Thermochemistry

Chapter 6

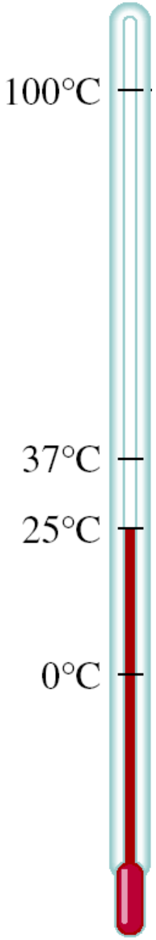
Energy Changes in Chemical Reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.

Temperature is a measure of the **thermal energy**.

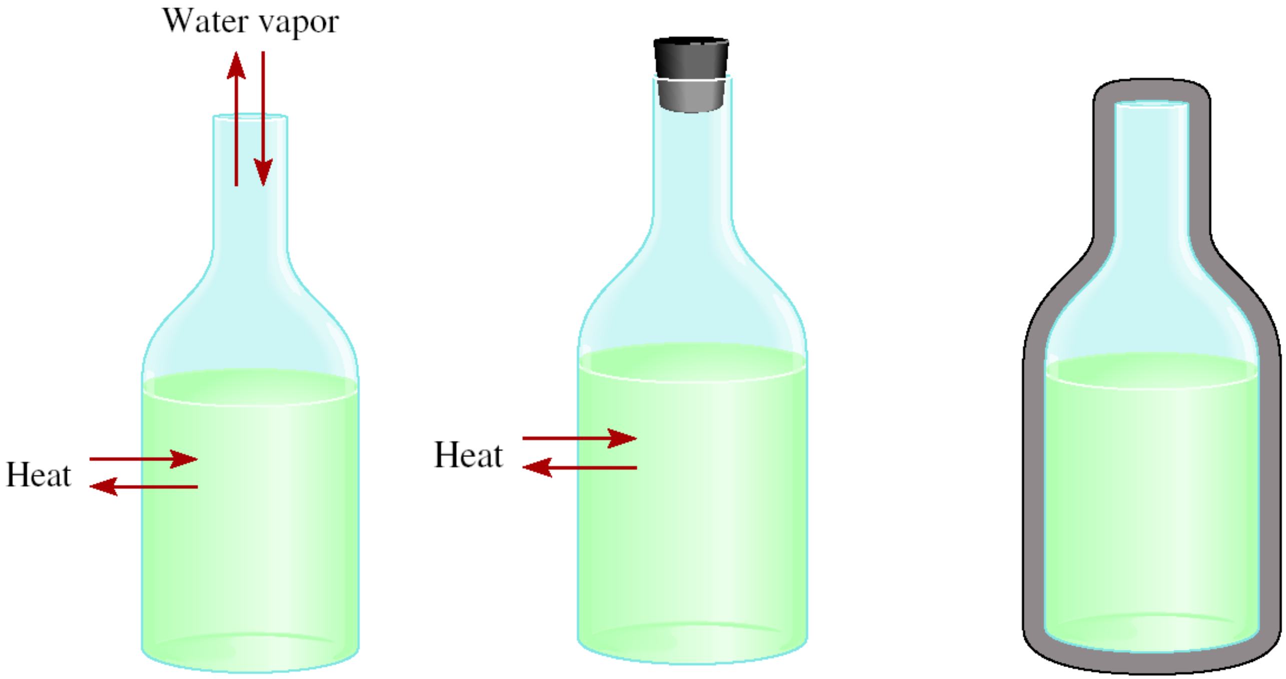
Temperature $\cancel{=}$ Thermal Energy

Thermochemistry is the study of heat change in chemical reactions.



The ***system*** is the specific part of the universe that is of interest in the study.

The surroundings are the rest of the universe outside the system.



	open	closed	isolated
Exchange:	mass & energy	energy	nothing

Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l) + \text{energy}$$

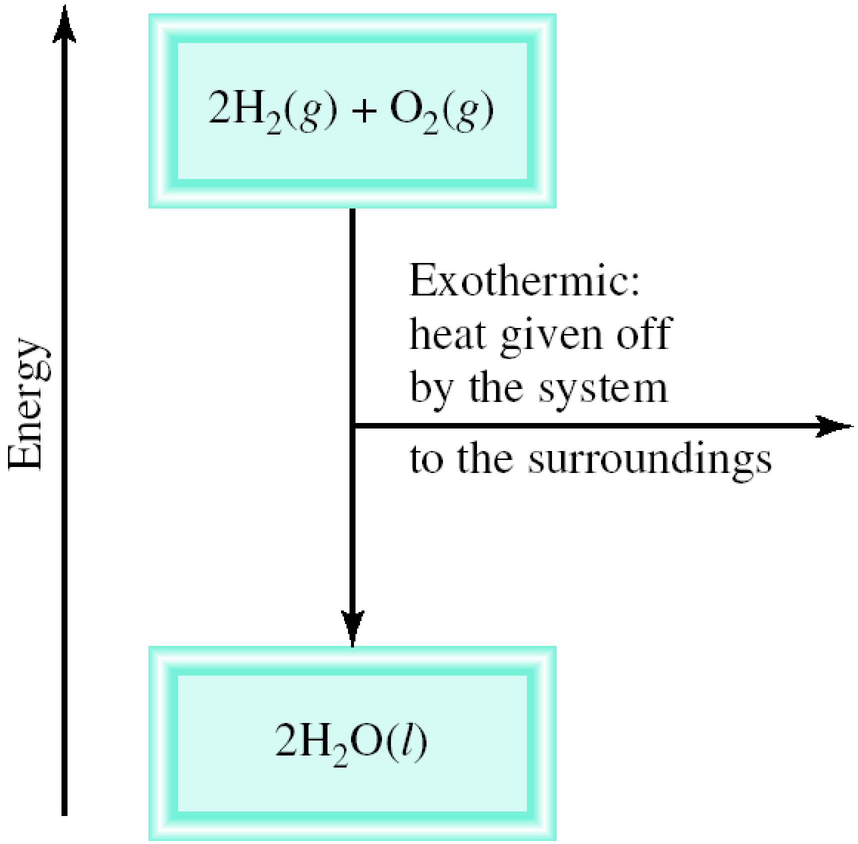
$$H_2O\ (g) \longrightarrow H_2O\ (l) + \text{energy}$$

Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

$$\text{energy} + 2HgO\ (s) \longrightarrow 2Hg\ (l) + O_2\ (g)$$

$$\text{energy} + H_2O\ (s) \longrightarrow H_2O\ (l)$$

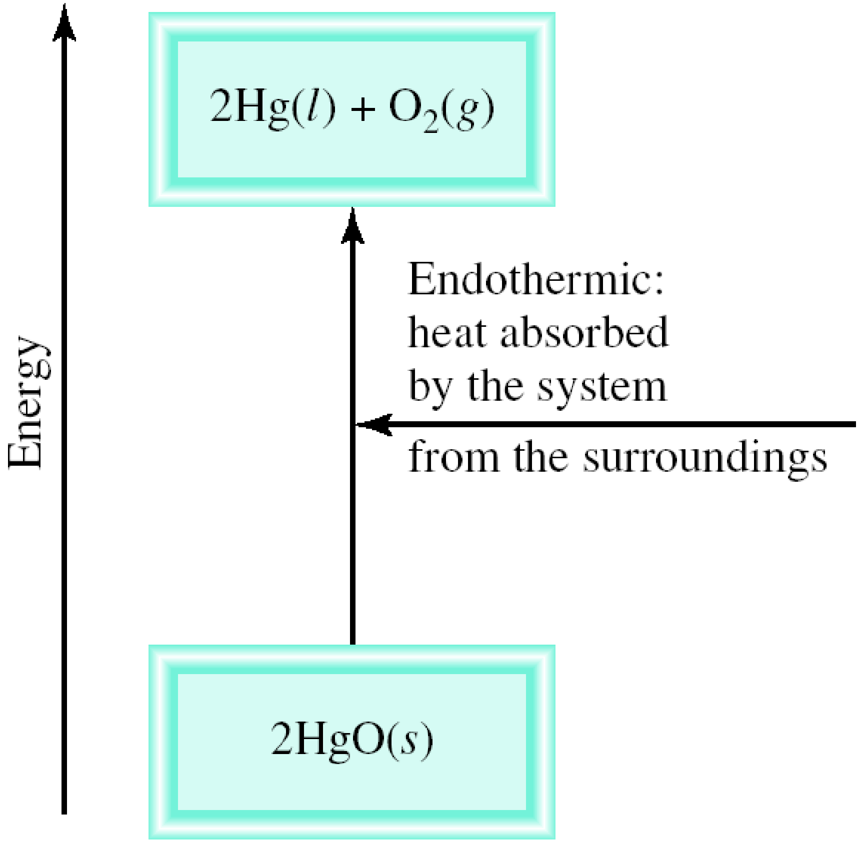
Schematic of Exothermic and Endothermic Processes



$2H_2(g) + O_2(g)$

Exothermic:
heat given off
by the system
to the surroundings

$2H_2O(l)$



$2Hg(l) + O_2(g)$

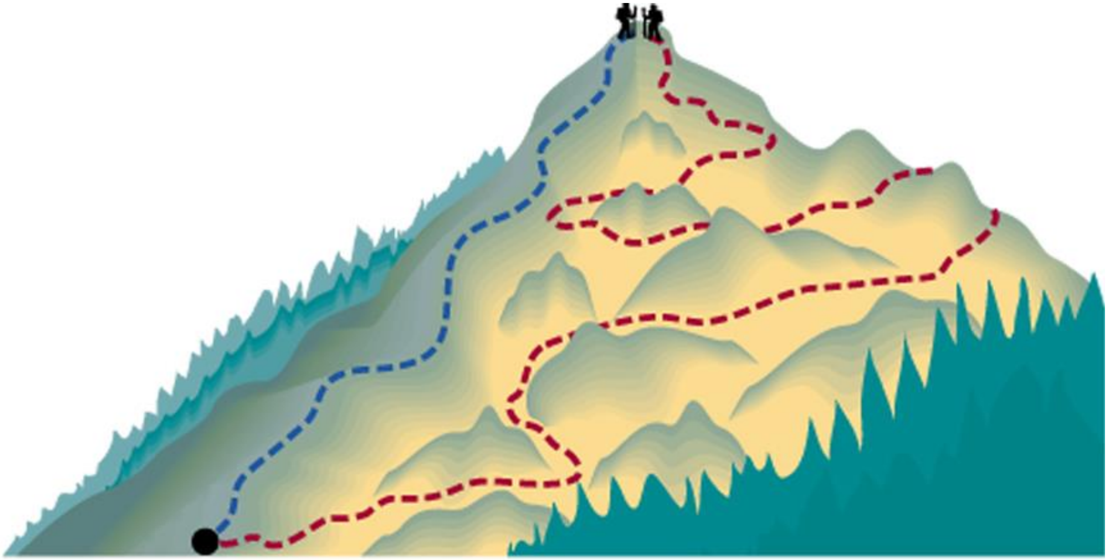
Endothermic:
heat absorbed
by the system
from the surroundings

$2HgO(s)$

Thermodynamics is the scientific study of the interconversion of heat and other kinds of energy.

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, pressure, volume, temperature



$$\Delta E = E_{final} - E_{initial}$$

$$\Delta P = P_{final} - P_{initial}$$

$$\Delta V = V_{final} - V_{initial}$$

$$\Delta T = T_{final} - T_{initial}$$

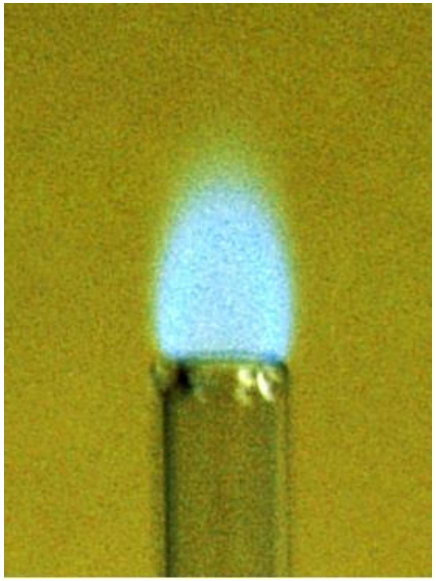
Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.

First law of thermodynamics – energy can be converted from one form to another but cannot be created or destroyed.

$$\Delta E_{system} + \Delta E_{surroundings} = 0$$

or

$$\Delta E_{system} = -\Delta E_{surroundings}$$



$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

Exothermic chemical reaction!

Chemical energy **lost** by combustion = Energy **gained** by the surroundings

system　　　　　　　　　　　　　　　surroundings

Another form of the ***first law*** for ΔE_{system}

$\Delta E = q + w$

ΔE is the change in internal energy of a system

q is the heat exchange between the system and the surroundings

w is the work done on (or by) the system

$w = -P\Delta V$ when a gas expands against a constant external pressure

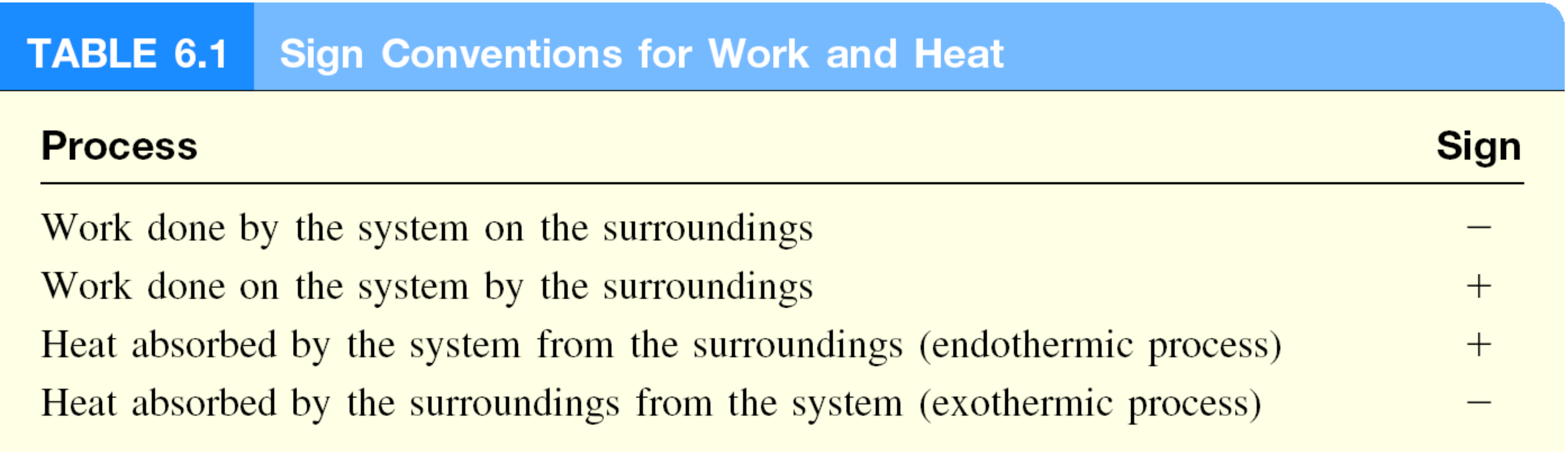


TABLE 6.1 Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	−
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	−

Work Done On the System

$w = F\ x\ d$

$\Delta V > 0$

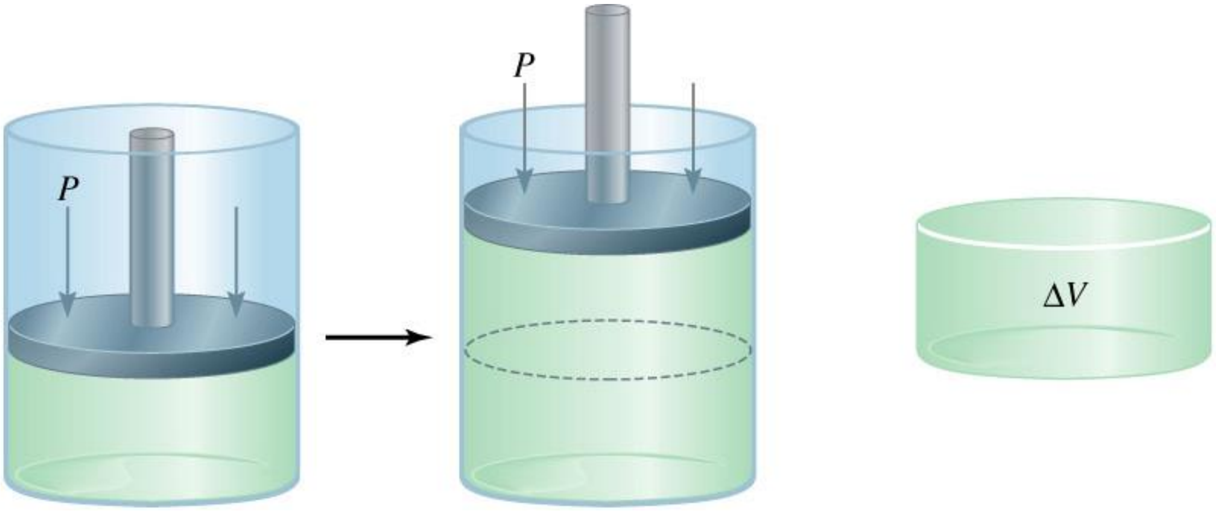
$w = -P\Delta V$

$-P\Delta V < 0$

$P\ x\ V = \frac{F}{d^2}\ x\ d^3 = F\ x\ d = w$

$w_{sys} < 0$

Work is not a state function.



$\Delta w \cancel{=} w_{final} - w_{initial}$

initial

final

The units for work done by or on a gas are liters atmospheres.

1 L . atm = 101.3 J

A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands (a) against a vacuum and (b) against a constant pressure of 3.7 atm?

$$w = -P\Delta V$$

(a) $\Delta V = 5.4\ \text{L} - 1.6\ \text{L} = 3.8\ \text{L}$ $\quad P = 0\ \text{atm}$

$$W = -0\ \text{atm} \times 3.8\ \text{L} = 0\ \text{L•atm} = 0\ \text{joules}$$

(b) $\Delta V = 5.4\ \text{L} - 1.6\ \text{L} = 3.8\ \text{L}$ $\quad P = 3.7\ \text{atm}$

$$w = -3.7\ \text{atm} \times 3.8\ \text{L} = -14.1\ \text{L•atm}$$

$$w = -14.1\ \cancel{\text{L•atm}} \times \frac{101.3\ \text{J}}{1\cancel{\text{L•atm}}} = -1430\ \text{J}$$

Enthalpy and the First Law of Thermodynamics

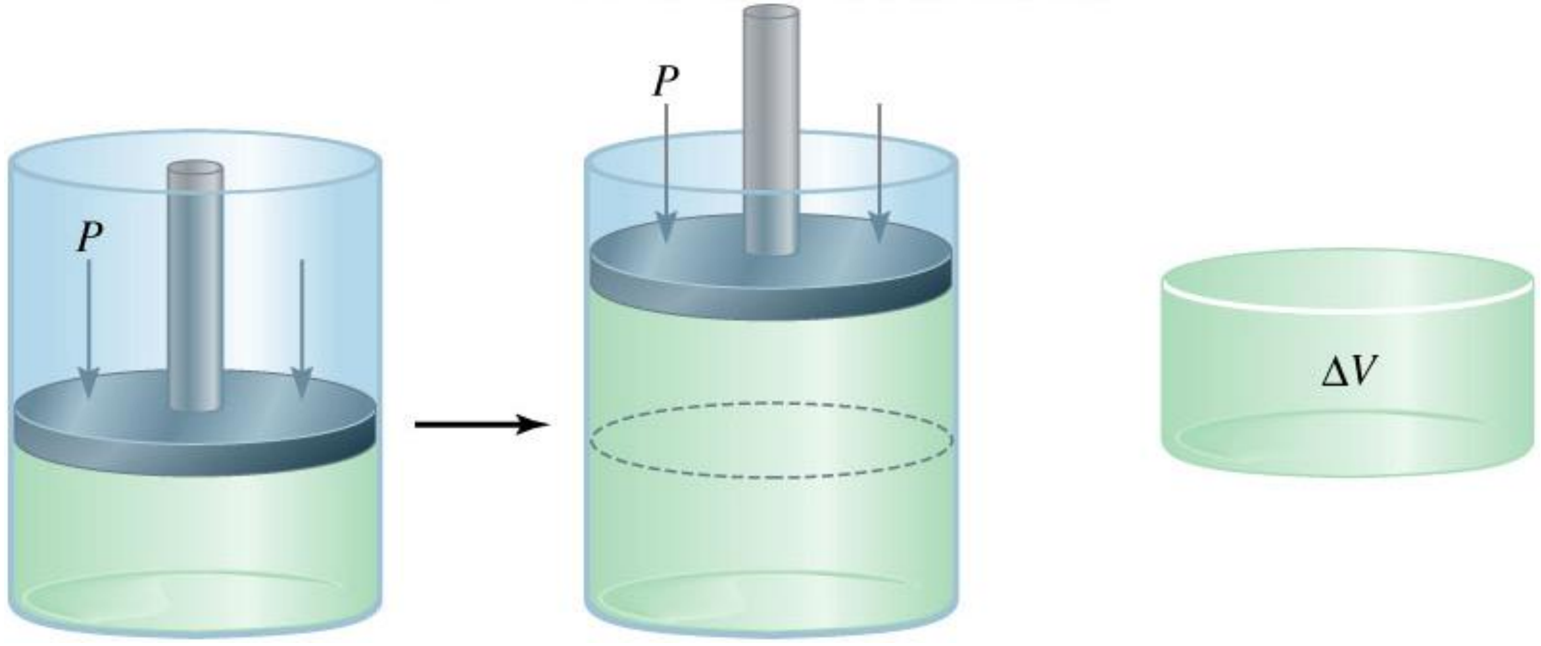
$$\Delta E = q + w$$

At constant pressure:

$q = \Delta H$ and $w = -P\Delta V$

$$\Delta E = \Delta H - P\Delta V$$

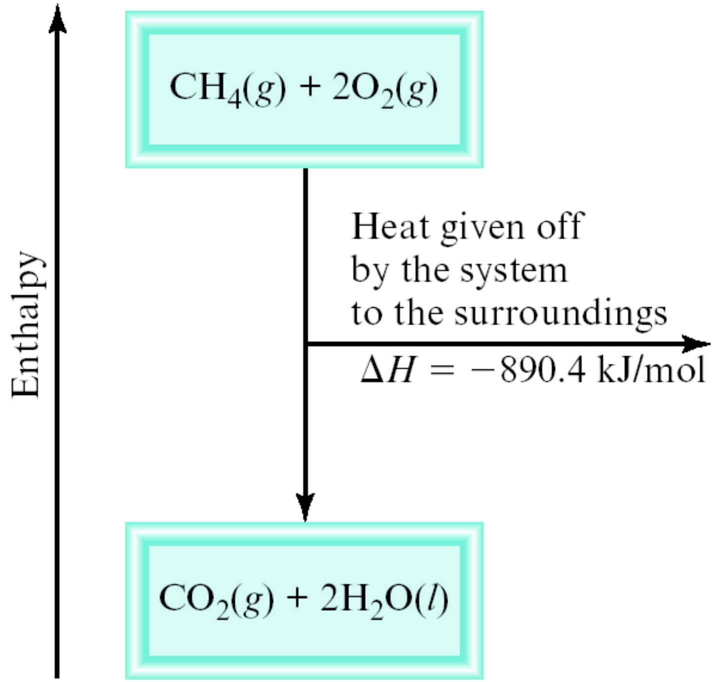
$$\Delta H = \Delta E + P\Delta V$$

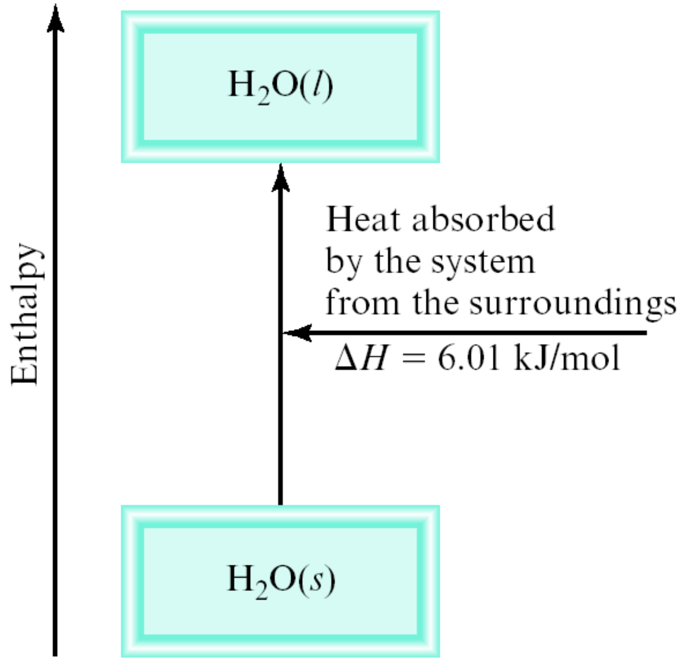


Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

$$\Delta H = H\,(\text{products}) - H\,(\text{reactants})$$

$\Delta H =$ heat given off or absorbed during a reaction **at constant pressure**

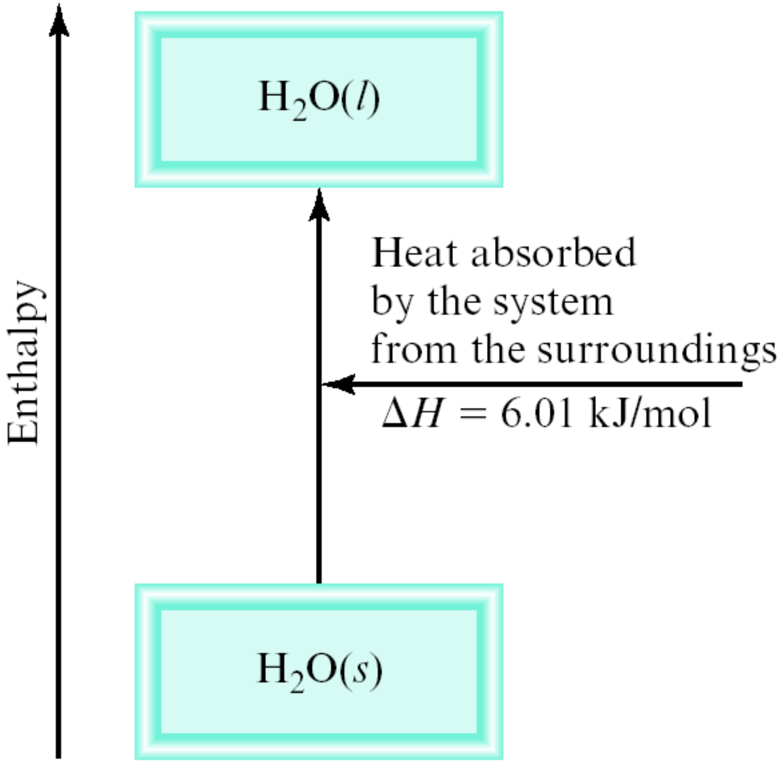




$H_{\text{products}} < H_{\text{reactants}}$
$\Delta H < 0$

$H_{\text{products}} > H_{\text{reactants}}$
$\Delta H > 0$

Thermochemical Equations



Is ΔH negative or positive?

System absorbs heat

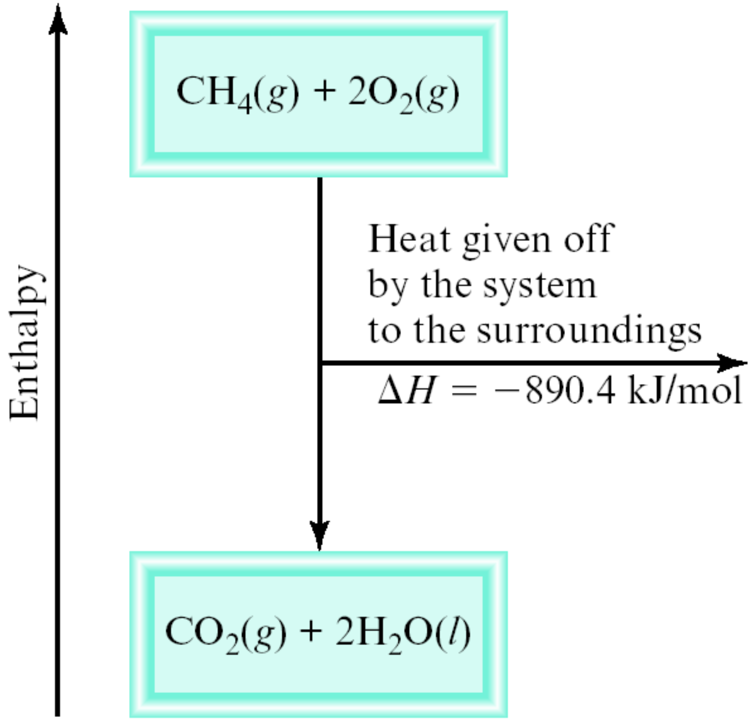
Endothermic

$\Delta H > 0$

6.01 kJ are absorbed for every 1 mole of ice that melts at 0^0C and 1 atm.

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \boxed{\Delta H = 6.01 \text{ kJ/mol}}$$

Thermochemical Equations



Is ΔH negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

890.4 kJ are released for every 1 mole of methane that is combusted at 25^0C and 1 atm.

$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l) \quad \boxed{\Delta H = -890.4 \text{ kJ/mol}}$$

Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance

$$H_2O\ (s) \longrightarrow H_2O\ (l) \qquad \Delta H = 6.01\ \text{kJ/mol}$$

- If you reverse a reaction, the sign of ΔH changes

$$H_2O\ (l) \longrightarrow H_2O\ (s) \qquad \Delta H = -6.01\ \text{kJ/mol}$$

- If you multiply both sides of the equation by a factor *n*, then ΔH must change by the same factor *n*.

$$2H_2O\ (s) \longrightarrow 2H_2O\ (l) \qquad \Delta H = 2 \times 6.01 = 12.0\ \text{kJ}$$

Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.

$$H_2O\,(s) \longrightarrow H_2O\,(l) \qquad \Delta H = 6.01\ \text{kJ/mol}$$

$$H_2O\,(l) \longrightarrow H_2O\,(g) \qquad \Delta H = 44.0\ \text{kJ/mol}$$

How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?

$$P_4\,(s) + 5O_2\,(g) \longrightarrow P_4O_{10}\,(s) \qquad \Delta H = -3013\ \text{kJ/mol}$$

$$266\ \cancel{\text{g}\ P_4} \times \frac{1\ \cancel{\text{mol}}\ P_4}{123.9\ \cancel{\text{g}\ P_4}} \times \frac{3013\ \text{kJ}}{1\ \cancel{\text{mol}\ P_4}} = 6470\ \text{kJ}$$

A Comparison of ΔH and ΔE

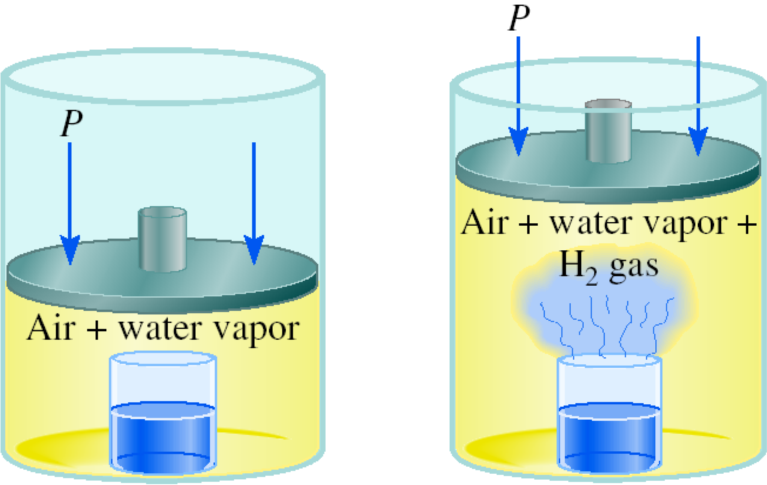
$2Na\ (s) + 2H_2O\ (l) \longrightarrow 2NaOH\ (aq) + H_2\ (g)\quad \Delta H = -367.5\ kJ/mol$

$\Delta E = \Delta H - P\Delta V$ At 25 ^{o}C, 1 mole H_2 = 24.5 L at 1 atm

$P\Delta V = 1\ atm \times 24.5\ L = 2.5\ kJ$

$\Delta E = -367.5\ kJ/mol - 2.5\ kJ/mol = -370.0\ kJ/mol$

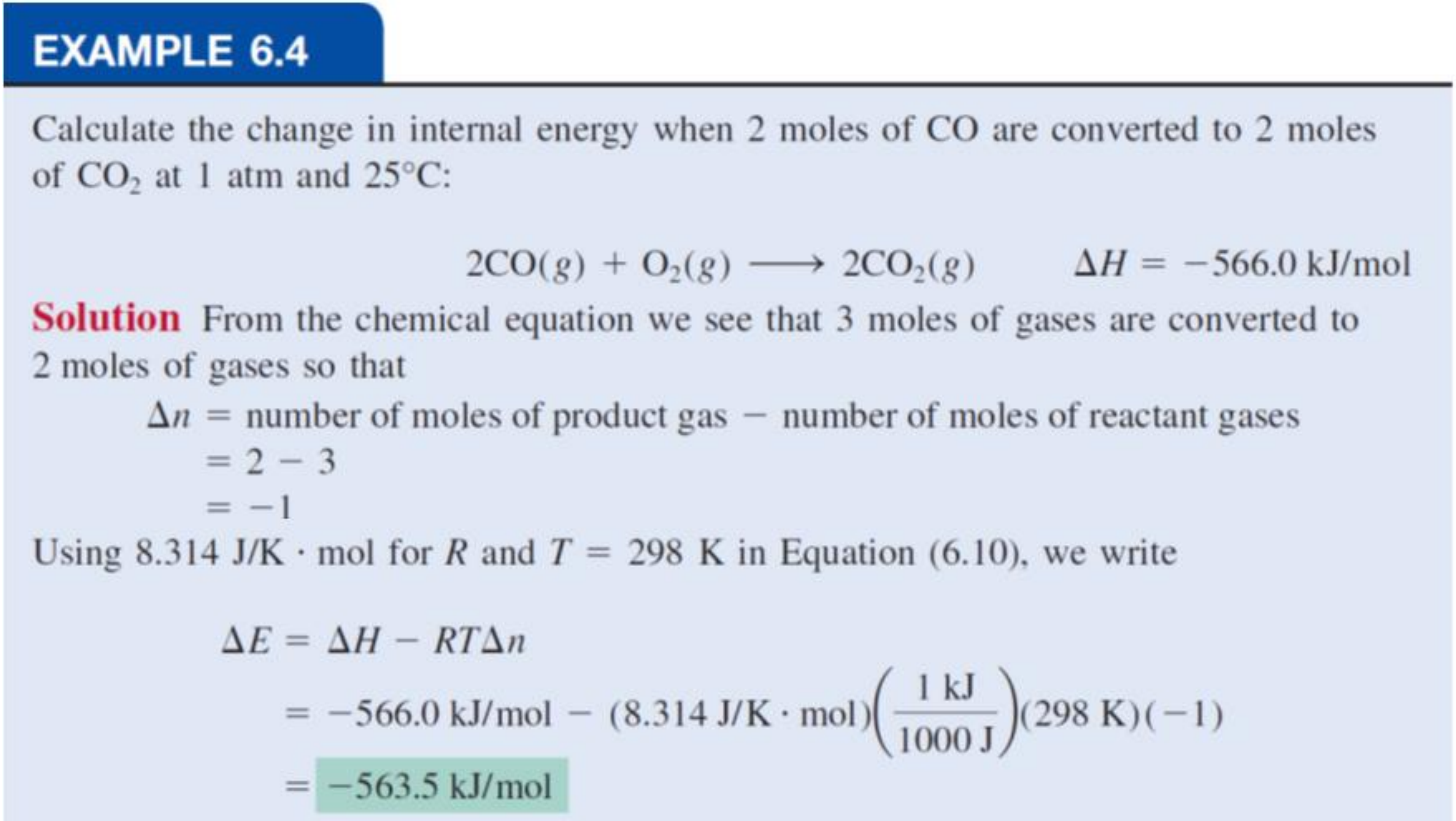
The reason ΔH is smaller than ΔE in magnitude is that some of the internal energy released is used to do gas expansion work, so less heat is evolved.



A Comparison of ΔH and ΔE

To calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature

$$\begin{aligned} \Delta E &= \Delta H - \Delta(PV) \\ &= \Delta H - \Delta(nRT) \\ &= \Delta H - RT\Delta n \end{aligned}$$



EXAMPLE 6.4

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO_2 at 1 atm and 25°C:

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

Solution From the chemical equation we see that 3 moles of gases are converted to 2 moles of gases so that

$$\begin{aligned}\Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases}\\ &= 2 - 3\\ &= -1\end{aligned}$$

Using 8.314 J/K · mol for R and $T = 298$ K in Equation (6.10), we write

$$\begin{aligned}\Delta E &= \Delta H - RT\Delta n\\ &= -566.0 \text{ kJ/mol} - (8.314 \text{ J/K} \cdot \text{mol})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(298 \text{ K})(-1)\\ &= -563.5 \text{ kJ/mol}\end{aligned}$$

The ***specific heat*** (***s***) of a substance is the amount of heat (*q*) required to raise the temperature of **one gram** of the substance by **one degree** Celsius.

The ***heat capacity*** (***C***) of a substance is the amount of heat (*q*) required to raise the temperature of **a given quantity** (*m*) of the substance by **one degree** Celsius.

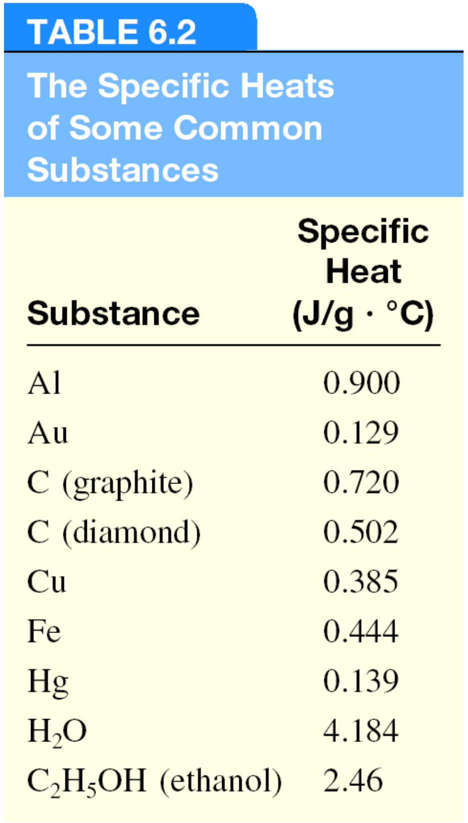


TABLE 6.2

The Specific Heats of Some Common Substances

Substance	Specific Heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184
C_2H_5OH (ethanol)	2.46

$$C = m \times s$$

<u>Heat (*q*) absorbed or released:</u>

$$q = m \times s \times \Delta t$$

$$q = C \times \Delta t$$

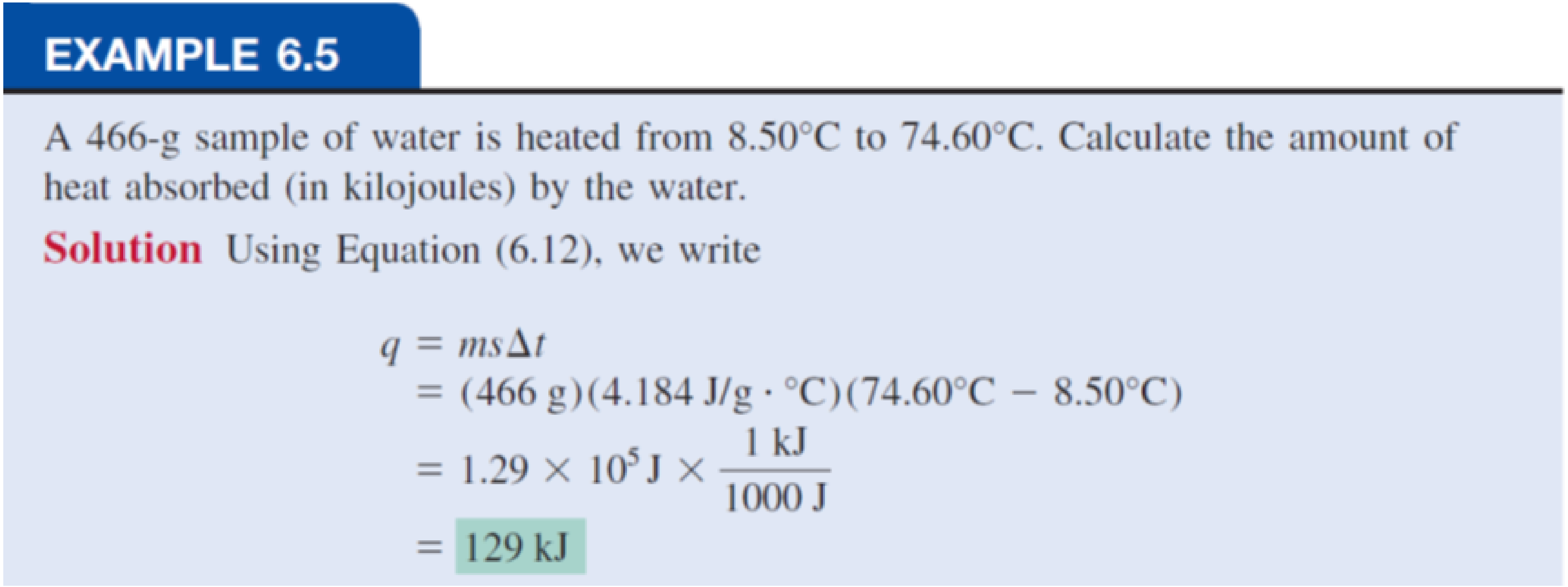
$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

How much heat is given off when an 869 g iron bar cools from 94°C to 5°C?

s of Fe = 0.444 J/g • °C

$\Delta t = t_{\text{final}} - t_{\text{initial}} = 5^{\circ}\text{C} - 94^{\circ}\text{C} = -89^{\circ}\text{C}$

$q = ms\Delta t = 869\ \cancel{\text{g}} \times 0.444\ \text{J}/\cancel{\text{g}} \bullet {}^{\circ}\cancel{\text{C}} \times -89^{\circ}\cancel{\text{C}} = -34{,}000\ \text{J}$



EXAMPLE 6.5

A 466-g sample of water is heated from 8.50°C to 74.60°C. Calculate the amount of heat absorbed (in kilojoules) by the water.

Solution Using Equation (6.12), we write

$$\begin{aligned} q &= ms\Delta t \\ &= (466\ \text{g})(4.184\ \text{J/g}\cdot{}^\circ\text{C})(74.60^\circ\text{C} - 8.50^\circ\text{C}) \\ &= 1.29 \times 10^5\ \text{J} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \\ &= \boxed{129\ \text{kJ}} \end{aligned}$$

Standard Enthalpy of Formation and Reaction

Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?

Establish an arbitrary scale with the **standard enthalpy of formation** (ΔH_f^0) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH_f^0) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.

The standard enthalpy of formation of any element in its most stable form is zero.

ΔH_f^0 (C, graphite) = 0

ΔH_f^0 (O_2) = 0

ΔH_f^0 (C, diamond) = 1.90 kJ/mol

ΔH_f^0 (O_3) = 142 kJ/mol

TABLE 6.4 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH°_f(kJ/mol)	Substance	ΔH°_f(kJ/mol)
$Ag(s)$	0	$H_2O_2(l)$	−187.6
$AgCl(s)$	−127.0	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	$HI(g)$	25.9
$Br_2(l)$	0	$Mg(s)$	0
$HBr(g)$	−36.2	$MgO(s)$	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
$CO(g)$	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	$NO(g)$	90.4
$Ca(s)$	0	$NO_2(g)$	33.85
$CaO(s)$	−635.6	$N_2O(g)$	81.56
$CaCO_3(s)$	−1206.9	$N_2O_4(g)$	9.66
$Cl_2(g)$	0	$O(g)$	249.4
$HCl(g)$	−92.3	$O_2(g)$	0
$Cu(s)$	0	$O_3(g)$	142.2
$CuO(s)$	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
$HF(g)$	−271.6	$SO_2(g)$	−296.1
$H(g)$	218.2	$SO_3(g)$	−395.2
$H_2(g)$	0	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	$Zn(s)$	0
$H_2O(l)$	−285.8	$ZnO(s)$	−348.0

The **standard enthalpy of reaction** (ΔH^0_{rxn}) is the enthalpy of a reaction carried out at 1 atm.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H^0_{rxn} = [c\Delta H^0_f(C) + d\Delta H^0_f(D)] - [a\Delta H^0_f(A) + b\Delta H^0_f(B)]$$

$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f(\text{products}) - \Sigma m\Delta H^0_f(\text{reactants})$$

Hess's Law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)

The direct Method

- Suppose we want to know the enthalpy of formation of carbon dioxide.
- We must measure the enthalpy of the reaction when carbon (graphite) and molecular oxygen in their standard states are converted to carbon dioxide in its standard state:

$$\mathrm{C(graphite)} + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -393.5\ \mathrm{kJ/mol}$$

$$\Delta H^0_{rxn} = \Sigma n \Delta H^0_f\ \text{(products)} - \Sigma m \Delta H^0_f\ \text{(reactants)}$$

$$\begin{aligned}\Delta H^\circ_{\mathrm{rxn}} &= \Delta H^\circ_{\mathrm{f}}(\mathrm{CO_2}, g) - [\Delta H^\circ_{\mathrm{f}}(\mathrm{C, graphite}) + \Delta H^\circ_{\mathrm{f}}(\mathrm{O_2}, g)] \\ &= -393.5\ \mathrm{kJ/mol}\end{aligned}$$

$$\Delta H^\circ_{\mathrm{rxn}} = \Delta H^\circ_{\mathrm{f}}(\mathrm{CO_2}, g) = -393.5\ \mathrm{kJ/mol}$$

or

$$\Delta H^\circ_{\mathrm{f}}(\mathrm{CO_2}, g) = -393.5\ \mathrm{kJ/mol}$$

Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.

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

$$\Delta H^0_{rxn} = \Sigma\, n\Delta H^0_f\,(\text{products}) - \Sigma\, m\Delta H^0_f\,(\text{reactants})$$

$$\Delta H^0_{rxn} = [12\Delta H^0_f\,(CO_2) + 6\Delta H^0_f\,(H_2O)] - [\,2\Delta H^0_f\,(C_6H_6)]$$

$$\Delta H^0_{rxn} = [\,12\text{x}{-393.5} + 6\text{x}{-285.8}\,] - [\,2\text{x}49.04\,] = -6338\ \text{kJ}$$

$$\frac{-6338\ \text{kJ}}{2\ \text{mol}} = -\,3169\ \text{kJ/mol}\ C_6H_6$$

The Indirect Method (Hess's Law)

- Many compounds cannot be directly synthesized from their elements.
- The reaction proceeds too slowly, or side reactions produce substances other than the desired compound.

Hess's Law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)

Let's say we are interested in the standard enthalpy of formation of carbon monoxide (CO).

$$\mathrm{C(graphite)} + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO}(g)$$

However, burning graphite also produces some carbon dioxide (CO_2), so we cannot measure the enthalpy change for CO directly.
We must employ an indirect route, based on Hess's law.
It is possible to carry out the following two separate reactions:

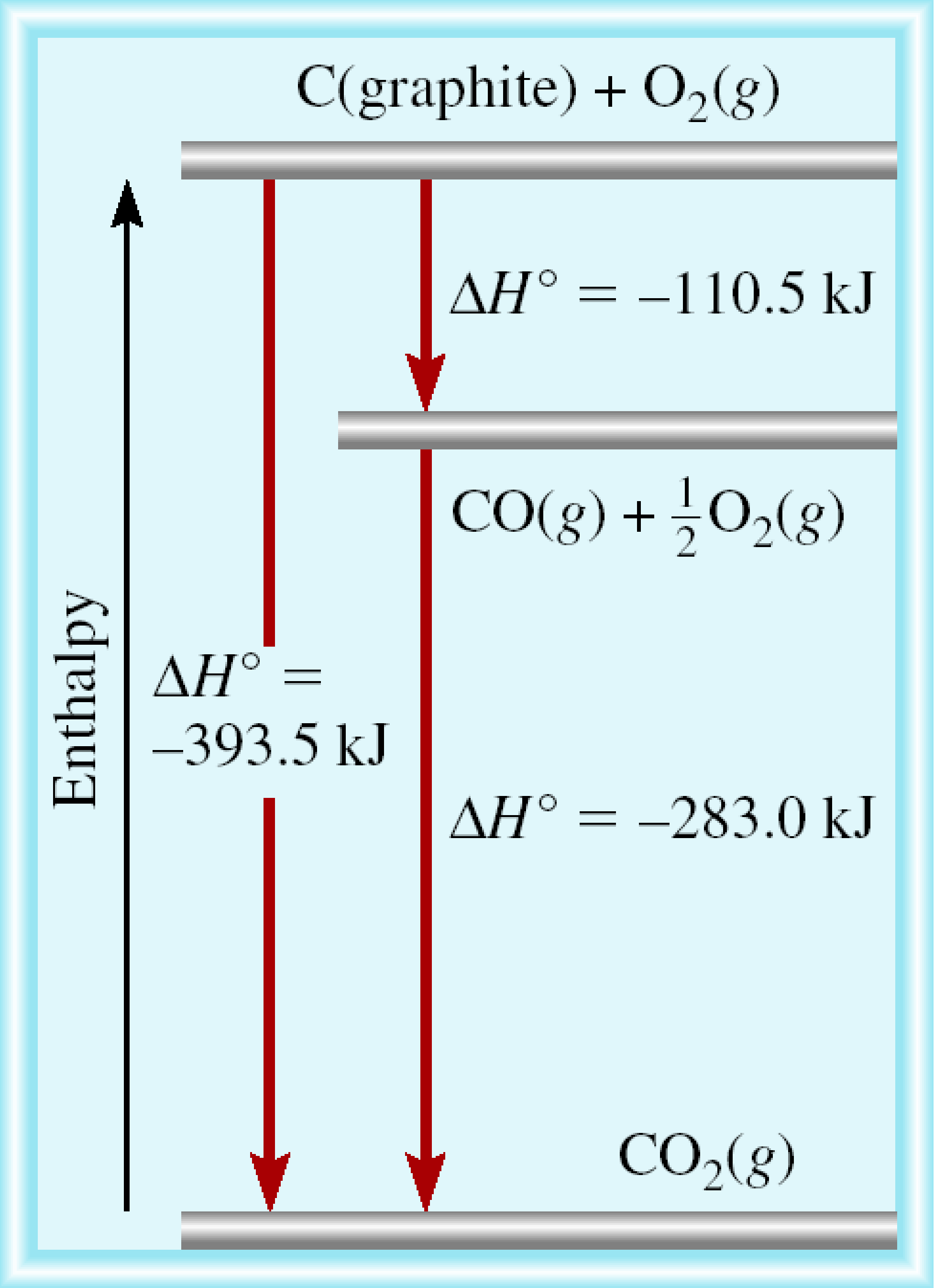
$$\begin{array}{llr}
\text{(a)} & \mathrm{C(graphite)} + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) & \Delta H^\circ_{\mathrm{rxn}} = -393.5\ \mathrm{kJ/mol} \\
\text{(b)} & \mathrm{CO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) & \Delta H^\circ_{\mathrm{rxn}} = -283.0\ \mathrm{kJ/mol}
\end{array}$$

First, we reverse Equation (b) to get

$$\begin{array}{llr}
\text{(c)} & \mathrm{CO_2}(g) \longrightarrow \mathrm{CO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) & \Delta H^\circ_{\mathrm{rxn}} = +283.0\ \mathrm{kJ/mol}
\end{array}$$

we carry out the operation (a) + (c) and obtain

$$\begin{array}{llr}
\text{(a)} & \mathrm{C(graphite)} + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) & \Delta H^\circ_{\mathrm{rxn}} = -393.5\ \mathrm{kJ/mol} \\
\text{(c)} & \mathrm{CO_2}(g) \longrightarrow \mathrm{CO}(g) + \tfrac{1}{2}\mathrm{O_2}(g) & \Delta H^\circ_{\mathrm{rxn}} = +283.0\ \mathrm{kJ/mol} \\
\hline
\text{(d)} & \mathrm{C(graphite)} + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO}(g) & \Delta H^\circ_{\mathrm{rxn}} = -110.5\ \mathrm{kJ/mol}
\end{array}$$



$$\text{C (graphite)} + 1/2\text{O}_2\ (g) \longrightarrow \text{CO}\ (g)$$

$$\text{CO}\ (g) + 1/2\text{O}_2\ (g) \longrightarrow \text{CO}_2\ (g)$$

$$\text{C (graphite)} + \text{O}_2\ (g) \longrightarrow \text{CO}_2\ (g)$$

Calculate the standard enthalpy of formation of CS_2 (*l*) given that:

$$C(\text{graphite}) + O_2\,(g) \longrightarrow CO_2\,(g) \qquad \Delta H^0_{rxn} = -393.5\ \text{kJ/mol}$$

$$S(\text{rhombic}) + O_2\,(g) \longrightarrow SO_2\,(g) \qquad \Delta H^0_{rxn} = -296.1\ \text{kJ/mol}$$

$$CS_2(l) + 3O_2\,(g) \longrightarrow CO_2\,(g) + 2SO_2\,(g) \qquad \Delta H^0_{rxn} = -1072\ \text{kJ/mol}$$

1. Write the enthalpy of formation reaction for CS_2

$$C(\text{graphite}) + 2S(\text{rhombic}) \longrightarrow CS_2\,(l)$$

2. Add the given rxns so that the result is the desired rxn.

$$C(\text{graphite}) + \cancel{O_2}\,(g) \longrightarrow \cancel{CO_2}\,(g) \qquad \Delta H^0_{rxn} = -393.5\ \text{kJ/mol}$$

$$2S(\text{rhombic}) + 2\cancel{O_2}\,(g) \longrightarrow 2\cancel{SO_2}\,(g) \qquad \Delta H^0_{rxn} = -296.1\ \text{kJ/mol} \times 2$$

$$+\ \cancel{CO_2}(g) + 2\cancel{SO_2}\,(g) \longrightarrow CS_2\,(l) + 3\cancel{O_2}\,(g) \qquad \Delta H^0_{rxn} = +1072\ \text{kJ/mol}$$

$$C(\text{graphite}) + 2S(\text{rhombic}) \longrightarrow CS_2\,(l)$$

$$\Delta H^0_{rxn} = -393.5 + (2\text{x}{-296.1}) + 1072 = 86.3\ \text{kJ/mol}$$