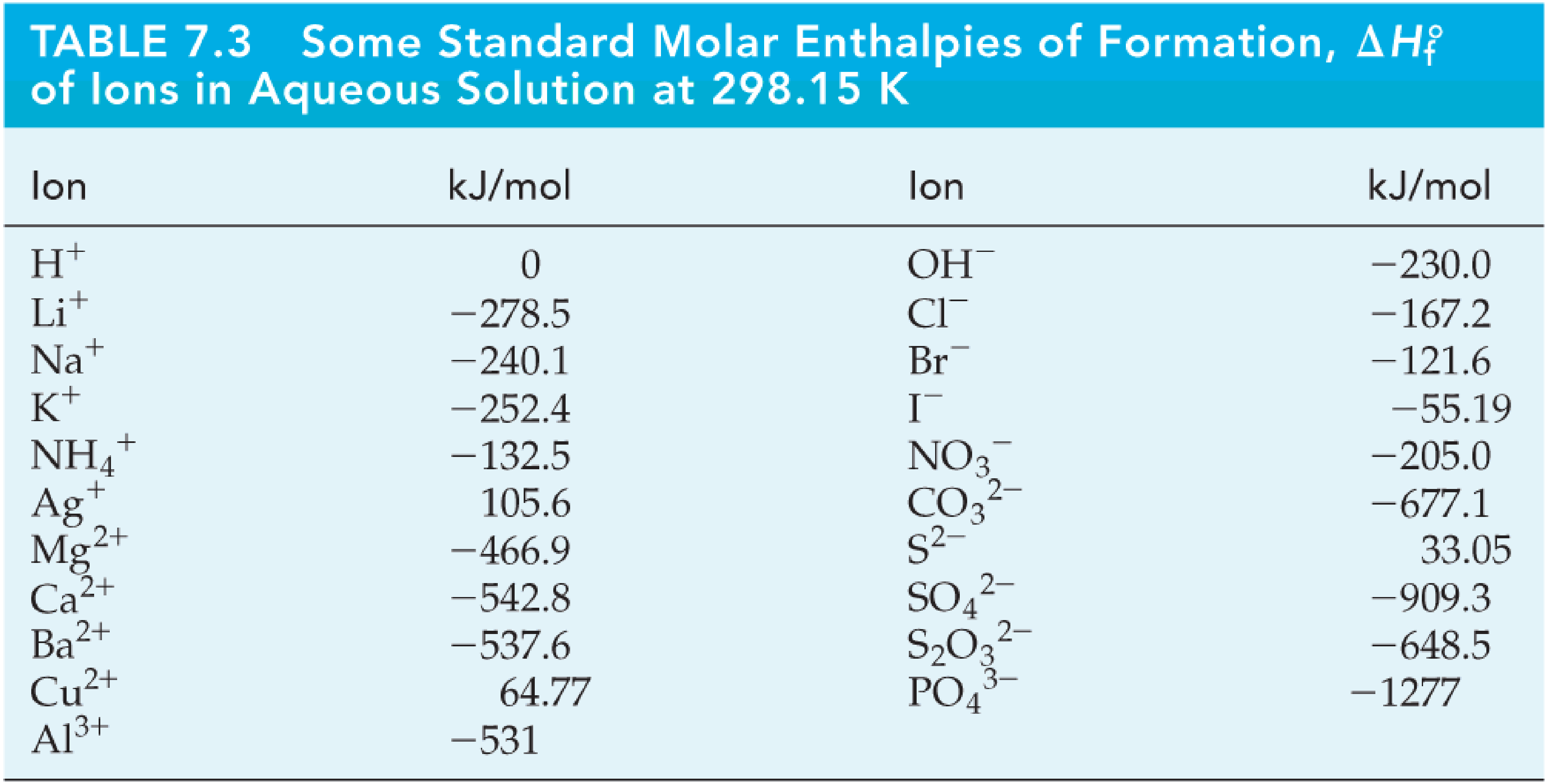
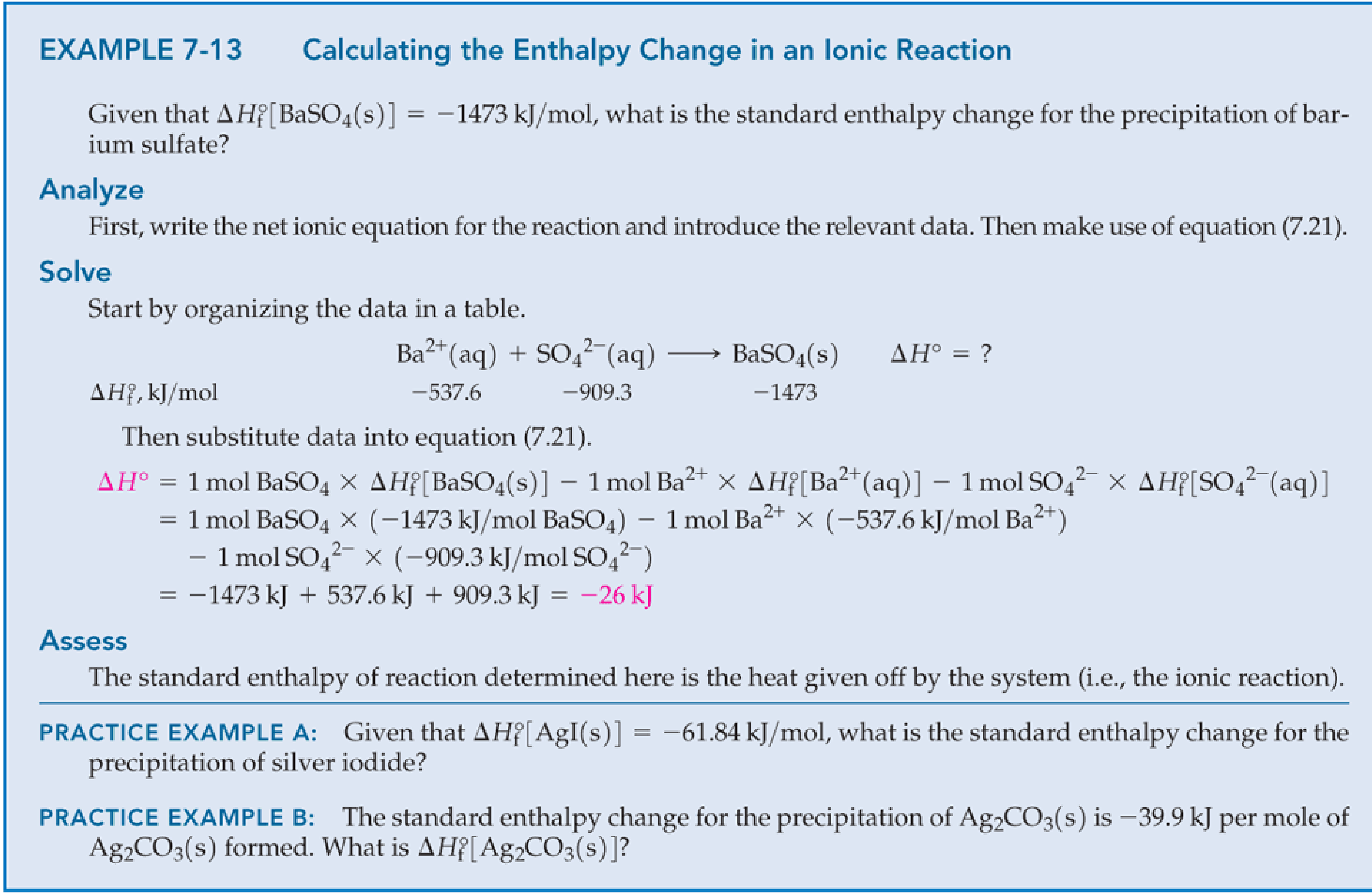


TABLE 7.3 Some Standard Molar Enthalpies of Formation, ΔH_f° of Ions in Aqueous Solution at 298.15 K

Ion	kJ/mol	Ion	kJ/mol
H^+	0	OH^-	−230.0
Li^+	−278.5	Cl^-	−167.2
Na^+	−240.1	Br^-	−121.6
K^+	−252.4	I^-	−55.19
NH_4^+	−132.5	NO_3^-	−205.0
Ag^+	105.6	CO_3^{2-}	−677.1
Mg^{2+}	−466.9	S^{2-}	33.05
Ca^{2+}	−542.8	SO_4^{2-}	−909.3
Ba^{2+}	−537.6	$S_2O_3^{2-}$	−648.5
Cu^{2+}	64.77	PO_4^{3-}	−1277
Al^{3+}	−531		



EXAMPLE 7-13 Calculating the Enthalpy Change in an Ionic Reaction

Given that $\Delta H_f^\circ[\mathrm{BaSO_4(s)}] = -1473$ kJ/mol, what is the standard enthalpy change for the precipitation of barium sulfate?

Analyze

First, write the net ionic equation for the reaction and introduce the relevant data. Then make use of equation (7.21).

Solve

Start by organizing the data in a table.

	$\mathrm{Ba^{2+}(aq)}$	$+\ \mathrm{SO_4{}^{2-}(aq)}$	$\longrightarrow \mathrm{BaSO_4(s)}$	$\Delta H^\circ = ?$
ΔH_f°, kJ/mol	-537.6	-909.3	-1473	

Then substitute data into equation (7.21).

$$\begin{aligned}\Delta H^\circ &= 1\ \mathrm{mol\ BaSO_4} \times \Delta H_f^\circ[\mathrm{BaSO_4(s)}] - 1\ \mathrm{mol\ Ba^{2+}} \times \Delta H_f^\circ[\mathrm{Ba^{2+}(aq)}] - 1\ \mathrm{mol\ SO_4{}^{2-}} \times \Delta H_f^\circ[\mathrm{SO_4{}^{2-}(aq)}]\\ &= 1\ \mathrm{mol\ BaSO_4} \times (-1473\ \mathrm{kJ/mol\ BaSO_4}) - 1\ \mathrm{mol\ Ba^{2+}} \times (-537.6\ \mathrm{kJ/mol\ Ba^{2+}})\\ &\quad - 1\ \mathrm{mol\ SO_4{}^{2-}} \times (-909.3\ \mathrm{kJ/mol\ SO_4{}^{2-}})\\ &= -1473\ \mathrm{kJ} + 537.6\ \mathrm{kJ} + 909.3\ \mathrm{kJ} = -26\ \mathrm{kJ}\end{aligned}$$

Assess

The standard enthalpy of reaction determined here is the heat given off by the system (i.e., the ionic reaction).

PRACTICE EXAMPLE A: Given that $\Delta H_f^\circ[\mathrm{AgI(s)}] = -61.84$ kJ/mol, what is the standard enthalpy change for the precipitation of silver iodide?

PRACTICE EXAMPLE B: The standard enthalpy change for the precipitation of $\mathrm{Ag_2CO_3(s)}$ is -39.9 kJ per mole of $\mathrm{Ag_2CO_3(s)}$ formed. What is $\Delta H_f^\circ[\mathrm{Ag_2CO_3(s)}]$?

General Chemistry

Principles & Modern Applications

10th Edition

Petrucci/Herring/Madura/Bissonnette

Chapter 7

Thermochemistry

Dr. Wendy Pell

University of Ottawa

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1. positive.
2. negative.
3. 0

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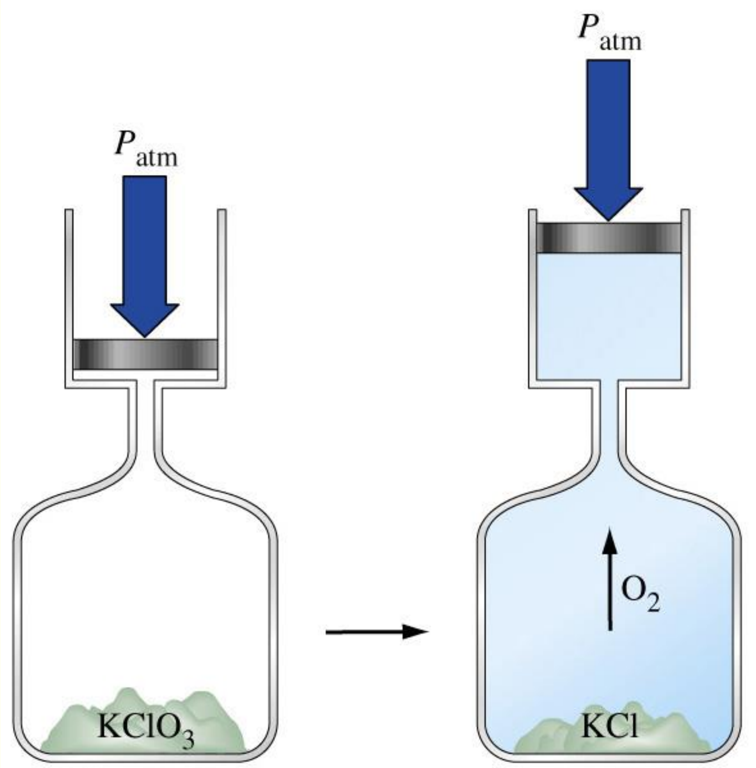
When potassium chlorate decomposes it produces oxygen gas. From the system's point of view (which is the convention), w is

1. positive.
2. negative.
3. No work done.



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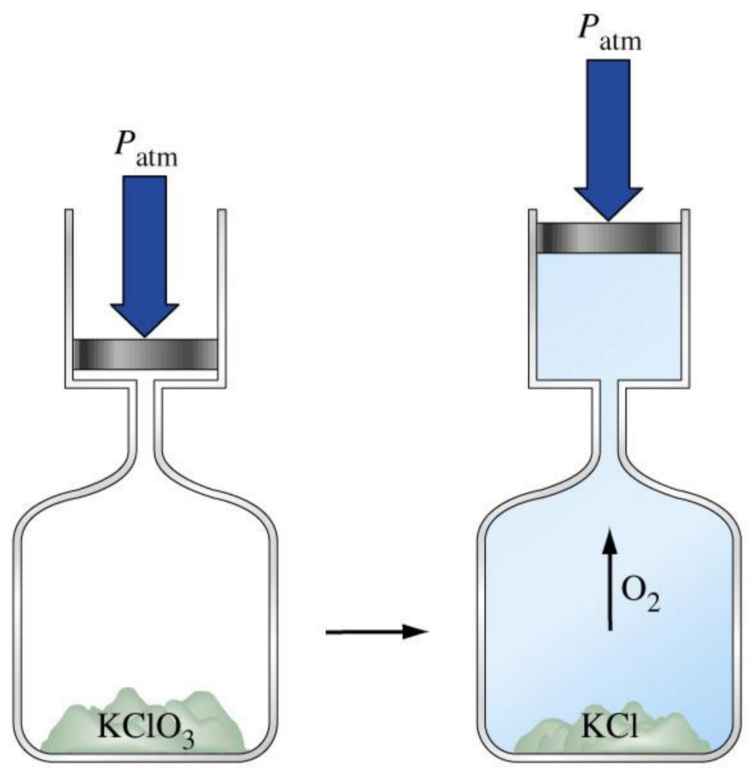
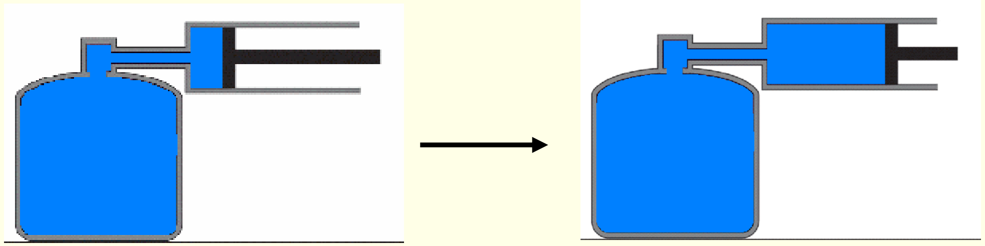


Heat is added to the container below while being allowed to expand freely against atmospheric pressure. The temperature and pressure, however, remain constant before and after.

ΔU is,



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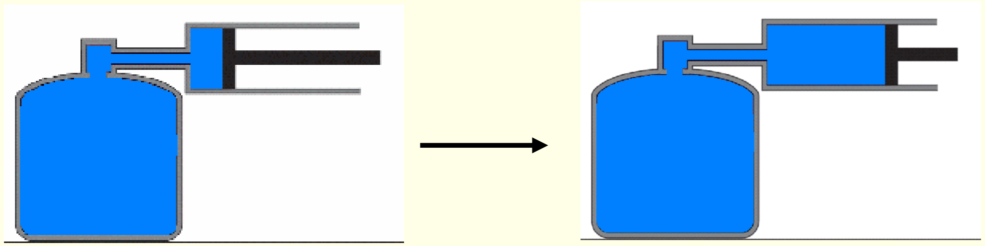

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For the following reaction:

$2\ H_2\ (g) + O_2\ (g) \rightarrow H_2O\ (l)$ $\Delta H^o = -572$ kJ

What is the work associated with this reaction at 25ºC?

1. 7.4 kJ
2. -7.4 kJ
3. 5.0 kJ
4. -5.0 kJ
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The volume of the Atlantic Ocean is about 300 km^3. Without the use of a calculator, estimate the heat that is required to raise the temperature of the Atlantic Ocean by 1 ^oC (assume the density of water is 1 g cm^{-3} and the specific heat is 4 J g^{-1} $^oC^{-1}$.

1. ~10^3 J
2. ~10^6 J
3. ~10^{12} J
4. ~10^{18} J
5. ~10^{25} J

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3. $\sim 10^{12}$ J
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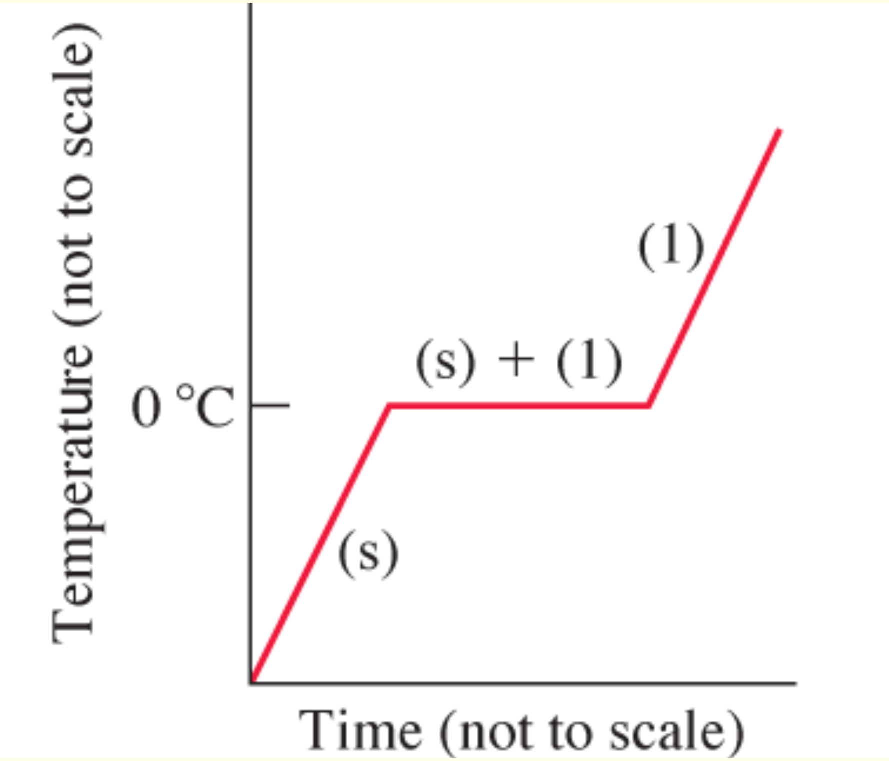
The figure below shows the heating curve for water. It traces the changes in temperature as ice, initially at -20 °C, is gradually heated to produce liquid water at +20 °C. When the ice (the system) melts,



1. Temperature remains constant, therefore no heat is being added to or removed from the system during the melting of the ice.

2. Although T is constant, heat is added to convert $H_2O(s)$ to $H_2O(l)$

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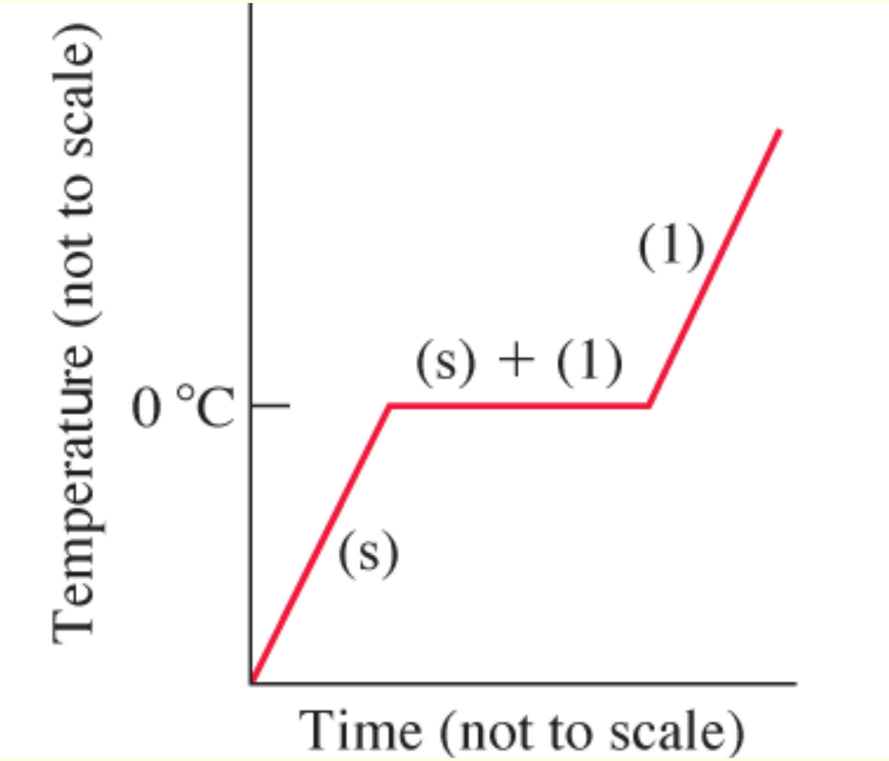

The figure below shows the cooling curve for water. It traces the changes in temperature as water, initially at 20 °C, is gradually cooled to produce ice at -20 °C. When the water (the system) freezes,

1. the temperature remains constant at 0 °C and the process is endothermic.

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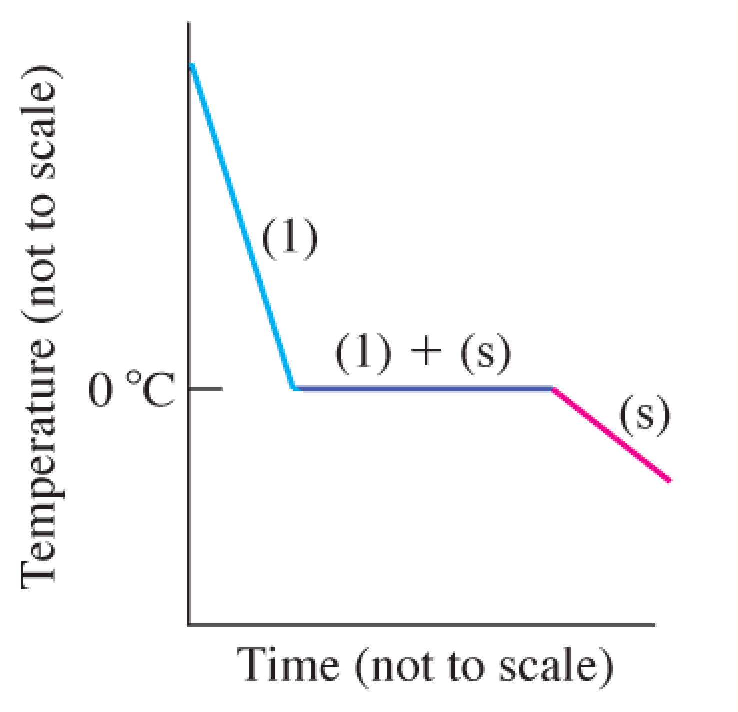
3. the temperature remains constant at 0 °C, thus the process is neither endothermic nor exothermic.



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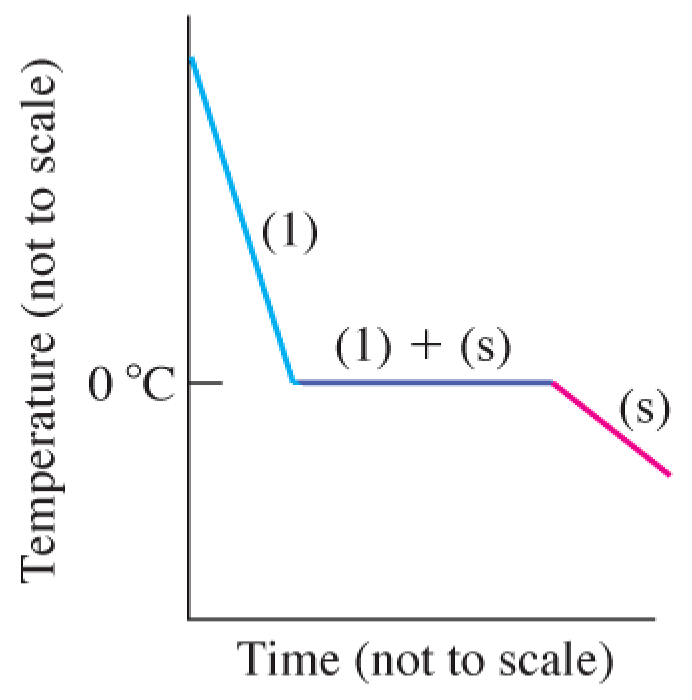

You take two frozen steaks and put them into room temperature water for a few hours to thaw. The heat gained by the steak (system) equals the heat lost by the water (surroundings). The ***best*** equation to express this, where subscript ‘s’ refers to steak and the subscript w refers to the water, is,

1. $s_w\ m_w\ \Delta T_w = s_s\ m_s\ \Delta T_s$
2. $s_w\ m_w\ \Delta T_w = -s_s\ m_s\ \Delta T_s$
3. $-s_w\ m_w\ \Delta T_w = s_s\ m_s\ \Delta T_s$

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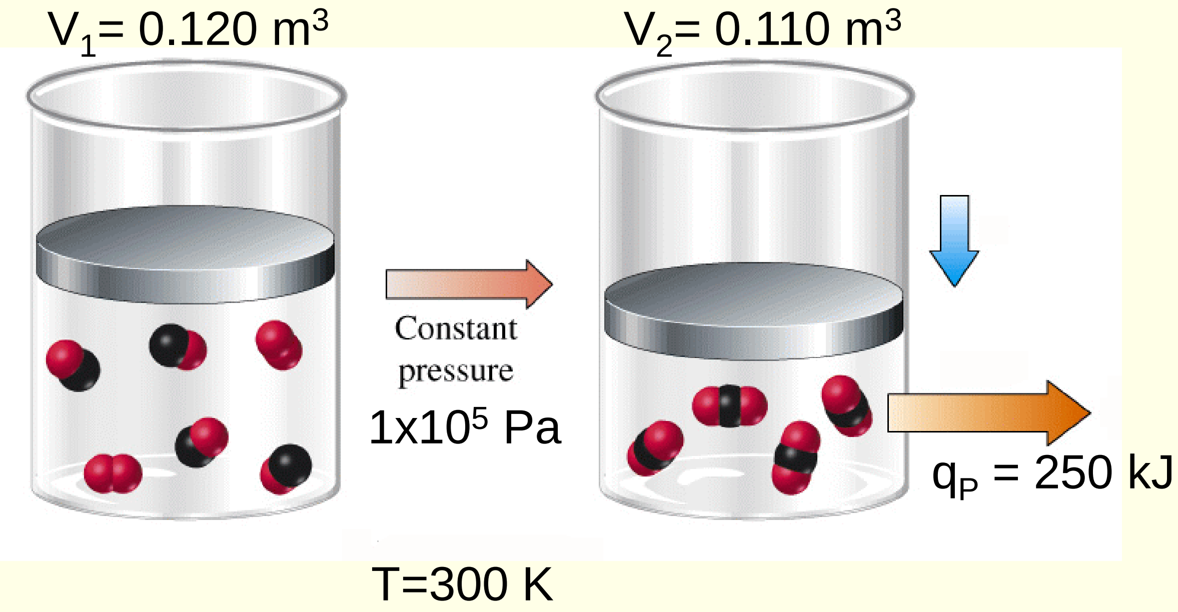
3. $\boxed{-s_w \ m_w \ \Delta T_w = s_s \ m_s \ \Delta T_s}$

Determine ΔH and ΔU for the reaction and conditions depicted below.
Note: 1 Pa = 1 N m^{-2}.

	ΔH	ΔU
1.	250 kJ,	251 kJ
2.	250 kJ,	249 kJ
3.	-250 kJ,	-251 kJ
4.	-250 kJ,	-249 kJ
5.	-250 kJ,	-250 kJ



$V_1 = 0.120\ m^3$

$V_2 = 0.110\ m^3$

Constant pressure

1×10^5 Pa

$q_P = 250$ kJ

T=300 K

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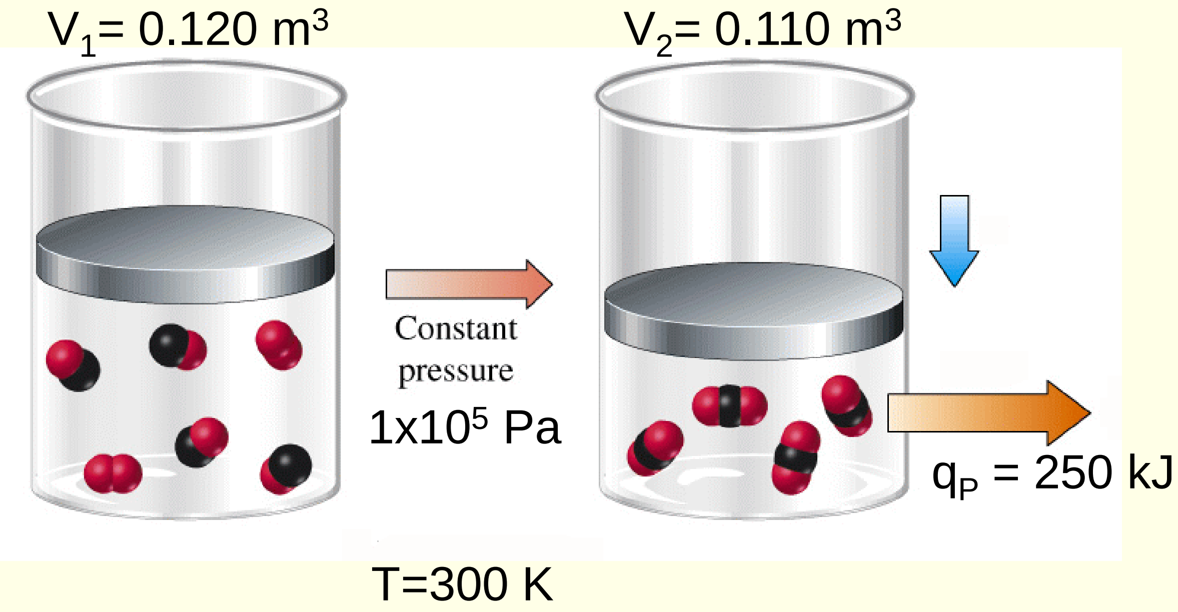

Ice (the system) melting is

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Note: a bit tricky perhaps until chapter 13.

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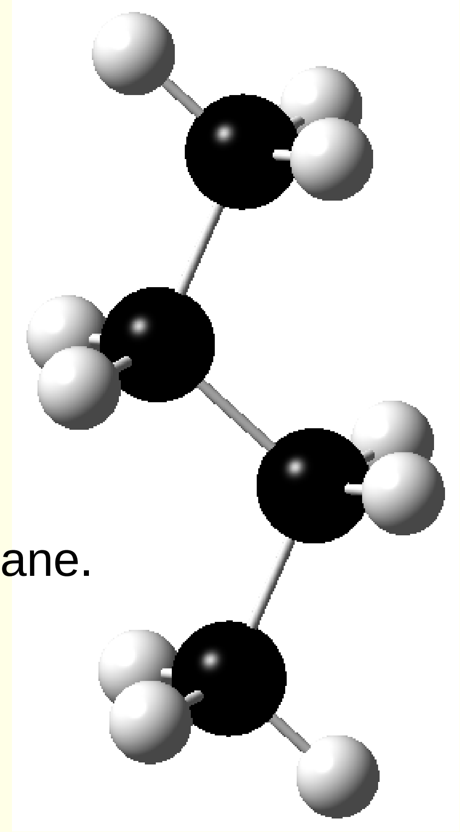
The equation for the combustion of butane is,

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$$



Which one of the following generates the least heat?

1. Burning one mole of butane in excess oxygen.
2. Reacting one mole of oxygen with excess butane.
3. Producing one mole of carbon dioxide by burning butane.
4. Producing one mole of water by burning butane.
5. Burning 0.25 moles of butane with excess oxygen.

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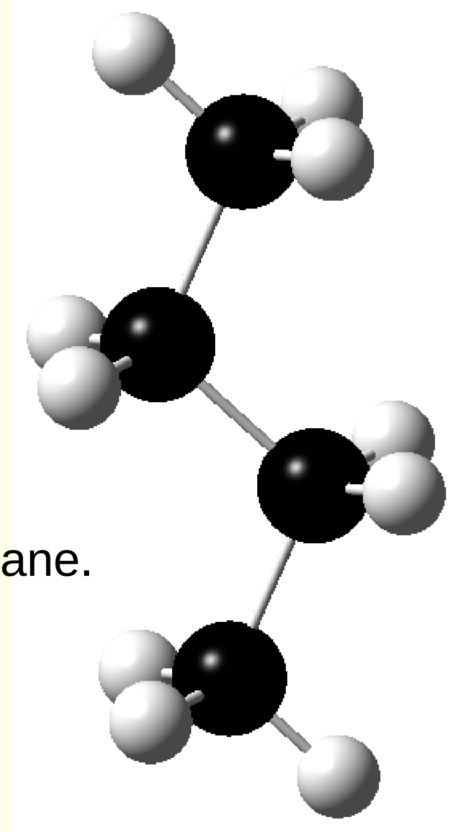
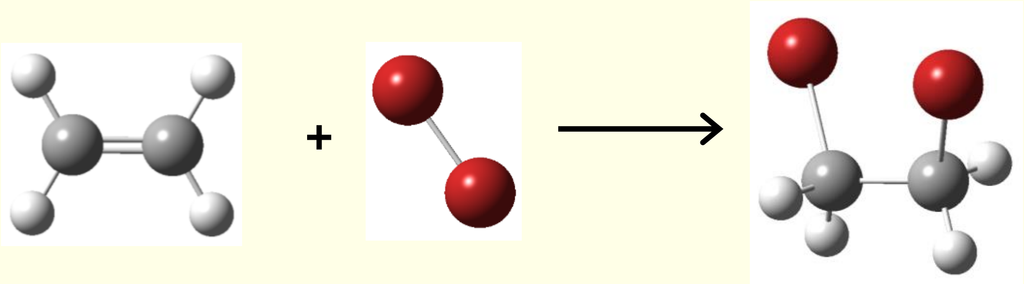


Given the bond energies below, estimate the enthalpy change for the addition of Br across the double bond in ethene.



C—C	**350 kJ mol^{-1}**
C=C	**600 kJ mol^{-1}**
C—Br	**300 kJ mol^{-1}**
Br—Br	**200 kJ mol^{-1}**

1. 150 kJ
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3. 220 kJ
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5. Not enough data to determine $\Delta_r H$

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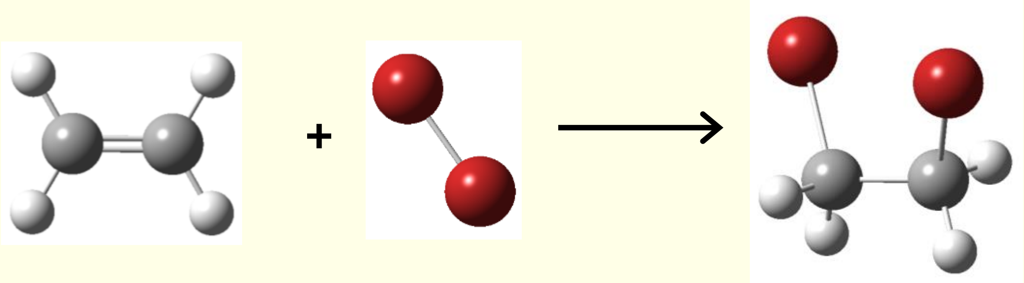

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5. Not enough data to determine $\Delta_r H$

1) A closed system can exchange matter but not energy with the surroundings. **(True or false)**

2) Kinetic energy is the energy of motion.

3) Heat is usually transferred from a cold object to a hot object.

4) A system that absorbs heat is an exothermic system.

5) An expansion of gas by a system means that the system does work.

6) An expansion of gas by a system means that the internal energy of the system increases.

7) The maximum amount of work is provided by a reversible process because equilibrium between the system and the surroundings is always maintained.

8) The enthalpy of a system is the internal energy minus work

9) Enthalpy is an extensive property.

10) The standard enthalpy for diamond and graphite are the same value.

12) Choose the INCORRECT statement.
A) Kinetic energy is the energy of motion.
B) Potential energy is energy in action.
C) Heat is energy transferred as a result of a temperature difference.
D) Pressure volume work is calculated by $w = P \cdot V$.
E) Heat moves from a warmer body to a colder one.

13) Choose the INCORRECT statement.
A) The surroundings are the part of the universe that is studied.
B) Thermal energy is energy associated with random molecular motion.
C) Chemical energy is associated with chemical bonds and intermolecular forces.
D) Energy is the capacity to do work.
E) Work is done when a force acts through a distance.

14) Choose the INCORRECT statement.
A) Temperatures of two bodies are equal when the average kinetic energies of the two bodies become the same.
B) The heat capacity is the quantity of heat required to change the temperature of the system by one degree.
C) The specific heat is the heat capacity for one mole of substance.
D) The law of conservation of energy can be written: $q$system + $q$surroundings = 0.
E) Most metals have low specific heats, as metals can be heated quickly.

15) 14.0 g of metal at 24.0° C has 250 joules of heat added to it. The metal's specific heat is 0.105 J/g ° C. What is its final temperature?

A) (250)(14.0)/0.105 ° C
B) [250/(14.0)(0.105)] ° C
C) [(914.0)(0.105)/250] + 24.0 ° C
D) (14.0)(0.105)/250 ° C
E) (14.0)(0.105)(250) ° C

16) Lead, water, sulfur, and arsenic have specific heats of 0.128, 4.18, 0.706, and 0.329 J g-1° C-1, respectively. Which of the following would need the smallest quantity of heat to change the temperature of 5 g by 10° C?

A) lead

B) water

C) sulfur

D) arsenic

17) How much work, in joules, is done when the pressure is suddenly released from 4.56 atm to
1.23 atm on 45.4 g of O2 at 44° C?

A) 386 J

B) -477 J

C) -2.74×10^3 J

D) 2.74×10^3 J

E) 477 J

18) A system absorbs 623 J of heat while doing 457 J of work. What is the value of ΔU?

A) +1080 J

B) -166 J

C) +166 J

D) -1080 J

E) +623 J

19) 2 NOCl(g) → 2 NO(g) + Cl2(g) ΔH° = +75.56 kJ
2 NO(g) + O2(g) → 2 NO2(g) ΔH° = -113.05 kJ
2 NO2(g) → N2O4(g) ΔH° = -58.03 kJ

Compute ΔH° of

N2O4(g) + Cl2(g) → 2 NOCl(g) + O2(g) in kJ.

A) +246.65
B) -95.52
C) -246.65
D) +95.52
E) none of these