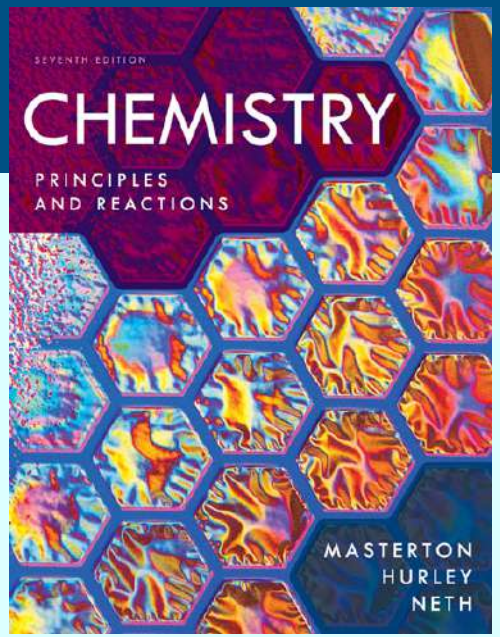

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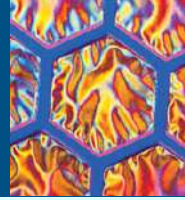
Chapter 8
Thermochemistry

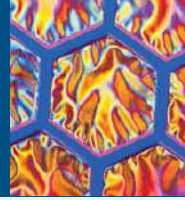
Edward J. Neth • University of Connecticut

Outline



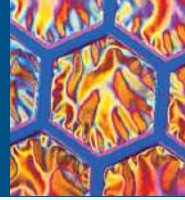
1. Principles of heat flow
2. Measurement of heat flow; calorimetry
3. Enthalpy
4. Thermochemical equations
5. Enthalpies of formation
6. Bond enthalpy
7. The first law of thermodynamics

Heat – Some Things to Think About



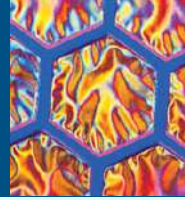
- What is heat?
- How do we measure heat?
- What connection is there between heat and matter at the molecular level?

Heat



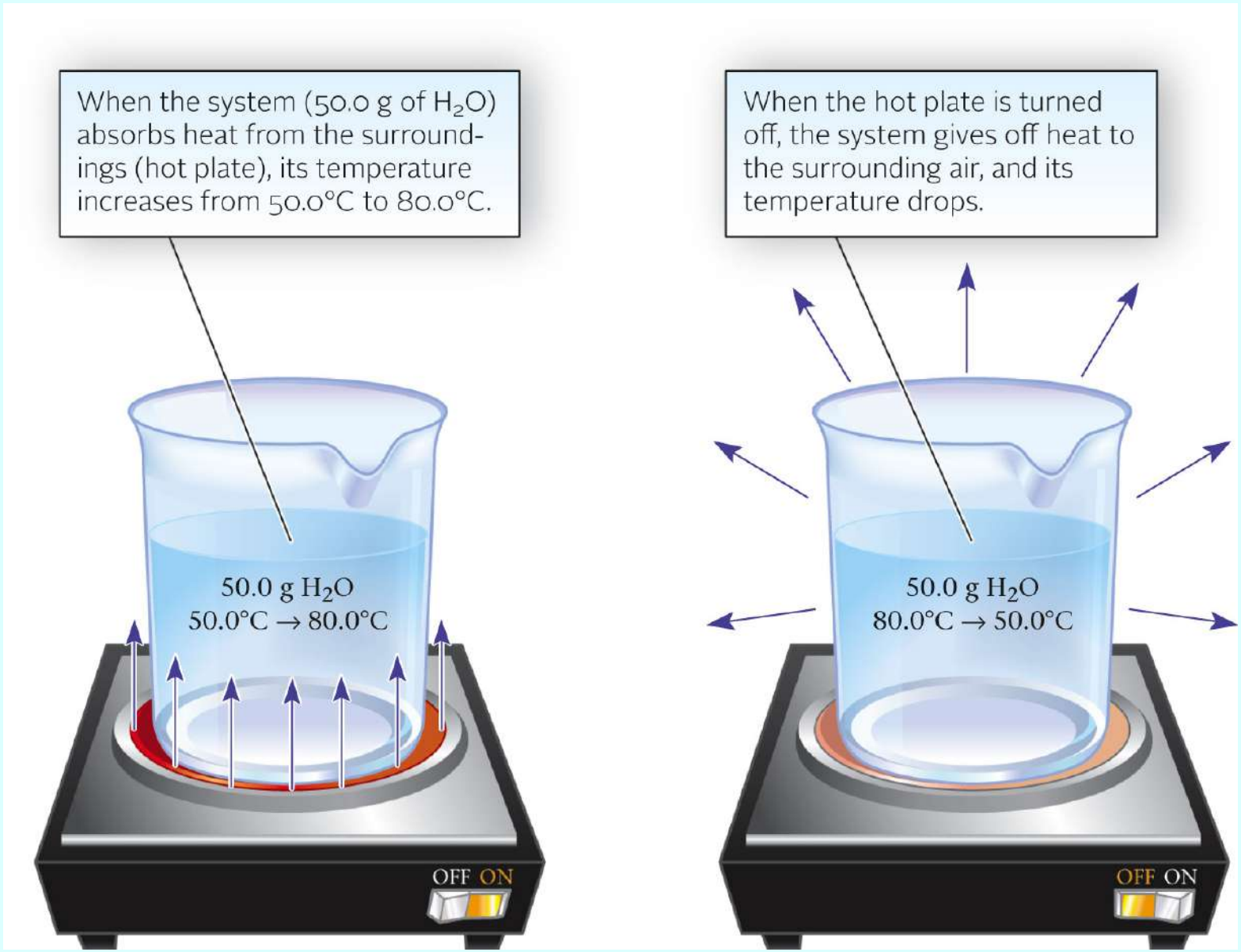
- Heat will flow from a hotter object to a colder object
  - Mix boiling water with ice
  - Temperature of the ice rises after it melts
  - Temperature of the water falls

Principles of Heat Flow

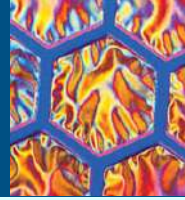


- Definitions
  - The system: that part of the universe on which attention is focused
  - The surroundings: the rest of the universe
    - Practically speaking, it is possible to consider only the surroundings that directly contact the system

Figure 8.1 – Systems and Surroundings

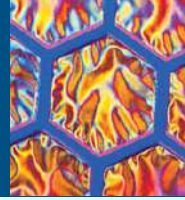


Chemical Reactions



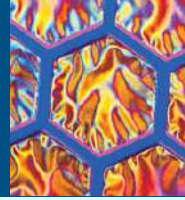
- When we study a chemical reaction, we consider the system to be the reactants and products
- The surroundings are the vessel (beaker, test tube, flask) in which the reaction takes place plus the air or other material in thermal contact with the reaction system

State Properties



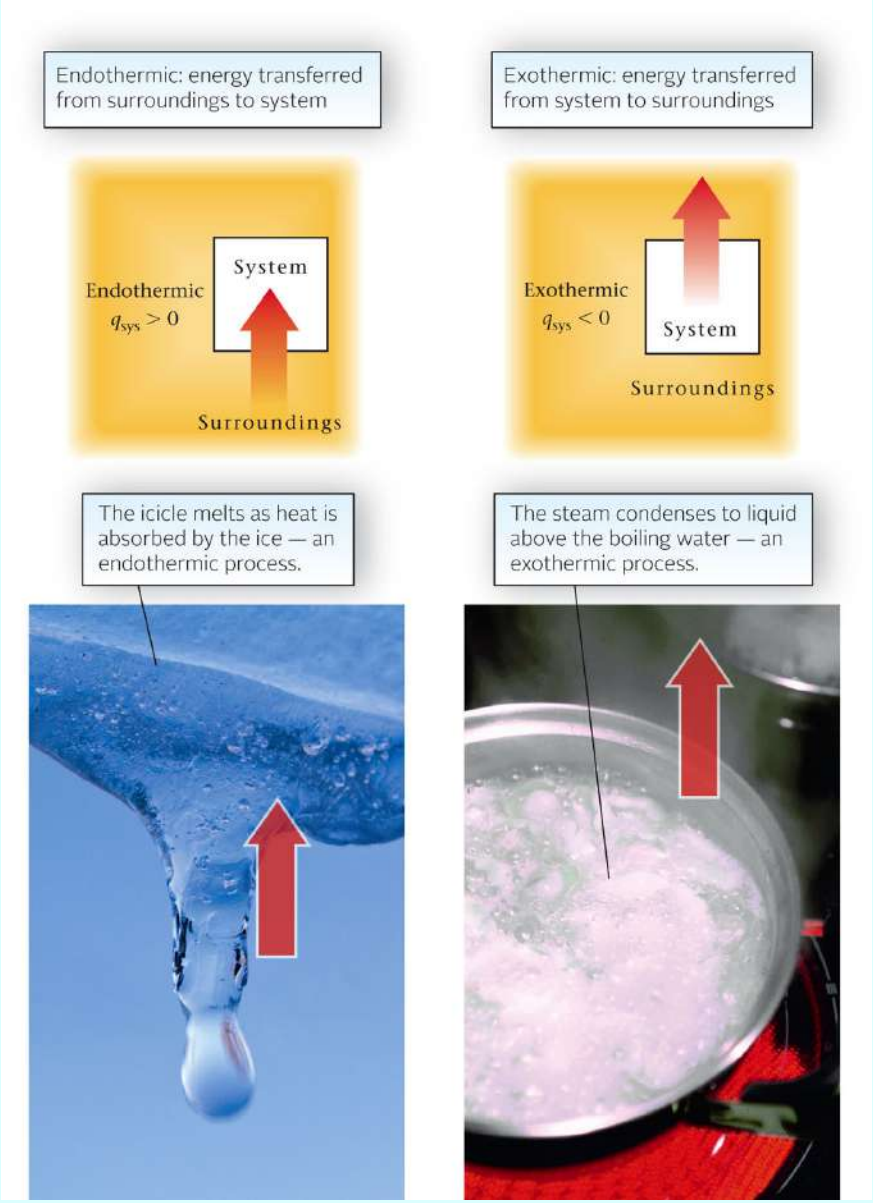
- The state of a system is specified by enumerating:
  - Composition
  - Temperature
  - Pressure
- State properties depend only on the state of the system, not on the path the system took to reach the state
- Mathematically for a state property X:
  - ΔX is the ***change*** in X
  - $\Delta X = X_{final} - X_{initial}$

Direction and Sign of Heat Flow

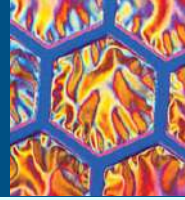


- Heat is given the symbol, q
  - q is positive when heat flows into the system from the surroundings
  - q is negative when heat flows from the system into the surroundings
- Endothermic processes have positive q
  - H_2O (s) → H_2O (ℓ)q > 0
- Exothermic processes have negative q
  - CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (ℓ) q < 0

Exothermic and Endothermic Processes

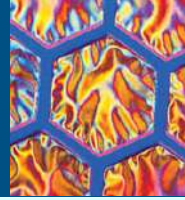


Magnitude of Heat Flow



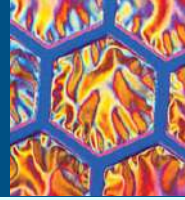
- In any process, we are interested in both the direction of heat flow and in its magnitude
  - q is expressed in joules (or kilojoules)
  - James Joule (1818-1889); calorimetry
  - Alternate unit: calorie
    - 1 calorie = 4.184 J
    - 1 kilocalorie = 4.184 kJ
    - Nutritional calories are kcal

The Calorimetry Equation



- $q = C \times \Delta t$
  - $\Delta t = t_{final} - t_{initial}$
  - ***C (uppercase)*** is the heat capacity of the system: it is the quantity of heat needed to raise the temperature of the system by 1 °C
- $q = m \times c \times \Delta t$
  - ***c (lowercase)*** is the specific heat: the quantity of heat needed to raise the temperature of one gram of a substance by 1 °C
- c depends on the identity and phase of the substance

Specific Heat



- The specific heat of a substance, like the density or melting point, is an intensive property that can be used to identify a substance or determine its purity
- Water
  - Water has an unusually large specific heat (4.18 J/g-°C)
  - A large quantity of heat is required to raise the temperature of water
  - Climate is moderated by the specific heat of water
    - Only two states in the US have never recorded temperatures over 100 °F – one is Alaska (cold North) and the other is Hawaii (moderated by water)

Table 8.1

TABLE 8.1 Specific Heats of a Few Common Substances

	c (J/g · °C)		c (J/g · °C)
$Br_2(l)$	0.474	Cu(s)	0.382
$Cl_2(g)$	0.478	Fe(s)	0.446
$C_2H_5OH(l)$	2.43	$H_2O(g)$	1.87
$C_6H_6(l)$	1.72	$H_2O(l)$	4.18
$CO_2(g)$	0.843	NaCl(s)	0.866

Example 8.1

EXAMPLE 8.1

Compare the amount of heat given off by 1.40 mol of liquid water when it cools from 100.0°C to 30.0°C to that given off when 1.40 mol of steam cools from 200.0°C to 110.0°C.

ANALYSIS

Information given:	$H_2O(l)$: mols (1.40), t_{final} (30.0°C), $t_{initial}$ (100.0°C) $H_2O(g)$: mols (1.40), t_{final} (110.0°C), $t_{initial}$ (200.0°C)
Information implied:	molar mass of water and steam specific heats of water and steam
Asked for:	q for both water and steam

STRATEGY

1. Recall that $\Delta t = t_{final} - t_{initial}$.
2. Convert mols to mass (in grams).
3. Use Table 8.1 to obtain the specific heats of water and steam.
4. Substitute into Equation 8.1.

Example 8.1, (Cont'd)

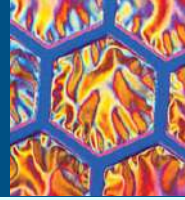
SOLUTION

For $H_2O(l)$: Δt	$\Delta t = t_{final} - t_{initial} = 30.0°C - 100.0°C = -70.0°C$
mass	$1.40 \text{ mol} \times \frac{18.02 \text{ g}}{1 \text{ mol}} = 25.2 \text{ g}$
c	From Table 8.1, $c = 4.18 \text{ J/g}\cdot°C$.
q	$q = \text{mass} \times \Delta t \times c = (25.2 \text{ g})(4.18 \text{ J/g}\cdot°C)(-70.0°C) = -7.37 \times 10^3 \text{ J}$
For $H_2O(g)$: Δt	$\Delta t = t_{final} - t_{initial} = 110.0°C - 200.0°C = -90.0°C$
mass	$1.40 \text{ mol} \times \frac{18.02 \text{ g}}{1 \text{ mol}} = 25.2 \text{ g}$
c	From Table 8.1, $c = 1.87 \text{ J/g}\cdot°C$.
q	$q = \text{mass} \times \Delta t \times c = (25.2 \text{ g})(1.87 \text{ J/g}\cdot°C)(-90.0°C) = -4.24 \times 10^3 \text{ J}$

END POINTS

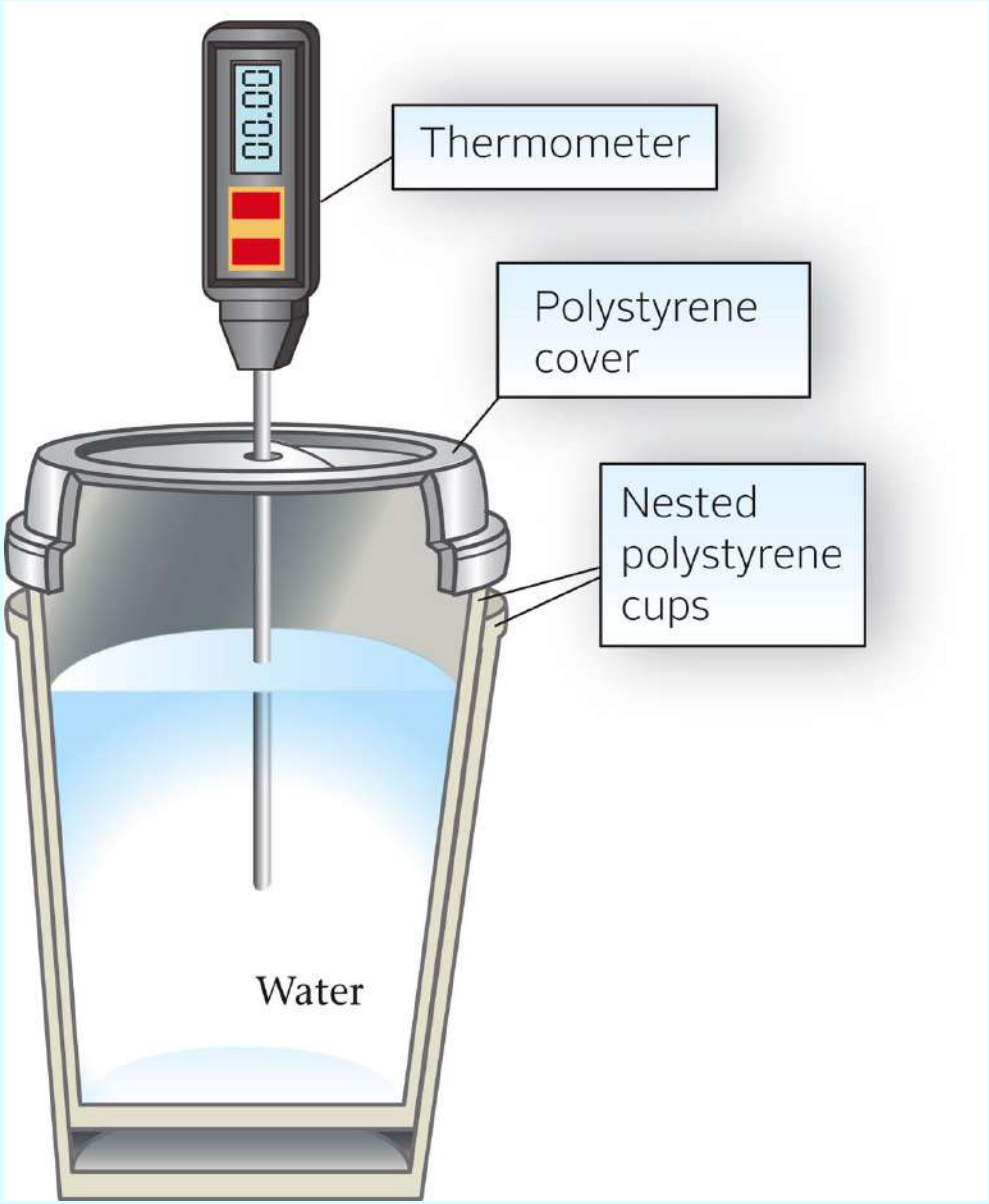
1. The negative sign indicates that heat flows from the system (water and steam) to the surroundings.
2. Be careful when deciding on initial and final temperatures. The higher temperature is not necessarily the final temperature.

Measurement of Heat Flow: Calorimetry



- A calorimeter is a device used to measure the heat flow of a reaction
  - The walls of the calorimeter are insulated to block heat flow between the reaction and the surroundings
  - The heat flow for the system is equal in magnitude and opposite in sign from the heat flow of the calorimeter
    - $q_{reaction} = - q_{calorimeter}$
    - $q_{reaction} = - C_{cal} \Delta t$

Figure 8.2: Coffee-cup Calorimeter



Coffee-cup Calorimeter

- For a reaction performed in a coffee-cup calorimeter

$$q_{reaction} = -m_{water} \times 4.18 \frac{J}{g \cdot {}^{o}C} \times \Delta t$$

Example 8.2

EXAMPLE 8.2 GRADED

Calcium chloride, $CaCl_2$, is added to canned vegetables to maintain the vegetables' firmness. When added to water, it dissolves:

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

A calorimeter contains 50.0 g of water at 25.00°C. When 1.00 g of calcium chloride is added to the calorimeter, the temperature rises to 28.51°C. Assume that all the heat given off by the reaction is transferred to the water.

a Calculate q for the reaction system.

b How much $CaCl_2$ must be added to raise the temperature of the solution 9.00°C?

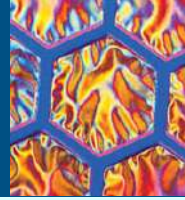
a

ANALYSIS

Information given:	mass of water (50.0 g); mass of $CaCl_2$ (1.00 g) initial temperature (25.00°C); final temperature (28.51°C)
Information implied:	specific heat of water
Asked for:	$q_{reaction}$

continued

Example 8.2, (Cont'd)



STRATEGY

1. Find Δt, and substitute into Equation 8.1 to find q_{H_2O}
2. Recall that q reaction $= -q_{H_2O}$.

SOLUTION

Δt	$\Delta t = t_{final} - t_{initial} = 28.51°C - 25.00°C = 3.51°C$
q_{H_2O}	$q_{H_2O} = \text{mass} \times \Delta t \times c = (50.0\ \text{g})(4.18\ \text{J/g}\cdot°C)(3.51°C) = 734\ \text{J}$
$q_{reaction}$	$q_{reaction} = -q_{H_2O} = -734\ \text{J}$

Example 8.2, (Cont'd)

ANALYSIS

Information given:	mass of water (50.0 g) From part (a), $q_{reaction}$ for 1.00 g of $CaCl_2$ used (−734 J). Δt (9.00°C)
Information implied:	specific heat of water
Asked for:	mass $CaCl_2$ to be added

STRATEGY

1. Find $q_{reaction}$ by substituting into Equation 8.1.
2. Use −734 J/g $CaCl_2$ obtained in part (a) as a conversion factor.

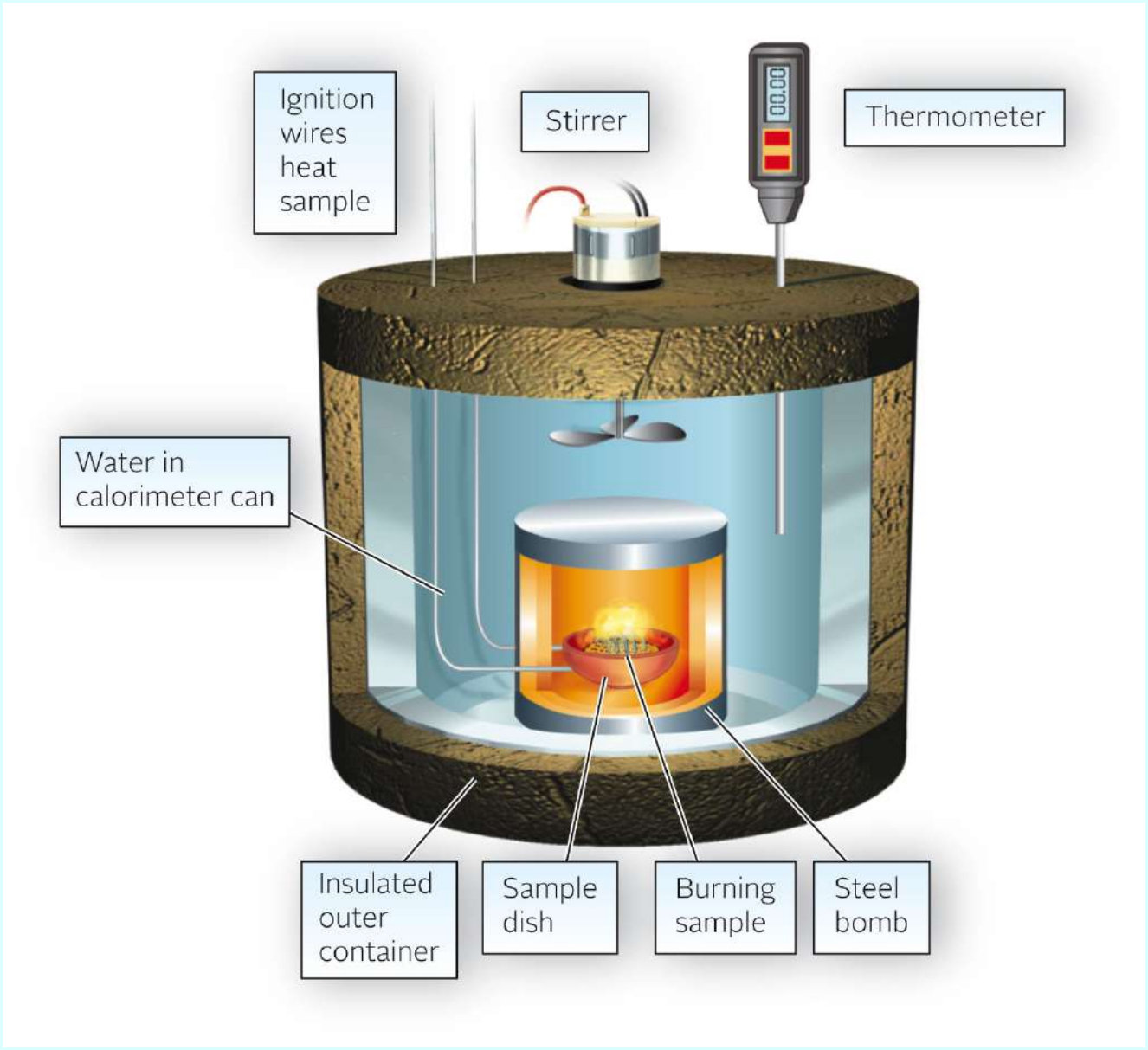
SOLUTION

q_{H_2O}	$q_{H_2O} = \text{mass} \times \Delta t \times c = (50.0\text{ g})(4.18\text{ J/g·°C})(9.00\text{°C}) = 1.88 \times 10^3\text{ J}$
$q_{reaction}$	$q_{reaction} = -q_{H_2O} = -1.88 \times 10^3\text{ J}$
Mass $CaCl_2$ needed	$-1.88 \times 10^3\text{ J} \times \dfrac{1.00\text{ g } CaCl_2}{-734\text{ J}} = 2.56\text{ g}$
Mass $CaCl_2$ to be added	$2.56 - 1.00 = 1.56\text{ g}$

END POINT

Since the final temperature is larger than the initial temperature after the addition of $CaCl_2$, the reaction must be exothermic. Thus $q_{reaction}$ must be negative. It is!

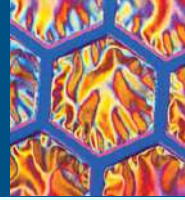
Figure 8.3: Bomb Calorimeter



Bomb Calorimeter

- The bomb calorimeter is more versatile than the coffee-cup calorimeter
  - Reactions involving high temperature
  - Reactions involving gases
- The bomb is a heavy metal vessel that is usually surrounded by water
- $q_{reaction} = -q_{calorimeter}$
- $q_{reaction} = -C_{cal}\Delta t$
- C_{cal} is a function of the calorimeter and can be measured experimentally

Example 8.3



EXAMPLE 8.3

Hydrogen chloride is used in etching semiconductors. It can be prepared by reacting hydrogen and chlorine gases.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

It is found that when 1.00 g of H_2 is made to react completely with Cl_2 in a bomb calorimeter with a heat capacity of 5.15 kJ/°C, the temperature in the bomb rises from 20.00°C to 29.82°C. The calorimeter can hold 1.000 kg of water. How much heat is evolved by the reaction?

ANALYSIS

Information given:	mass of H_2 (1.00 g); mass of water (1.000 kg = 1.000×10^3 g) C_{cal} (5.15 kJ/°C) t_{final} (29.82°C), $t_{initial}$ (20.00°C)
Information implied:	specific heat (c) of water
Asked for:	q for the reaction

Example 8.3, (Cont'd)

STRATEGY

1. Find q_{H_2O} by substituting into Equation 8.2.
2. Find q_{cal} by substituting into Equation 8.3.
3. Recall: $q_{reaction} = -(q_{H_2O} + q_{cal})$.

SOLUTION

1. q_{H_2O}

$$q_{H_2O} = c_{H_2O} \times \text{mass}_{H_2O} \times \Delta t$$

$$= 4.18 \frac{\text{J}}{\text{g} \cdot {}^\circ\text{C}} \times 1.000 \times 10^3 \text{ g} \times (29.82 - 20.00){}^\circ\text{C}$$

$$= 4.10 \times 10^4 \text{ J} = 41.0 \text{ kJ}$$

2. q_{cal}

$$q_{cal} = C_{cal} \times \Delta t = (5.15 \text{ kJ/}{}^\circ\text{C})(29.82 - 20.00){}^\circ\text{C} = 50.6 \text{ kJ}$$

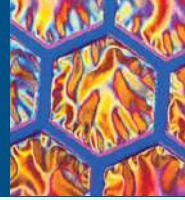
3. $q_{reaction}$

$$q_{reaction} = -(q_{cal} + q_{H_2O}) = -(41.0 + 50.6)\text{kJ} = -91.6 \text{ kJ}$$

END POINT

The amount of hydrogen gas (1.00 g) that reacted is not relevant to the solution of this problem.

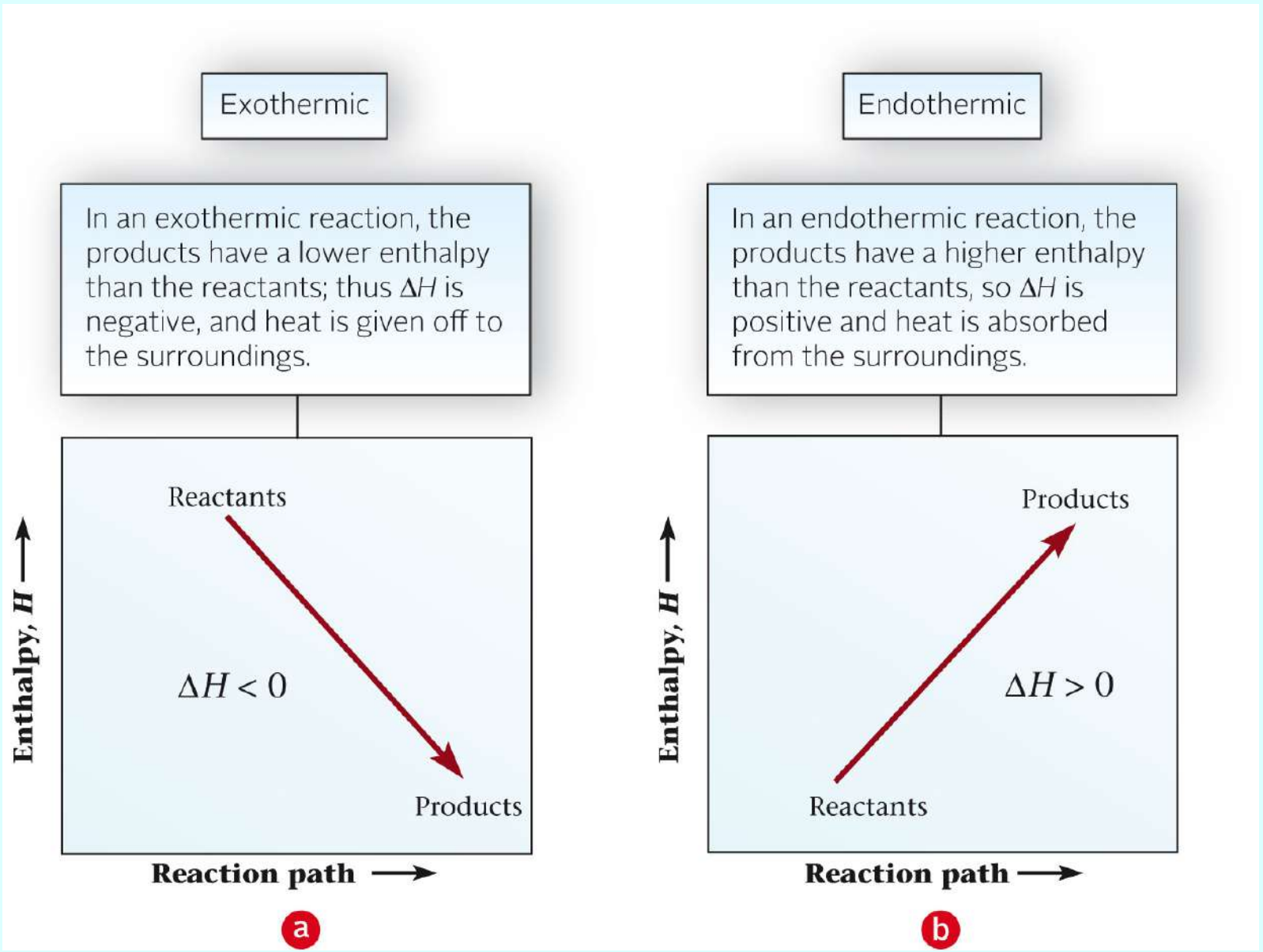
Enthalpy



- The heat flow at constant pressure is equal to the difference in enthalpy (heat content) between products and reactants
- The symbol for enthalpy is H
- We measure changes in enthalpy using a calorimeter and a reaction run at constant pressure:
  - $\Delta H = H_{products} - H_{reactants}$
- The sign of the enthalpy change is the same as for heat flow:
  - $\Delta H > 0$ for endothermic reactions
  - $\Delta H < 0$ for exothermic reactions
  - ***Enthalpy is a state variable***

Exothermic Reactions

Figure 8.4 – Enthalpy of Reaction



Thermochemical Equations

- A thermochemical equation is a chemical equation with the ΔH for the reaction included
- Example
  - NH_4NO_3 (s) → NH_4^+ (aq) + NO_3^- (aq)
    - Experiment gives $q_{reaction}$ = 351 J for one gram of ammonium nitrate
    - For one mole, this is

$$\frac{351\,J}{1.00\,g} \times \frac{80.05\,g}{1\,mol} = 2.81 \times 10^4\,J = 28.1\,kJ$$

  - The thermochemical equation is
    - NH_4NO_3 (s) → NH_4^+ (aq) + NO_3^- (aq) ΔH = +28.1 kJ

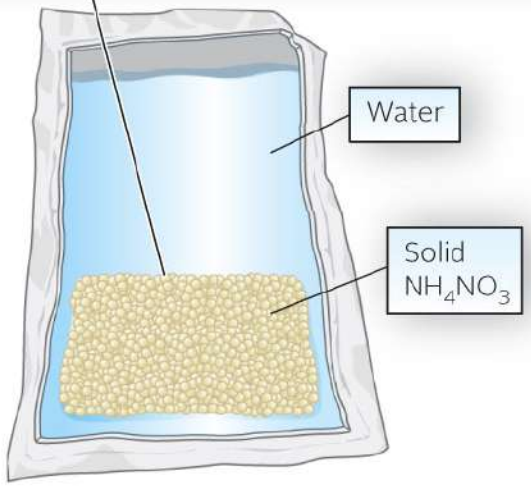
Figure 8.5 – An Endothermic Reaction

The cold pack contains two separate compartments; one with ammonium nitrate and one with water.

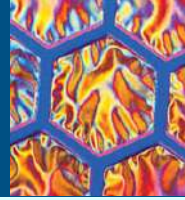
When the seal separating the compartments is broken the following endothermic reaction occurs:

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq) \quad \Delta H = +28.1\ kJ$

As a result, the temperature, as read on the thermometer, drops.



Conventions for Thermochemical Equations



1. The sign of ΔH indicates whether the reaction is endothermic or exothermic
2. The coefficients of the thermochemical equation represent the number of moles of reactant and product
3. The phases of all reactant and product species must be stated
4. The value of ΔH applies when products and reactants are at the same temperature, usually 25 °C

Rules of Thermochemistry

1. The magnitude of ΔH is directly proportional to the amount of reactant or product
2. ΔH for the reaction is equal in magnitude but opposite in sign for ΔH for the reverse of the reaction
3. The value of ΔH is the same whether the reaction occurs in one step or as a series of steps

   This rule is a direct consequence of the fact that ΔH is a state variable

   This rule is a statement of Hess's Law

Example 8.4

EXAMPLE 8.4 GRADED

The Bunsen burners in your labs are fueled by natural gas, which is mostly methane, CH_4. The thermochemical equation for the combustion (burning in oxygen) of methane is

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.3 \text{ kJ}$$

Calculate ΔH when

a. 5.00 g of CH_4 react with an excess of oxygen.

b. 2.00 L of O_2 at 49.0°C and 782 mm Hg react with an excess of methane.

c. 2.00 L of CH_4 react with 5.00 L of O_2 in a reaction vessel kept at 25°C and 1.00 atm.

(a)

ANALYSIS

Information given:	mass of CH_4 (5.00 g), excess O_2
Information implied:	molar mass of CH_4 ΔH for the reaction
Asked for:	ΔH

STRATEGY

1. Use the relationship obtained from the thermochemical equation: -890.3 kJ/mol CH_4 as a conversion factor.
2. Follow the following schematic plan.

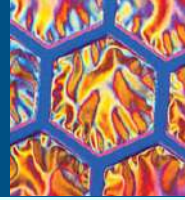
$$\text{mass}_{CH_4} \xrightarrow{MM} \text{mol}_{CH_4} \xrightarrow{-890.3 \text{ kJ/mol } CH_4} \Delta H$$

SOLUTION

ΔH

$$5.00 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.04 \text{ g } CH_4} \times \frac{-890.3 \text{ kJ}}{1 \text{ mol } CH_4} = -278 \text{ kJ}$$

Example 8.4, (Cont'd)



(b)

ANALYSIS

Information given:	O_2 data: V (2.00 L), T (49.0°C), P (782 mm Hg). Excess CH_4
Information implied:	ΔH for the reaction gas constant, R
Asked for:	ΔH

continued

STRATEGY

Follow the following schematic plan.

$$V_{O_2} \xrightarrow{PV/RT} \text{mol}_{O_2} \xrightarrow{-890.3\ \text{kJ}/2\ \text{mol}\ O_2} \Delta H$$

SOLUTION

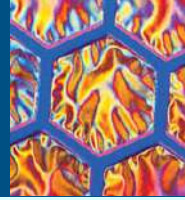
mol O_2

$$n = \frac{PV}{RT} = \frac{(782/760)\text{atm} \times 2.00\ \text{L}}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K}) \times 322\ \text{K}} = 0.0778\ \text{mol}$$

ΔH

$$0.0778\ \text{mol}\ O_2 \times \frac{-890.3\ \text{kJ}}{2\ \text{mol}\ O_2} = -34.7\ \text{kJ}$$

Example 8.4, (Cont'd)



(c)

ANALYSIS

Information given:	V_{CH_4} (2.00 L), V_{O_2} (5.00 L), T and P are constant.
Information implied:	stoichiometric ratios ΔH for the reaction gas constant, R
Asked for:	ΔH

STRATEGY

1. Note that data about both reactants is given (limiting reactant problem) and that the reaction is at constant temperature and pressure.
2. Find V_{CO_2} obtained if CH_4 is limiting and again if O_2 is limiting. Choose the smaller value, then use the following schematic plan:

$$V_{CO_2} \xrightarrow{PV/RT} \text{mol}_{CO_2} \xrightarrow{-890.3\ \text{kJ/1 mol } CO_2} \Delta H$$

SOLUTION

V_{CO_2} produced

If CH_4 is limiting: $2.00\ \text{L } CH_4 \times \dfrac{1\ \text{L } CO_2}{1\ \text{L } CH_4} = 2.00\ \text{L}$

If O_2 is limiting: $5.00\ \text{L } O_2 \times \dfrac{1\ \text{L } CO_2}{2\ \text{L } O_2} = 2.50\ \text{L}$

CH_4 is limiting and 2.00 L of CO_2 are produced.

mol CO_2

$$n = \frac{PV}{RT} = \frac{1.00\ \text{atm} \times 2.00\ \text{L}}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K}) \times 298\ \text{K}} = 0.0817\ \text{mol}$$

ΔH

$$0.0817\ \text{mol } CO_2 \times \frac{-890.3\ \text{kJ}}{1\ \text{mol } CO_2} = -72.8\ \text{kJ}$$

Enthalpy of Phase Changes

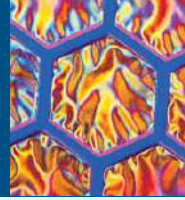
- Phase changes involve enthalpy
  - There is no change in temperature during a phase change
  - Endothermic: melting or vaporization
  - Exothermic: freezing or condensation
- Pure substances have a value of ΔH that corresponds to melting (reverse, fusion) or vaporization (reverse, condensation)

TABLE 8.2 ΔH (kJ/mol) for Phase Changes

Substance		mp (°C)	ΔH_{fus}*	bp (°C)	ΔH_{vap}*
Benzene	C_6H_6	5	9.84	80	30.8
Bromine	Br_2	−7	10.8	59	29.6
Mercury	Hg	−39	2.33	357	59.4
Naphthalene	$C_{10}H_8$	80	19.3	218	43.3
Water	H_2O	0	6.00	100	40.7

*Values of ΔH_{fus} are given at the melting point, values of ΔH_{vap} at the boiling point. The heat of vaporization of water decreases from 44.9 kJ/mol at 0°C to 44.0 kJ/mol at 25°C to 40.7 kJ/mol at 100°C.

Example 8.5



EXAMPLE 8.5

Given

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = -571.6 \text{ kJ}$$

calculate ΔH for the equation

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2} O_2(g)$$

STRATEGY

1. Note that the second equation is the reverse of the first. Apply Rule 2.
2. The coefficients of the second equation are half those of the given equation. Apply Rule 1.

SOLUTION

Apply Rule 2.	$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$	$\Delta H = -(-571.6 \text{ kJ}) = 571.6 \text{ kJ}$
Apply Rule 1.	$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2} O_2(g)$	$\Delta H = \frac{1}{2}(+ 571.6 \text{ kJ}) = 285.8 \text{ kJ}$

Example 8.6

EXAMPLE 8.6

Carbon monoxide, CO, is a poisonous gas. It can be obtained by burning carbon in a limited amount of oxygen. Given

(1) $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5\ \text{kJ}$

(2) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -566.0\ \text{kJ}$

calculate ΔH for the reaction

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = ?$$

STRATEGY

1. Work with the given equations until you arrive at two equations that will add to give the equation

   $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

2. Focus on species that appear in only one of the thermochemical equations. In this case C appears only in Equation (1) and CO appears only in Equation (2).

3. For CO

   Compare position and number of moles of CO in Equation 2 and in the desired equation.

Position: Equation (2)—on the left	Desired equation—on the right
Moles: Equation (2)—2 moles	Desired equation—1 mole

   Apply Rule 2 to reverse Equation (2) (to put CO on the right).

   Apply Rule 1 and divide Equation (2) by 2 (to get a coefficient of 1 for CO).

4. For C

   Compare position and number of moles of C in Equation (1) and in the desired equation.

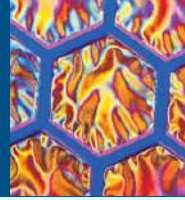
Position: Equation (1)—on the left	Desired equation—on the left
Moles: Equation (2)—1 mole	Desired equation—1 mole

   Both the position and coefficient for C are okay, so use Equation (1) "as is."

5. Add the "revised" Equation (2c) to Equation (1).

continued

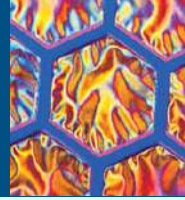
Example 8.6, (Cont'd)



SOLUTION

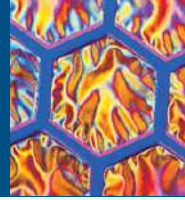
For Equation (2)		
Apply Rule 2	(2a) $2CO_2(g) \longrightarrow 2CO(g) + O_2(g)$	$\Delta H = -(-566.0\ \text{kJ}) = 566.0\ \text{kJ}$
Apply Rule 1	(2b) $CO_2(g) \longrightarrow CO(g) + \frac{1}{2} O_2(g)$	$\Delta H = \frac{1}{2}(566.0\ \text{kJ}) = 283.0\ \text{kJ}$
"Revised" Equation 2	(2c) $CO_2(g) \longrightarrow CO(g) + \frac{1}{2} O_2(g)$	$\Delta H_2 = \frac{1}{2}(566.0\ \text{kJ}) = 283.0\ \text{kJ}$
Equation (1) "as is"	(1) $C(s) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H_1 = -393.5\ \text{kJ}$
Apply Hess's law	Add "revised" Equation (2c) to Equation (1)	
	(2c) ~~$CO_2(g)$~~ $\longrightarrow CO(g) + \frac{1}{2}$ ~~$O_2(g)$~~	$\Delta H_2 = 283.0\ \text{kJ}$
	(1) $C(s) +$ ~~$O_2(g)$~~ $\longrightarrow$ ~~$CO_2(g)$~~	$\Delta H_1 = -393.5\ \text{kJ}$
	↓	
	$\frac{1}{2} O_2(g)$	
$\Delta H = \Delta H_1 + \Delta H_2$	$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$	$\Delta H = 283.0\ \text{kJ} + (-393.5)\ \text{kJ} = -110.5\ \text{kJ}$

Recap of the Rules of Thermochemistry



- ΔH is directly proportional to the amount of reactant or product
  - If a reaction is divided by 2, so is ΔH
  - If a reaction is multiplied by 6, so is ΔH
- ΔH changes sign when the reaction is reversed
- ΔH has the same value regardless of the number of steps

Enthalpies of Formation



- The standard molar enthalpy of formation, ΔH_f°, is equal to the enthalpy change
  - For one mole of a compound
  - At constant pressure of 1 atm
  - At a fixed temperature of 25°C
  - From elements in their stable states at that temperature and pressure
- Enthalpies of formation are tabulated in Table 8.3 and in Appendix 1 in the back of the textbook

Table 8.3

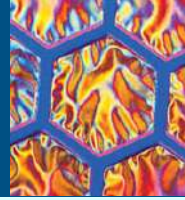


TABLE 8.3 Standard Enthalpies of Formation at 25°C (kJ/mol) of Compounds at 1 atm, Aqueous Ions at 1 *M*

Compounds							
$AgBr(s)$	−100.4	$CaCl_2(s)$	−795.8	$H_2O(g)$	−241.8	$NH_4NO_3(s)$	−365.6
$AgCl(s)$	−127.1	$CaCO_3(s)$	−1206.9	$H_2O(l)$	−285.8	$NO(g)$	+90.2
$AgI(s)$	−61.8	$CaO(s)$	−635.1	$H_2O_2(l)$	−187.8	$NO_2(g)$	+33.2
$AgNO_3(s)$	−124.4	$Ca(OH)_2(s)$	−986.1	$H_2S(g)$	−20.6	$N_2O_4(g)$	+9.2
$Ag_2O(s)$	−31.0	$CaSO_4(s)$	−1434.1	$H_2SO_4(l)$	−814.0	$NaCl(s)$	−411.2
$Al_2O_3(s)$	−1675.7	$CdCl_2(s)$	−391.5	$HgO(s)$	−90.8	$NaF(s)$	−573.6
$BaCl_2(s)$	−858.6	$CdO(s)$	−258.2	$KBr(s)$	−393.8	$NaOH(s)$	−425.6
$BaCO_3(s)$	−1216.3	$Cr_2O_3(s)$	−1139.7	$KCl(s)$	−436.7	$NiO(s)$	−239.7
$BaO(s)$	−553.5	$CuO(s)$	−157.3	$KClO_3(s)$	−397.7	$PbBr_2(s)$	−278.7
$BaSO_4(s)$	−1473.2	$Cu_2O(s)$	−168.6	$KClO_4(s)$	−432.8	$PbCl_2(s)$	−359.4
$CCl_4(l)$	−135.4	$CuS(s)$	−53.1	$KNO_3(s)$	−494.6	$PbO(s)$	−219.0
$CHCl_3(l)$	−134.5	$Cu_2S(s)$	−79.5	$MgCl_2(s)$	−641.3	$PbO_2(s)$	−277.4
$CH_4(g)$	−74.8	$CuSO_4(s)$	−771.4	$MgCO_3(s)$	−1095.8	$PCl_3(g)$	−287.0
$C_2H_2(g)$	+226.7	$Fe(OH)_3(s)$	−823.0	$MgO(s)$	−601.7	$PCl_5(g)$	−374.9
$C_2H_4(g)$	+52.3	$Fe_2O_3(s)$	−824.2	$Mg(OH)_2(s)$	−924.5	$SiO_2(s)$	−910.9
$C_2H_6(g)$	−84.7	$Fe_3O_4(s)$	−1118.4	$MgSO_4(s)$	−1284.9	$SnO_2(s)$	−580.7
$C_3H_8(g)$	−103.8	$HBr(g)$	−36.4	$MnO(s)$	−385.2	$SO_2(g)$	−296.8
$CH_3OH(l)$	−238.7	$HCl(g)$	−92.3	$MnO_2(s)$	−520.0	$SO_3(g)$	−395.7
$C_2H_5OH(l)$	−277.7	$HF(g)$	−271.1	$NH_3(g)$	−46.1	$ZnI_2(s)$	−208.0
$CO(g)$	−110.5	$HI(g)$	+26.5	$N_2H_4(l)$	+50.6	$ZnO(s)$	−348.3
$CO_2(g)$	−393.5	$HNO_3(l)$	−174.1	$NH_4Cl(s)$	−314.4	$ZnS(s)$	−206.0

Table 8.3, (Cont'd)

TABLE 8.3 Standard Enthalpies of Formation at 25°C (kJ/mol) of Compounds at 1 atm, Aqueous Ions at 1 *M*

Cations				Anions			
$Ag^+(aq)$	+105.6	$Hg^{2+}(aq)$	+171.1	$Br^-(aq)$	−121.6	$HPO_4^{2-}(aq)$	−1292.1
$Al^{3+}(aq)$	−531.0	$K^+(aq)$	−252.4	$CO_3^{2-}(aq)$	−677.1	$HSO_4^-(aq)$	−887.3
$Ba^{2+}(aq)$	−537.6	$Mg^{2+}(aq)$	−466.8	$Cl^-(aq)$	−167.2	$I^-(aq)$	−55.2
$Ca^{2+}(aq)$	−542.8	$Mn^{2+}(aq)$	−220.8	$ClO_3^-(aq)$	−104.0	$MnO_4^-(aq)$	−541.4
$Cd^{2+}(aq)$	−75.9	$Na^+(aq)$	−240.1	$ClO_4^-(aq)$	−129.3	$NO_2^-(aq)$	−104.6
$Cu^+(aq)$	+71.7	$NH_4^+(aq)$	−132.5	$CrO_4^{2-}(aq)$	−881.2	$NO_3^-(aq)$	−205.0
$Cu^{2+}(aq)$	+64.8	$Ni^{2+}(aq)$	−54.0	$Cr_2O_7^{2-}(aq)$	−1490.3	$OH^-(aq)$	−230.0
$Fe^{2+}(aq)$	−89.1	$Pb^{2+}(aq)$	−1.7	$F^-(aq)$	−332.6	$PO_4^{3-}(aq)$	−1277.4
$Fe^{3+}(aq)$	−48.5	$Sn^{2+}(aq)$	−8.8	$HCO_3^-(aq)$	−692.0	$S^{2-}(aq)$	+33.1
$H^+(aq)$	0.0	$Zn^{2+}(aq)$	−153.9	$H_2PO_4^-(aq)$	−1296.3	$SO_4^{2-}(aq)$	−909.3

Enthalpies of Formation of Elements and of H^+ (aq)

- The enthalpy of formation of an element in its standard state at 25 °C is zero
- $\Delta H_f^o\ Br_2(\ell) = \Delta H_f^o\ H_2(g) = 0$

- The enthalpy of formation of H^+ (aq) is also zero

Calculation of ΔH°

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

- The symbol Σ refers to “the sum of”
- Elements in their standard states may be omitted, as their enthalpies of formation are zero
- The coefficients of reactants and products in the balanced equation must be accounted for

Example 8.7

EXAMPLE 8.7 GRADED

Benzene, C_6H_6, used in the manufacture of plastics, is a carcinogen affecting the bone marrow. Long-term exposure has been shown to cause leukemia and other blood disorders. The combustion of benzene is given by the following equation:

$$C_6H_6(l) + \tfrac{15}{2}\,O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l) \qquad \Delta H^\circ = -3267.4\ \text{kJ}$$

(a) Calculate the heat of formation of benzene.

(b) Calculate ΔH° for the reaction

$$12CO_2(g) + 6H_2O(l) \longrightarrow 2C_6H_6(l) + 15\,O_2(g)$$

(c) Calculate ΔH° for the reaction

$$C_6H_6(g) + \tfrac{15}{2}\,O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$$

(a)

ANALYSIS

Information given:	thermochemical equation for the combustion of benzene
Information implied:	ΔH_f° for all species except benzene (Table 8.3).
Asked for:	ΔH_f° for benzene

STRATEGY

1. Find ΔH° for all the species (besides benzene) in Table 8.3 and substitute into Equation 8.4.
2. Recall that ΔH° for $O_2(g)$ is zero.

SOLUTION

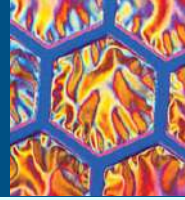
Equation 8.4

$$-3267.4\ \text{kJ} = 6(\Delta H_f^\circ\ CO_2) + 3(\Delta H_f^\circ\ H_2O) - (\Delta H_f^\circ\ C_6H_6)$$

ΔH_f° for $C_6H_6(l)$

$$\Delta H_f^\circ = 3267.4\ \text{kJ} + 6\ \text{mol}\left(-393.5\ \frac{\text{kJ}}{\text{mol}}\right) + 3\ \text{mol}\left(-285.8\ \frac{\text{kJ}}{\text{mol}}\right) = +\,49.0\ \text{kJ/mol}$$

Example 8.7, (Cont'd)



(b)

ANALYSIS

Information given:	thermochemical equation for the combustion of benzene
Asked for:	ΔH° for the reaction: $12CO_2(g) + 6H_2O(l) \longrightarrow 2C_6H_6(l) + 15\ O_2(g)$

continued

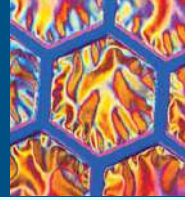
STRATEGY

Note that the given equation is the reverse of the combustion equation and that the coefficients have been doubled. Apply Rules 1 and 2.

SOLUTION

Rule 2	$\Delta H^\circ = -(-3267.4)\ \text{kJ} = 3267.4\ \text{kJ}$
Rule 1	$\Delta H^\circ = 2(3267.4\ \text{kJ}) = 6534.8\ \text{kJ}$

Example 8.7, (Cont'd)



(c)

ANALYSIS

Information given:	thermochemical equation for the combustion of benzene
Information implied:	ΔH_{vap} for water and benzene (Table 8.2)
Asked for:	$C_6H_6(g) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$

STRATEGY

1. Notice that the given equation is identical to the combustion equation except for the physical states of benzene and water.
2. a. Write the thermochemical equation for the vaporization of water.
   b. Multiply the equation by 3 since there are three moles of H_2O in the combustion reaction.
3. a. Write the thermochemical equation for the vaporization of benzene.
   b. Note that $C_6H_6(g)$ is a reactant in the equation where $\Delta H°$ is needed.
   c. Reverse the vaporization equation for benzene and change the sign of its $\Delta H°$.
4. Apply Hess's law by adding all the equations so you come up with $\Delta H°$ for the overall given equation.

SOLUTION

$\Delta H_1°$: ($3 \times \Delta H_{vap}$ H_2O)	$3(H_2O(l) \longrightarrow H_2O(g)) = 3(40.7 \text{ kJ/mol})$	$\Delta H_1° = 122.1$ kJ
$\Delta H_2°$: (reverse ΔH_{vap} C_6H_6)	$C_6H_6(g) \longrightarrow C_6H_6(l) = -(30.8)$ kJ/mol	$\Delta H_2° = -30.8$ kJ
Apply Hess's law	Equation (1) + Equation (2) + combustion equation	
	(1) $3H_2O(l) \longrightarrow 3H_2O(g)$	$\Delta H_1° = 122.1$ kJ
	(2) $C_6H_6(g) \longrightarrow C_6H_6(l)$	$\Delta H_2° = -30.8$ kJ
	$C_6H_6(l) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$	$\Delta H° = -3267.4$ kJ
Overall equation	$C_6H_6(g) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$	
$\Delta H°$	$122.1 \text{ kJ} + (-30.8 \text{ kJ}) + (-3267.4 \text{ kJ}) = -3176.1$ kJ	

Example 8.8

EXAMPLE 8.8 GRADED

Sodium carbonate is a white powder used in the manufacture of glass. When hydrochloric acid is added to a solution of sodium carbonate, carbon dioxide gas is formed (Figure 8.8). The equation for the reaction is

$$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O(l)$$

(a) Calculate $\Delta H°$ for the thermochemical equation.

(b) Calculate $\Delta H°$ when 25.00 mL of 0.186 *M* HCl is added to sodium carbonate.

(a)

ANALYSIS

Information given:	Equation for the reaction: $[2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O(l)]$
Information implied:	$\Delta H_f°$ for all the species in the reaction (Table 8.3)
Asked for:	$\Delta H°$ for the reaction

STRATEGY

Use Table 8.3 and recall that $\Delta H_f°$ for H^+ is zero.

SOLUTION

$\Delta H°$

$$\Delta H° = \Delta H_f° \, CO_2 + \Delta H_f° \, H_2O - [2\,\Delta H_f° \, H^+ + \Delta H_f° \, CO_3^{2-}]$$

$$= 1\text{ mol}\left(-393.5\frac{\text{kJ}}{\text{mol}}\right) + 1\text{ mol}\left(-285.8\frac{\text{kJ}}{\text{mol}}\right) - \left[0 + 1\text{ mol}\left(-677.1\frac{\text{kJ}}{\text{mol}}\right)\right] = -2.2\text{ kJ}$$

Example 8.8, (Cont'd)

(b)

ANALYSIS

Information given:	V_{HCl} (25.00 mL); M_{HCl} (0.186) From part (a): $\Delta H°$ for the reaction (−2.2 kJ)
Asked for:	ΔH when given amounts of HCl are used.

STRATEGY

1. $\Delta H°$ calculated for (a) is for 2 moles of H^+.
2. Find moles of H^+ actually used and convert to kJ by using the following plan:

$$(V \times M) \longrightarrow \text{mol HCl} \xrightarrow{1 \text{ mol HCl}/1 \text{ mol } H^+} \text{mol } H^+ \xrightarrow{\Delta H°/2 \text{ mol } H^+} \text{kJ}$$

continued

SOLUTION

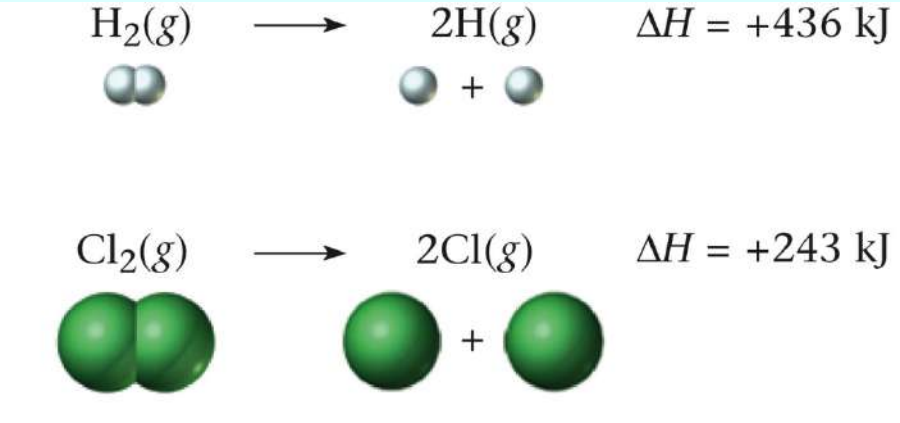
mol H^+	$V \times M = (0.02500 \text{ L})(0.186 \text{ mol/L}) = 0.00465 \text{ mol HCl} = \text{mol } H^+$
$\Delta H°$	$0.00465 \text{ mol } H^+ \times \dfrac{-2.2 \text{ kJ}}{2 \text{ mol } H^+} = -5.1 \times 10^{-3} \text{ kJ}$

END POINT

When you use Table 8.3 to figure out $\Delta H°$ for a reaction, make sure you consider the physical state of the species. Water, for example, has 2 different $\Delta H_f°$ values given: one for liquid and the other for gas. By the same token, do not forget to write the physical state of each species when you write an equation to represent a reaction.

Bond Enthalpy

- Chemical bonds store ***energy***
- The ***bond enthalpy is defined as ΔH when one mole of chemical bonds is broken in the gaseous state***



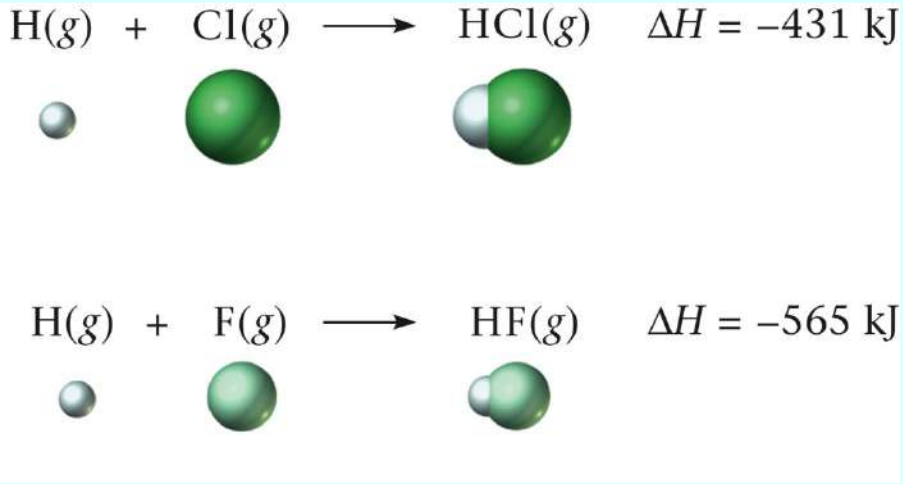
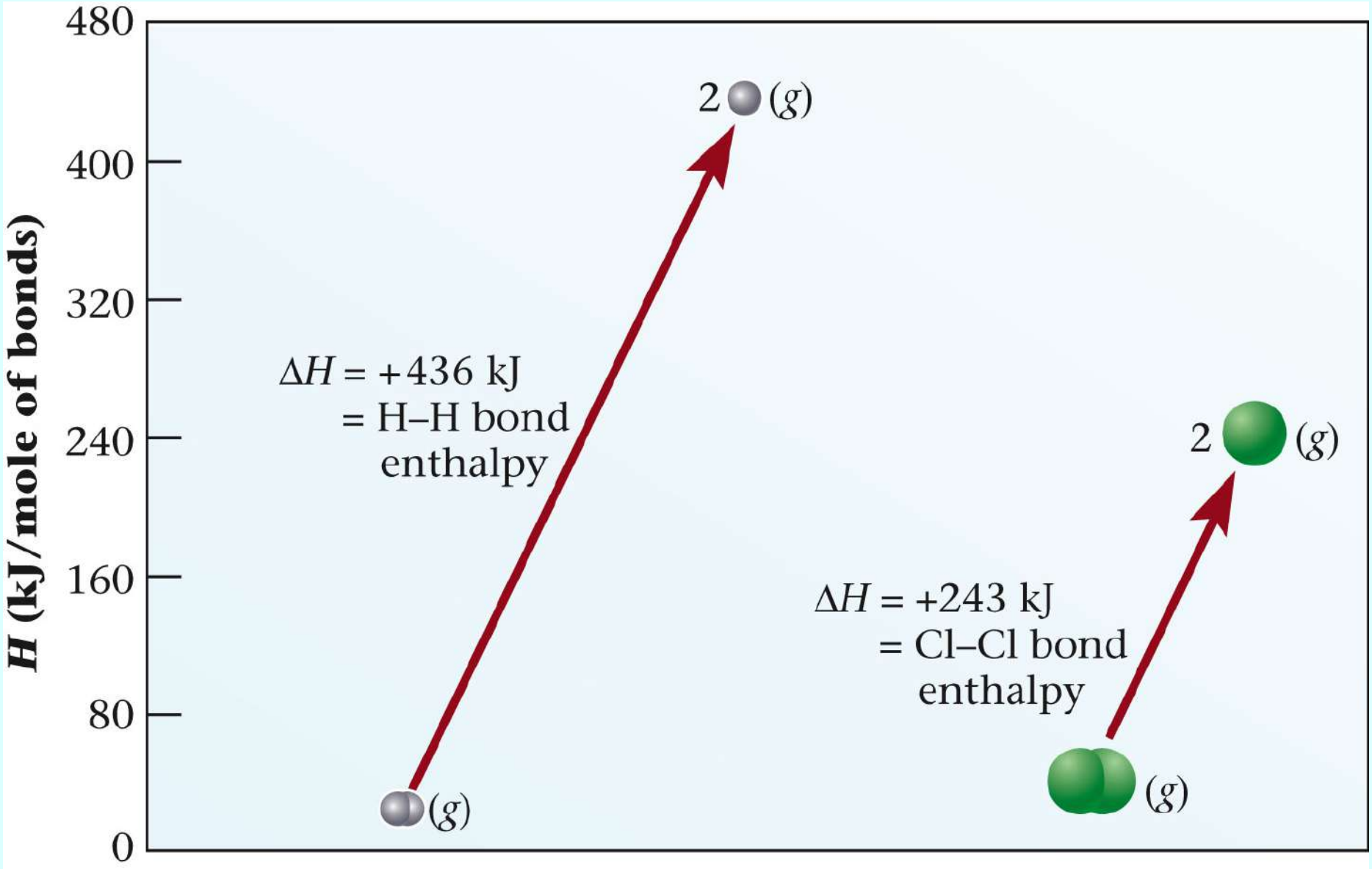
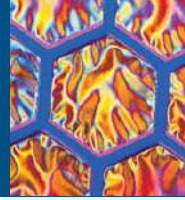


Figure 8.9


480
400
320
240
160
80
0
H (kJ/mole of bonds)
2 (g)
ΔH = +436 kJ
= H–H bond
enthalpy
(g)
2
(g)
ΔH = +243 kJ
= Cl–Cl bond
enthalpy
(g)

Notes on Bond Enthalpy



- ***The bond enthalpy is always a positive quantity***
  - Energy is required to break a chemical bond
- When a chemical bond forms, the sign of the enthalpy change is negative
- For ***endothermic*** reactions
  - The ***bonds are stronger in the reactants than in the products,*** and/or
  - There are ***more bonds in the reactants than in the products***

Table 8.4

TABLE 8.4 Bond Enthalpies

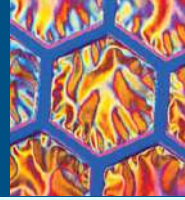
Single Bond Enthalpy (kJ/mol)

	H	C	N	O	S	F	Cl	Br	I
H	436	414	389	464	339	565	431	368	297
C		347	293	351	259	485	331	276	218
N			159	222	—	272	201	243	—
O				138	—	184	205	201	201
S					226	285	255	213	—
F						153	255	255	277
Cl							243	218	209
Br								193	180
I									151

Multiple Bond Enthalpy (kJ/mol)

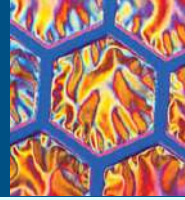
C=C	612	N=N	418	C≡C	820
C=N	615	N=O	607	C≡N	890
C=O	715	O=O	498	C≡O	1075
C=S	477	S=O	498	N≡N	941

Bond Enthalpies and Multiple Bonds



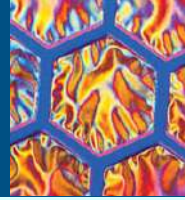
- As the order of a bond increases from single to double to triple, the bond enthalpy also increases
  - C-C single, 347 kJ/mol
  - C-C double, 612 kJ/mol
  - C-C triple, 820 kJ/mol
- Whenever a bond involves two different atoms, the enthalpy is an approximation, because it must be averaged over two different species
  - H-O-H (g) → H (g) + OH (g)ΔH = +499 J
  - H-O (g) → H (g) + O (g)ΔH = +428 kJ

Bond Enthalpy vs. Enthalpy of Formation



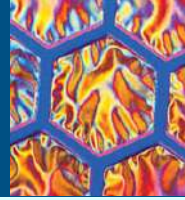
- When ΔH is calculated, we can use enthalpies of formation or bond enthalpies
  - Using enthalpy of formation, results are accurate to 0.1 kJ
  - Using bond enthalpies, results can produce an error of 10 kJ or more
- Use enthalpies of formation to calculate ΔH wherever possible

The First Law of Thermodynamics



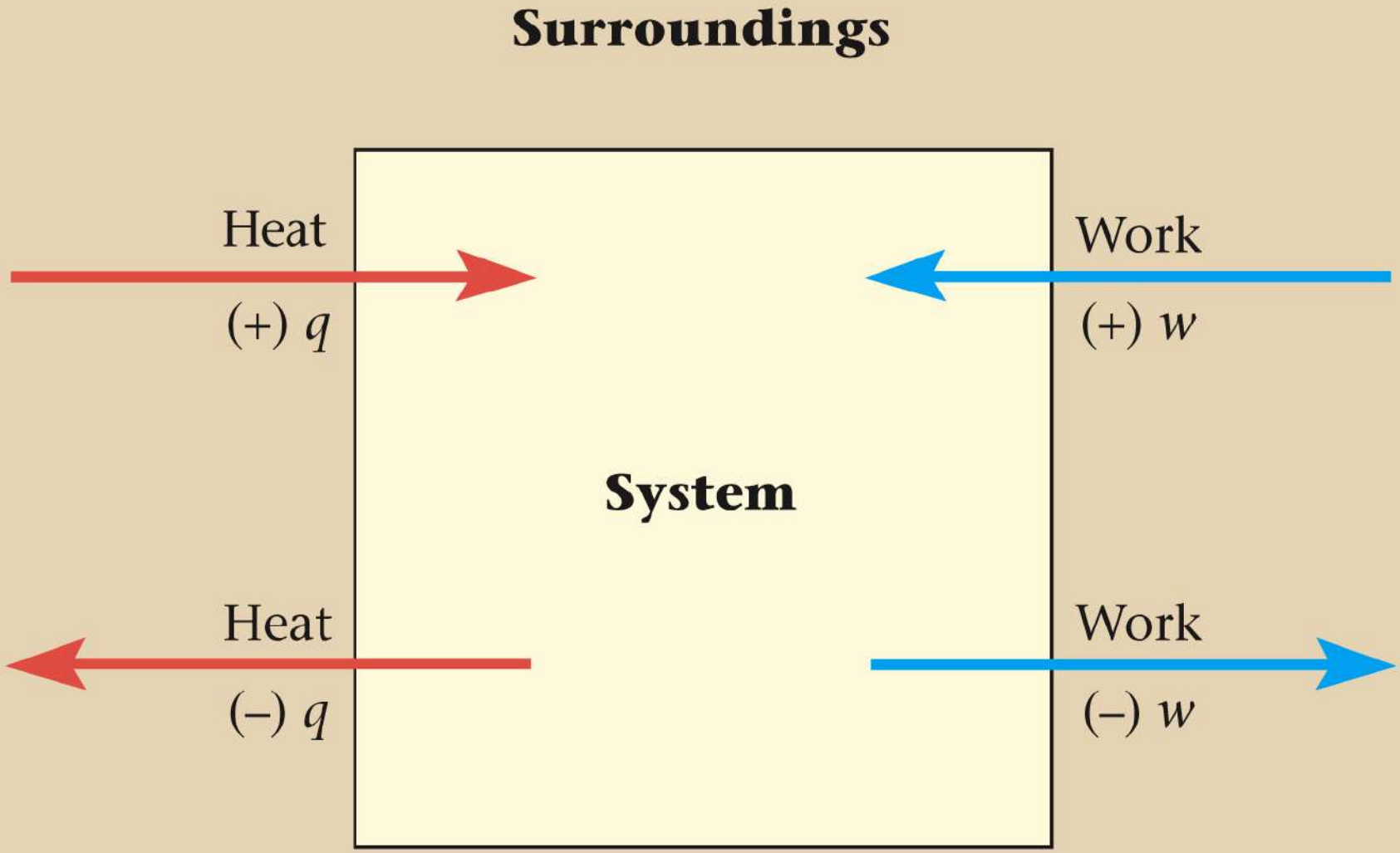
- Thermodynamics
  - Deals with all kinds of energy effects in all kinds of processes
  - Two types of energy
    - Heat (q)
    - Work (w)
  - The Law of Conservation of Energy
    - $\Delta E_{system} = - \Delta E_{surroundings}$
  - The First Law
    - $\Delta E = q + w$
    - The ***total change in energy*** is equal to the ***sum of the heat and work transferred*** between the system and the surroundings

Conventions



- q and w are positive
  - When the heat or work enters the system from the surroundings
- q and w are negative
  - When the heat or work leaves the system for the surroundings

Figure 8.10



Example 8.9

EXAMPLE 8.9

Calculate ΔE of a gas for a process in which the gas

(a) absorbs 20 J of heat and does 12 J of work by expanding.

(b) evolves 30 J of heat and has 52 J of work done on it as it contracts.

ANALYSIS

Information given:	(a) heat absorbed (20 kJ), work done by the system (12 kJ) (b) heat evolved (30 kJ), work done on the system (52 kJ)
Asked for:	ΔE for both (a) and (b)

continued

Example 8.9 (Cont'd)

STRATEGY

1. Decide on the signs for work (w) and heat (q).

   Recall that quantites are positive when they enter the system (absorbed, work done on the system) and negative when they leave the system (evolved, work done by the system).

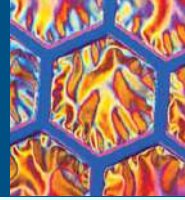
2. Substitute into Equation 8.5.

   $$\Delta E = w + q$$

SOLUTION

(a) Signs for w and q	w is negative (work is done by the system) q is positive (heat is absorbed)
ΔE	$\Delta E = q + w = 20\ \text{J} + (-12\ \text{J}) = 8\ \text{J}$
(b) Signs for w and q	w is positive (work is done on the system; enters the system) q is negative (heat is evolved)
ΔE	$\Delta E = q + w = -30\ \text{J} + 52\ \text{J} = 22\ \text{J}$

Heat

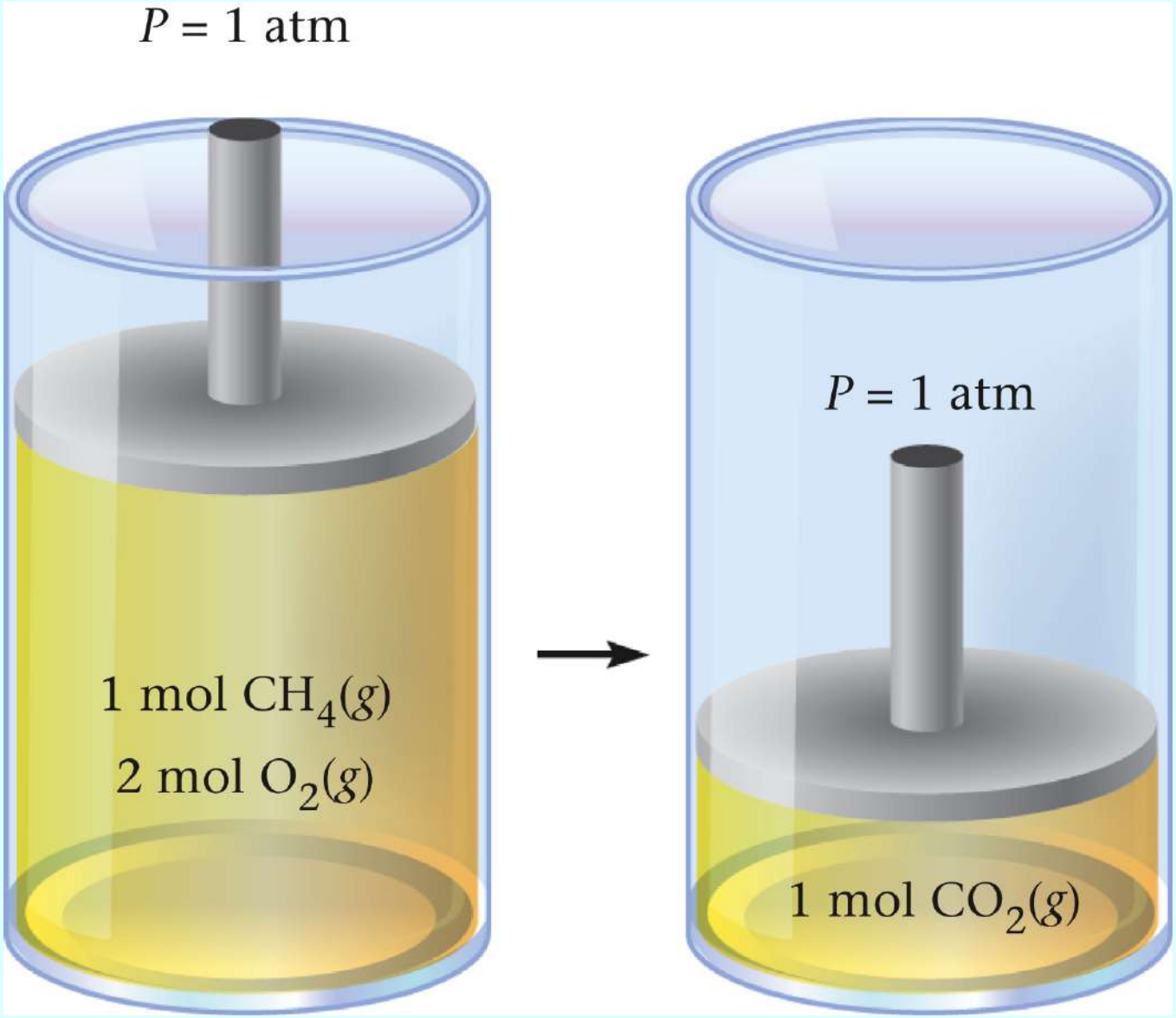


- Ordinarily, when a chemical reaction is carried out in the laboratory, energy is evolved as heat
  - CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (ℓ) ΔE = -885 kJ
  - The combustion of methane in a Bunsen burner produces nearly 885 kJ of heat per mol
  - The decrease in volume that takes place is a 1% work effect

Work

- In an internal combustion engine, a significant fraction of the energy of combustion is converted to useful work
  - The expansion of the combustion gases produces a volume and a pressure change
  - The system does work on its surroundings
    - Propels the car forward
    - Overcomes friction
    - Charges battery
  - Like ΔH, ***ΔE is a state variable***
    - ***q and w are not state variables***

Figure 8.11 – Pressure-Volume Work



ΔH and ΔE

- Constant pressure
  - Coffee-cup calorimeter
  - $\Delta H = q_p$
- Constant volume
  - In a bomb calorimeter, there is no pressure-volume work done
  - $\Delta E = q_v$

ΔH and ΔE, (Cont'd)

- $H = E + PV$
- $\Delta H = \Delta E + P\Delta V$
  - The PV product is important only where gases are involved; it is negligible when only liquids or solids are involved
- $\Delta H = \Delta E + \Delta n_g RT$
  - Δn_g is the change in the number of moles of gas as the reaction proceeds

Example 8.10

EXAMPLE 8.10

Calculate ΔH and ΔE at 25°C for the reaction that takes place when an oxyacetylene torch is used.

$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$$

ANALYSIS

Information given:	chemical equation; T (25°C)
Information implied:	ΔH_f° from Table 8.3 moles of products and reactants R with energy units
Asked for:	ΔH and ΔE

STRATEGY

1. Use Table 8.3 to calculate ΔH for the reaction. Remember ΔH_f° for $O_2(g)$ is zero.
2. Find Δn: $\Delta n = n_{products} - n_{reactants}$
3. Recall that R is 8.31 J/mol · K when energy units are involved (Table 5.1).
4. Substitute into Equation 8.6 to find ΔE.

$$\Delta H = \Delta E + \Delta n_g RT$$

SOLUTION

1. ΔH

$$\Delta H = 2\Delta H_f^\circ\, CO_2(g) + \Delta H_f^\circ\, H_2O(g) - \Delta H_f^\circ\, C_2H_2(g)$$
$$= 2\,(-393.5\text{ kJ}) + (-241.8\text{ kJ}) - (226.7\text{ kJ}) = -1255.5\text{ kJ}$$

2. Δn_g

$$(2\text{ mol } CO_2 + 1\text{ mol } H_2O) - (1\text{ mol } C_2H_2 + \tfrac{5}{2}\text{ mol } O_2) = -\tfrac{1}{2}\text{ mol}$$

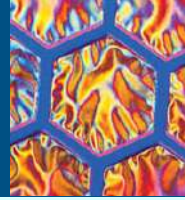
3. ΔE

$$\Delta H = \Delta E + \Delta n_g RT$$
$$1255.5\text{ kJ} = \Delta E - (-0.5\text{ mol})\left(8.31 \times 10^{-3}\,\frac{\text{kJ}}{\text{mol} \cdot \text{K}}\right)(298\text{ K})$$
$$\Delta E = -1255.5\text{ kJ} + 1.24\text{ kJ} = -1254.3\text{ kJ}$$

END POINT

Note that in this case ΔH and ΔE differ from one another only by 1.2 kJ (about 0.1%), a very small difference indeed.

Key Concepts



1. Relate heat flow to specific heat, m and Δt
2. Calculate q for a reaction from calorimetric data.
3. Apply the rules of thermochemistry
4. Apply Hess's law to calculate ΔH
5. Relate ΔH° to the enthalpies of formation
6. Relate ΔE, q and w
7. Relate ΔH and ΔE