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Thermochemistry


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Chapter 6

Energy

Energy is the capacity to do work.

- ***Radiant energy*** comes from the sun and is earth’s primary energy source
- ***Thermal energy*** is the energy associated with the random motion of atoms and molecules
- ***Chemical energy*** is the energy stored within the bonds of chemical substances
- ***Nuclear energy*** is the energy stored within the collection of neutrons and protons in the atom
- ***Potential energy*** is the energy available by virtue of an object’s position

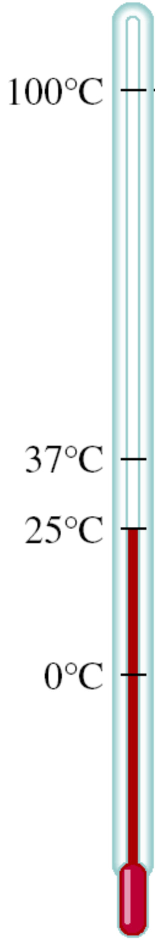
Energy Changes in Chemical Reactions

Thermochemistry is the study of heat change in chemical reactions.

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

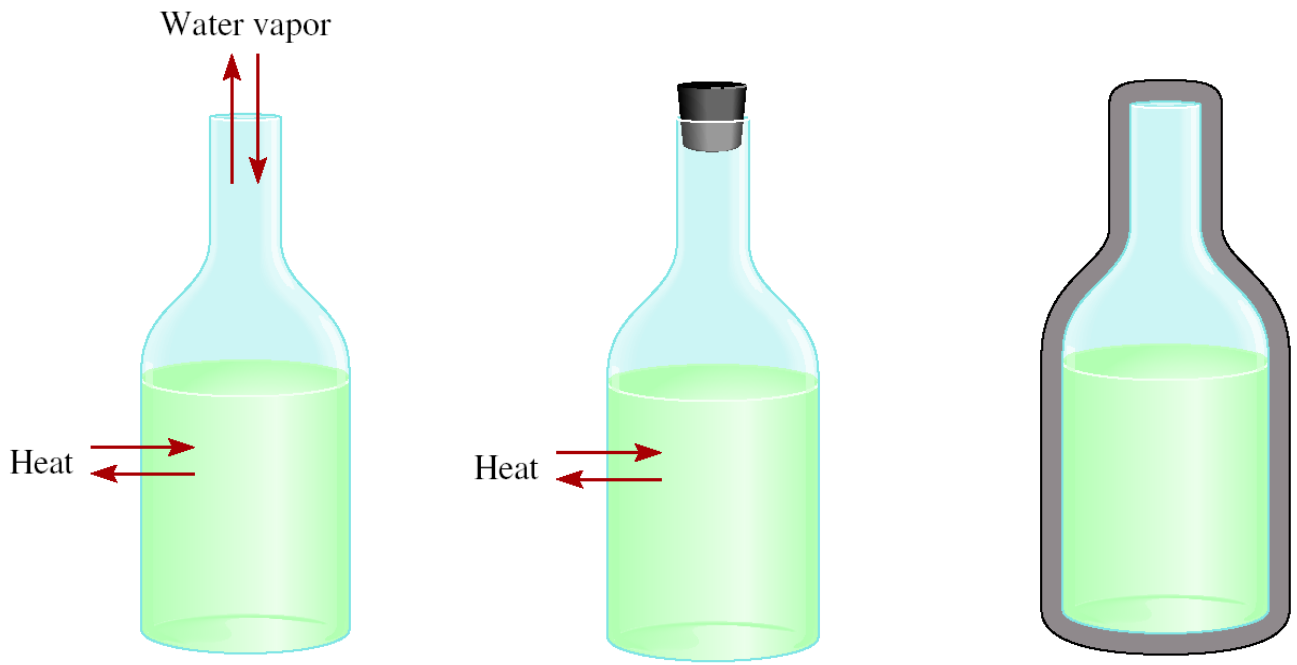
Temperature is a measure of the thermal energy.

Temperature $\neq$ Thermal Energy



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.

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

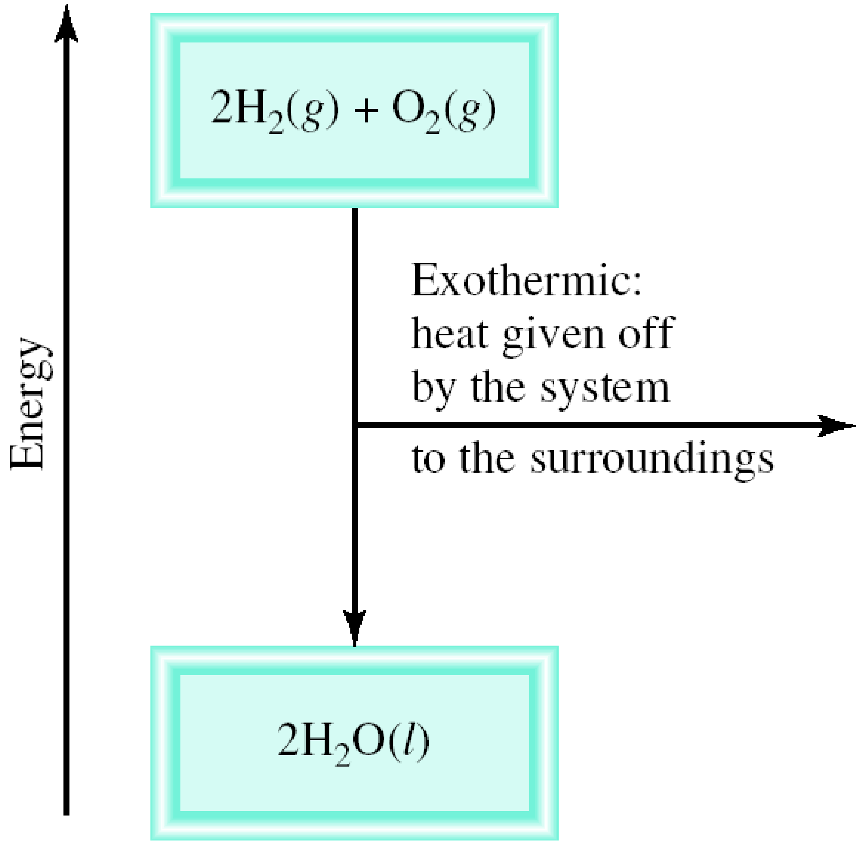
$$H_2O\,(g) \longrightarrow H_2O\,(l) + \text{energy}$$

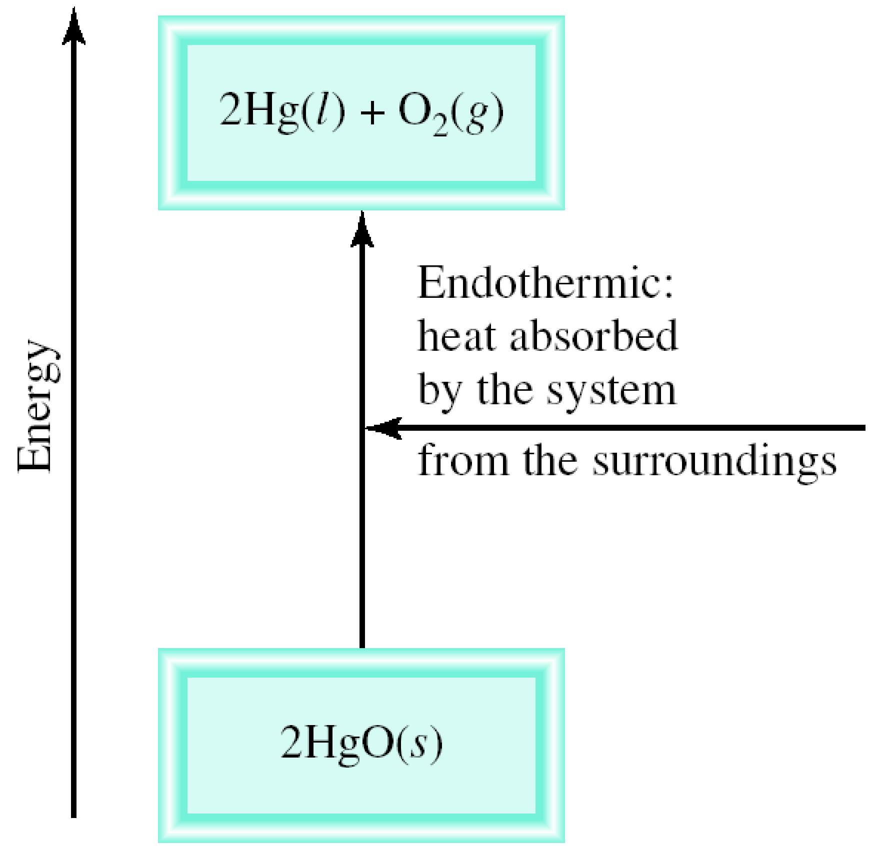
Endothermic *process* is any process in which heat has to be supplied to the system from the surroundings.

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

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

Schematic of Exothermic and Endothermic Processes

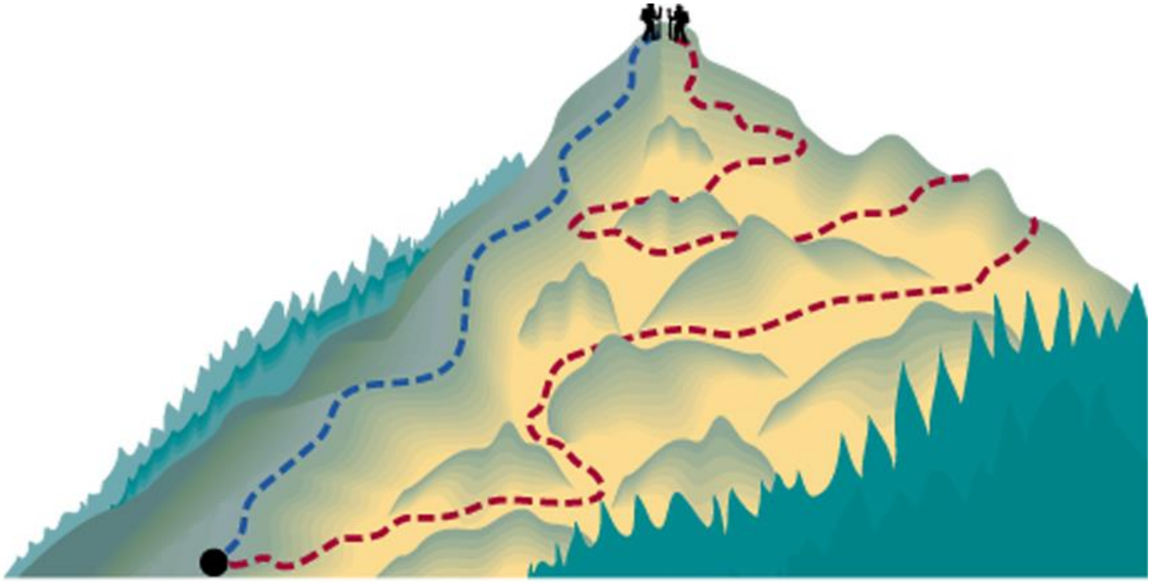




Thermodynamics is the scientific study of the interconversion of heat and other kinds of energy.

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

energy, pressure, volume, temperature



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

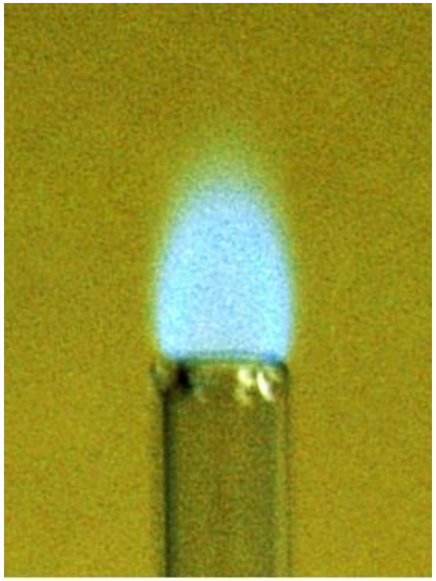
$\Delta P = P_{final} - P_{initial}$

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

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

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

$$w = F \times d$$

$$w = -P\Delta V$$

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

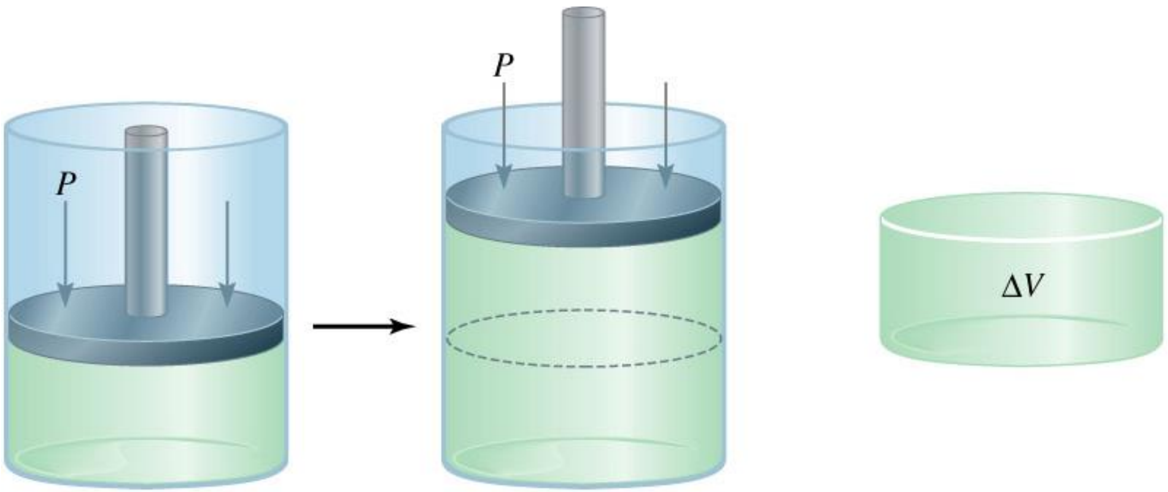
$$\Delta V > 0$$

$$-P\Delta V < 0$$

$$w_{sys} < 0$$

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

$$w = -0\text{ atm} \times 3.8\text{ L} = 0\text{ L}\bullet\text{atm} = 0\text{ joules}$$

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

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

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

Enthalpy and the First Law of Thermodynamics

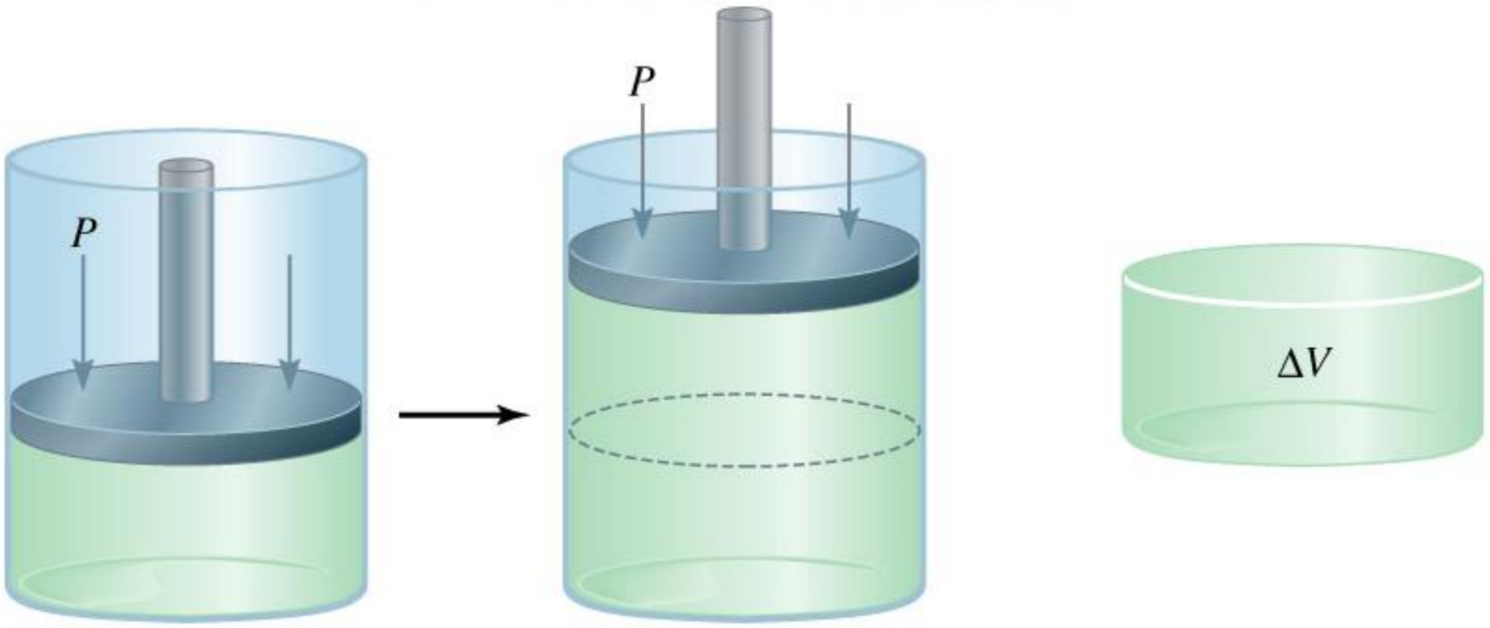
$$\Delta E = q + w$$

At constant pressure:

$$q = \Delta H \text{ and } w = -P\Delta V$$

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

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



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$$w = -0\ \text{atm} \times 3.8\ \text{L} = 0\ \text{L} \bullet \text{atm} = 0\ \text{joules}$$

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

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

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

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

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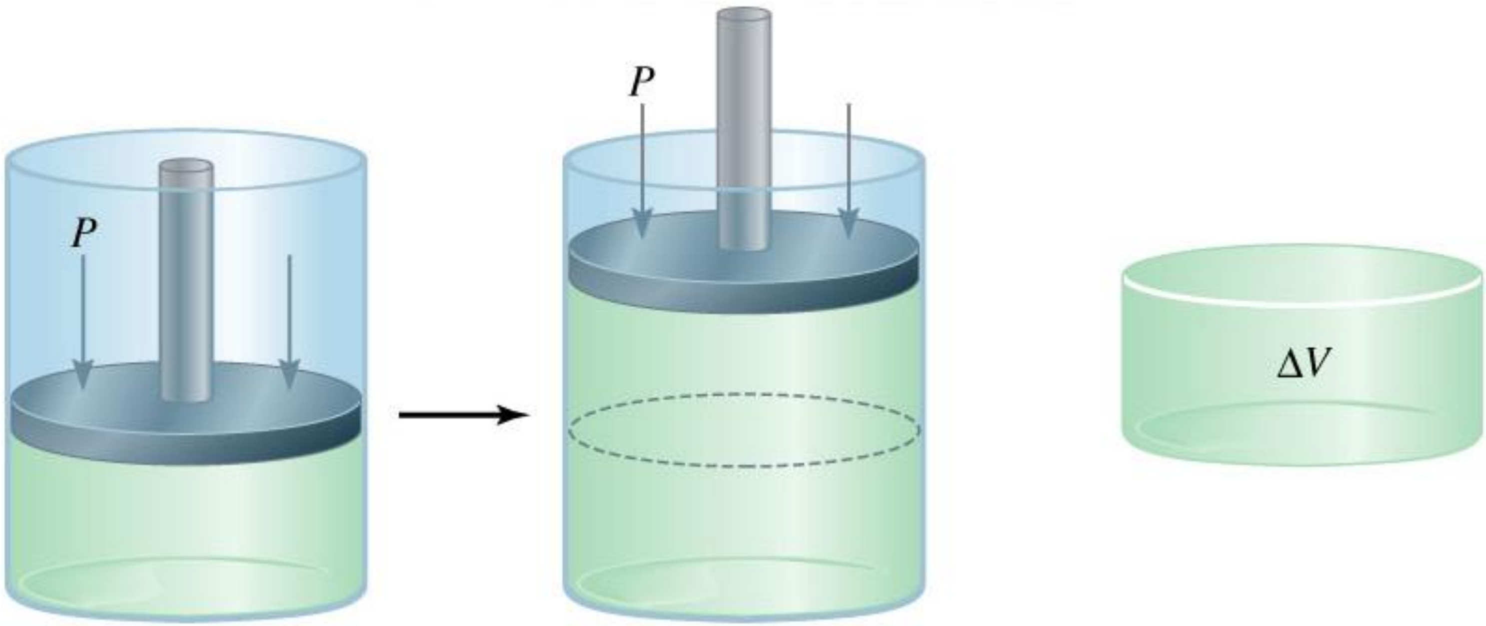
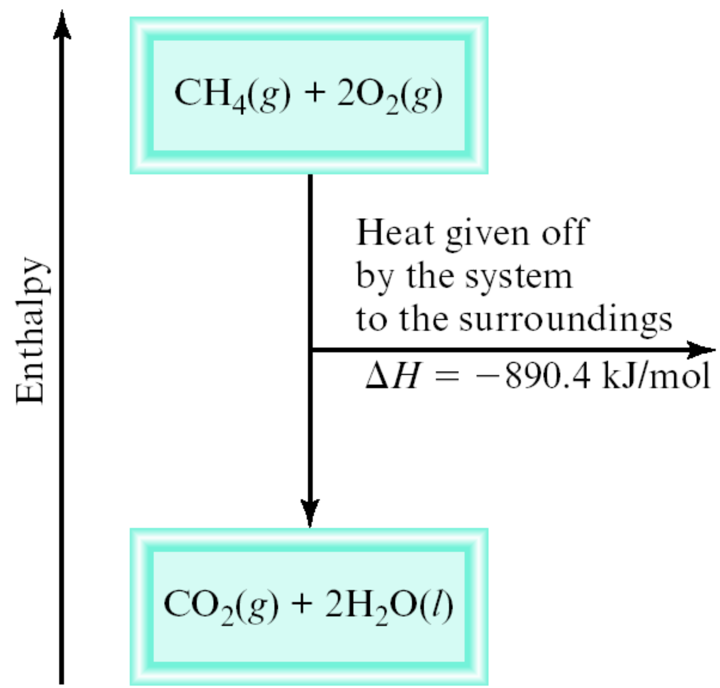


Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

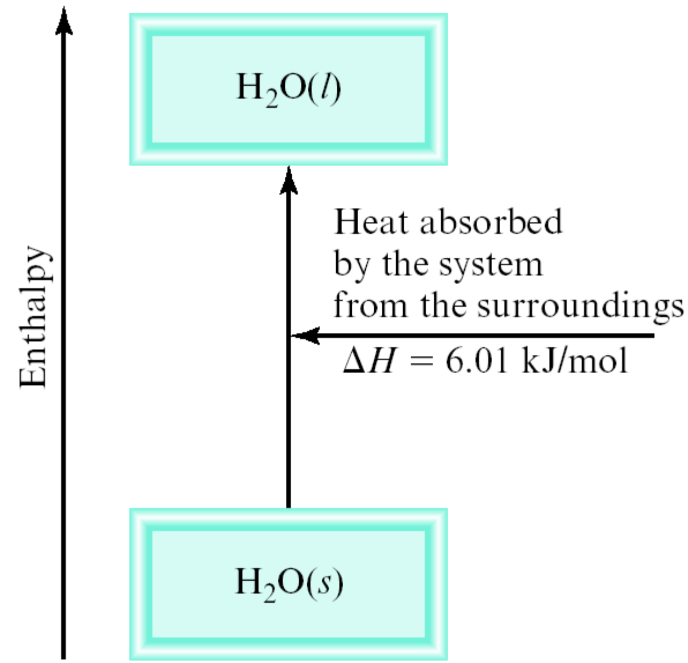
$$\Delta H = H\,(\text{products}) - H\,(\text{reactants})$$

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



$H_{products} < H_{reactants}$

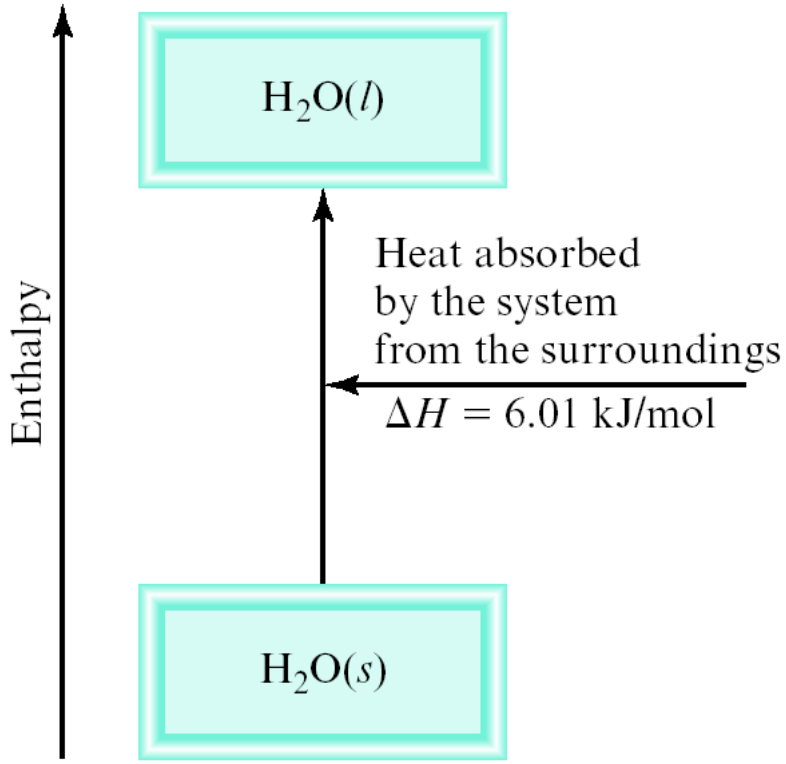
$\Delta H < 0$



$H_{products} > H_{reactants}$

$\Delta H > 0$

Thermochemical Equations



<u>Is ΔH negative or positive?</u>

System absorbs heat

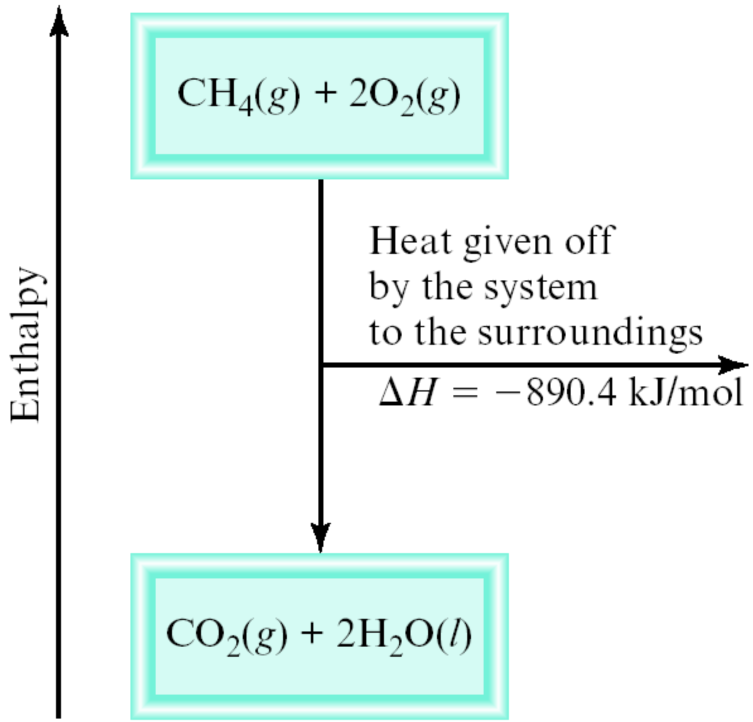
Endothermic

$\Delta H > 0$

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

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

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.

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

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:

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

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

A Comparison of ΔH and ΔE

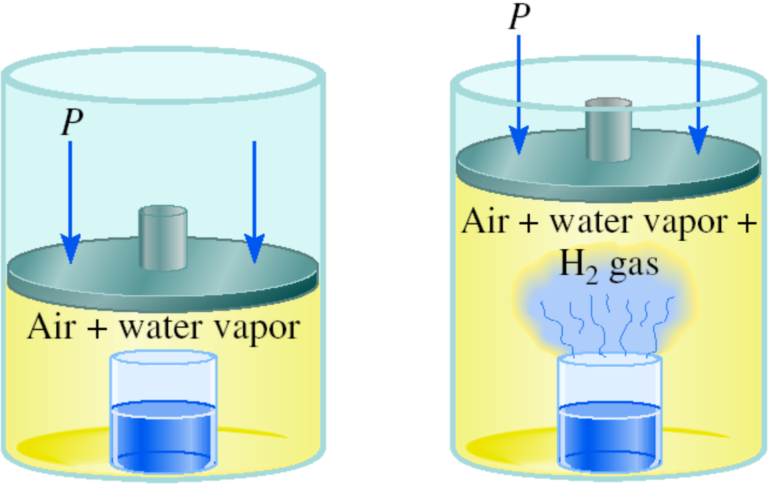
$$2Na\ (s) + 2H_2O\ (l) \longrightarrow 2NaOH\ (aq) + H_2\ (g) \quad \Delta H = -367.5\ \text{kJ/mol}$$

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

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

ΔE = -367.5 kJ/mol – 2.5 kJ/mol = -370 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

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

- 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

$$C = m \times s$$

Heat (q) absorbed or released:

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

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

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

t: in ^{o}C

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)

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

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

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.

Strategy We know the quantity of water and the specific heat of water. With this information and the temperature rise, we can calculate the amount of heat absorbed (q).

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.

$\Delta H_f^0 (O_2) = 0$

$\Delta H_f^0 (O_3) = 142$ kJ/mol

ΔH_f^0 (C, graphite) $= 0$

ΔH_f^0 (C, diamond) $= 1.90$ 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.

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

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

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

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:

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

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

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

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

or

$$\Delta H^\circ_f(CO_2, g) = -393.5 \text{ kJ/mol}$$

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.

$\Delta H_f^0\ (CO_2) = -393.5$ kJ/mol $\qquad \Delta H_f^0\ (H_2O) = -285.8$ kJ/mol

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

$$\Delta H_{rxn}^0 = \Sigma n\Delta H_f^0\ (\text{products}) - \Sigma m\Delta H_f^0\ (\text{reactants})$$

$$\Delta H_{rxn}^0 = [12\Delta H_f^0\ (CO_2) + 6\Delta H_f^0\ (H_2O)] - [2\Delta H_f^0\ (C_6H_6)]$$

$$\Delta H_{rxn}^0 = [12 \times -393.5 + 6 \times -285.8] - [2 \times 49.04] = -5946 \text{ kJ}$$

$$\frac{-5946 \text{ kJ}}{2 \text{ mol}} = -2973 \text{ kJ/mol } C_6H_6$$

The Indirect Method (Hess's Law)

- Many compounds <u>cannot</u> 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).

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

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:

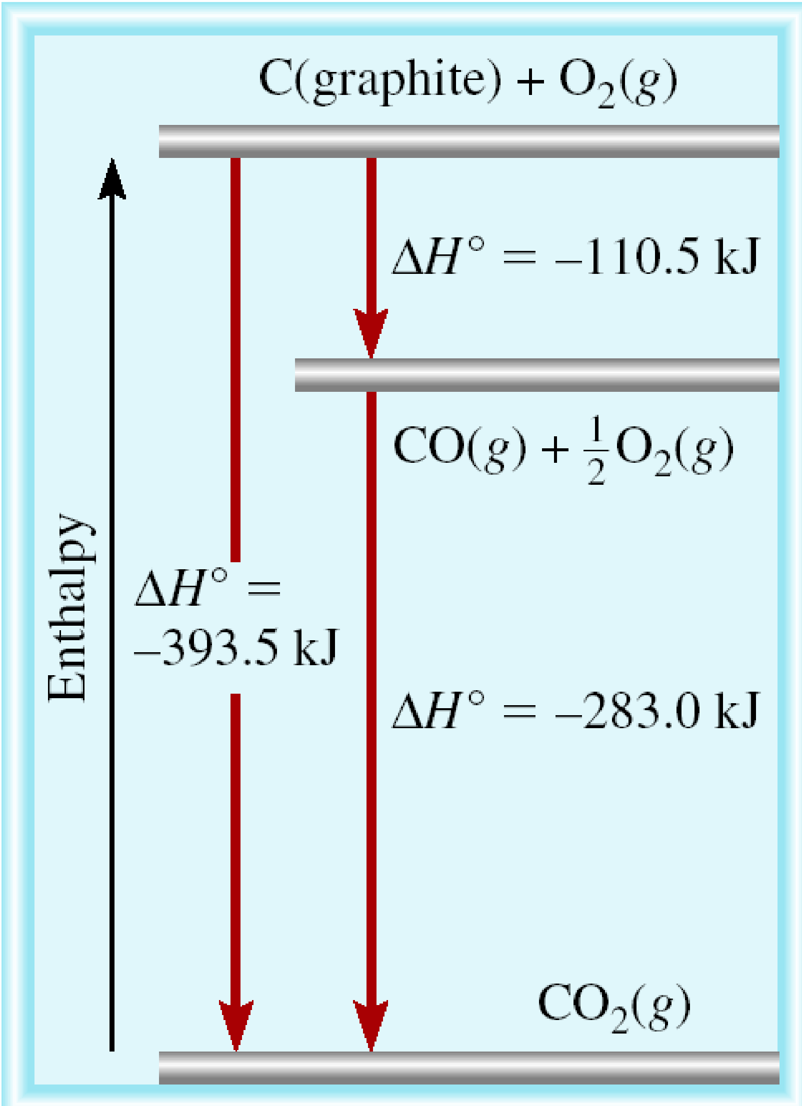
$$\begin{array}{lrcll} \text{(a)} & \text{C(graphite)} + \text{O}_2(g) & \longrightarrow & \text{CO}_2(g) & \Delta H^\circ_{\text{rxn}} = -393.5 \text{ kJ/mol} \\ \text{(b)} & \text{CO}(g) + \tfrac{1}{2}\text{O}_2(g) & \longrightarrow & \text{CO}_2(g) & \Delta H^\circ_{\text{rxn}} = -283.0 \text{ kJ/mol} \end{array}$$

First, we reverse Equation (b) to get

$$\text{(c)} \quad \text{CO}_2(g) \longrightarrow \text{CO}(g) + \tfrac{1}{2}\text{O}_2(g) \quad \Delta H^\circ_{\text{rxn}} = +283.0 \text{ kJ/mol}$$

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

$$\begin{array}{lrcll} \text{(a)} & \text{C(graphite)} + \text{O}_2(g) & \longrightarrow & \text{CO}_2(g) & \Delta H^\circ_{\text{rxn}} = -393.5 \text{ kJ/mol} \\ \text{(c)} & \text{CO}_2(g) & \longrightarrow & \text{CO}(g) + \tfrac{1}{2}\text{O}_2(g) & \Delta H^\circ_{\text{rxn}} = +283.0 \text{ kJ/mol} \\ \hline \text{(d)} & \text{C(graphite)} + \tfrac{1}{2}\text{O}_2(g) & \longrightarrow & \text{CO}(g) & \Delta H^\circ_{\text{rxn}} = -110.5 \text{ kJ/mol} \end{array}$$



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

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

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

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.

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

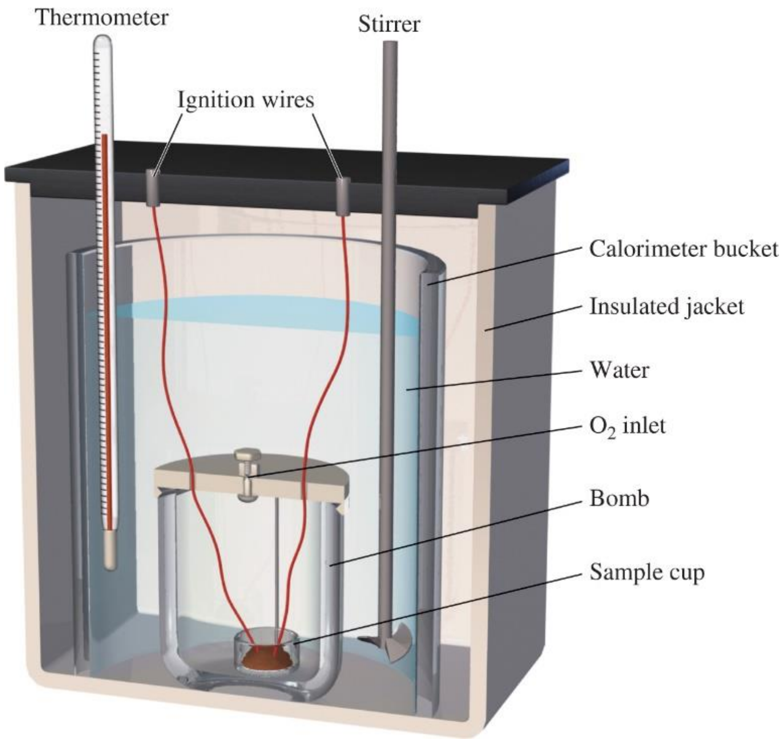
$$2S(\text{rhombic}) + 2\cancel{O_2}\,(g) \longrightarrow 2\cancel{SO_2}\,(g) \qquad \Delta H^0_{rxn} = -296.1\ \text{kJ/mol} \times 2$$

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

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

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

Constant-Volume Calorimetry



$$q_{sys} = q_{water} + q_{bomb} + q_{rxn}$$

$$q_{sys} = 0$$

$$q_{rxn} = -\left(q_{water} + q_{bomb}\right)$$

$$q_{water} = m \times s \times \Delta t$$

$$q_{bomb} = C_{bomb} \times \Delta t$$

No heat enters or leaves!

Reaction at Constant V

$$\Delta H \neq q_{rxn}$$

$$\Delta H \sim q_{rxn}$$

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EXAMPLE 6.6

A quantity of 1.435 g of naphthalene ($C_{10}H_8$), a pungent-smelling substance used in moth repellents, was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from 20.28°C to 25.95°C. If the heat capacity of the bomb plus water was 10.17 kJ/°C, calculate the heat of combustion of naphthalene on a molar basis; that is, find the molar heat of combustion.

Solution The heat absorbed by the bomb and water is equal to the product of the heat capacity and the temperature change. From Equation (6.16), assuming no heat is lost to the surroundings, we write

$$\begin{aligned} q_{\text{cal}} &= C_{\text{cal}}\Delta t \\ &= (10.17\text{ kJ/°C})(25.95\text{°C} - 20.28\text{°C}) \\ &= 57.66\text{ kJ} \end{aligned}$$

Because $q_{\text{sys}} = q_{\text{cal}} + q_{\text{rxn}} = 0$, $q_{\text{cal}} = -q_{\text{rxn}}$. The heat change of the reaction is -57.66 kJ. This is the heat released by the combustion of 1.435 g of $C_{10}H_8$; therefore, we can write the conversion factor as

$$\frac{-57.66\text{ kJ}}{1.435\text{ g } C_{10}H_8}$$

The molar mass of naphthalene is 128.2 g, so the heat of combustion of 1 mole of naphthalene is

$$\begin{aligned} \text{molar heat of combustion} &= \frac{-57.66\text{ kJ}}{1.435\ \cancel{\text{g } C_{10}H_8}} \times \frac{128.2\ \cancel{\text{g } C_{10}H_8}}{1\text{ mol } C_{10}H_8} \\ &= \boxed{-5.151 \times 10^3\text{ kJ/mol}} \end{aligned}$$

Chemistry in Action:

Fuel Values of Foods and Other Substances

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H = -2801\ \text{kJ/mol}$$

1 cal = 4.184 J

1 cal = 1000 cal = 4184 J

Fuel Values of Foods

Substance	$\Delta H_{combustion}(kJ/g)$
Apple	−2
Beef	8
Beer	−1.5
Bread	−11
Butter	−34
Cheese	−18
Eggs	6
Milk	−3
Potatoes	−3

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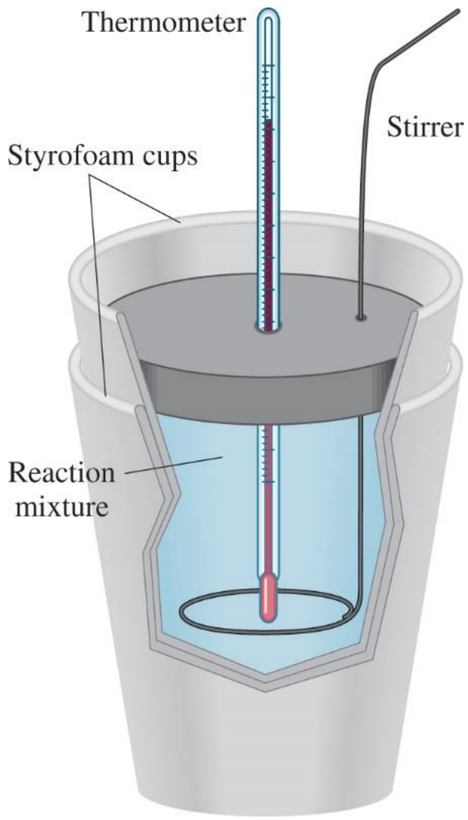
Constant-Pressure Calorimetry



$$q_{sys} = q_{water} + q_{cal} + q_{rxn}$$

$$q_{sys} = 0$$

$$q_{rxn} = -\left(q_{water} + q_{cal}\right)$$

$$q_{water} = m \times s \times \Delta t$$

Reaction at Constant *P*

$$\Delta H = q_{rxn}$$

No heat enters or leaves!

Access the text alternative for slide images.

EXAMPLE 6.7

A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from 22.50°C to 23.17°C. What is the specific heat of the lead pellet?

Solution Treating the calorimeter as an isolated system (no heat lost to the surroundings), we write

$$q_{Pb} + q_{H_2O} = 0$$

or

$$q_{Pb} = -q_{H_2O}$$

The heat gained by the water is given by

$$q_{H_2O} = ms\Delta t$$

where m and s are the mass and specific heat and $\Delta t = t_{final} - t_{initial}$. Therefore,

$$\begin{aligned} q_{H_2O} &= (100.0\ g)(4.184\ J/g \cdot °C)(23.17°C - 22.50°C) \\ &= 280.3\ J \end{aligned}$$

Because the heat lost by the lead pellet is equal to the heat gained by the water, so $q_{Pb} = -280.3$ J. Solving for the specific heat of Pb, we write

$$\begin{aligned} q_{Pb} &= ms\Delta t \\ -280.3\ J &= (26.47\ g)(s)(23.17°C - 89.98°C) \\ s &= \boxed{0.158\ J/g \cdot °C} \end{aligned}$$

Some Heats of Reaction

Table 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$	−56.2
Heat of ionization	$H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \rightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \rightarrow H_2O(g)$	44.0*
Heat of reaction	$MgCl_2(s) + 2Na(l) \rightarrow 2Nacl(s) + Mg(s)$	−180.2

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EXAMPLE 6.8

A quantity of 1.00×10^2 mL of 0.500 *M* HCl was mixed with 1.00×10^2 mL of 0.500 *M* NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solutions was the same, 22.50°C, and the final temperature of the mixed solution was 25.86°C. Calculate the heat change for the neutralization reaction on a molar basis

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL and 4.184 J/g · °C, respectively).

Strategy Because the temperature rose, the neutralization reaction is exothermic. How do we calculate the heat absorbed by the combined solution? What is the heat of the reaction? What is the conversion factor for expressing the heat of reaction on a molar basis?

Solution Assuming no heat is lost to the surroundings, $q_{sys} = q_{soln} + q_{rxn} = 0$, so $q_{rxn} = -q_{soln}$, where q_{soln} is the heat absorbed by the combined solution. Because

(Continued)

the density of the solution is 1.00 g/mL, the mass of a 100-mL solution is 100 g. Thus,

$$\begin{aligned} q_{\text{soln}} &= ms\Delta t \\ &= (1.00 \times 10^2\,\text{g} + 1.00 \times 10^2\,\text{g})(4.184\ \text{J/g}\cdot{}^\circ\text{C})(25.86^\circ\text{C} - 22.50^\circ\text{C}) \\ &= 2.81 \times 10^3\ \text{J} \\ &= 2.81\ \text{kJ} \end{aligned}$$

Because $q_{\text{rxn}} = -q_{\text{soln}}$, $q_{\text{rxn}} = -2.81$ kJ.

From the molarities given, the number of moles of both HCl and NaOH in 1.00×10^2 mL solution is

$$\frac{0.500\ \text{mol}}{1\ \text{L}} \times 0.100\ \text{L} = 0.0500\ \text{mol}$$

Therefore, the heat of neutralization when 1.00 mole of HCl reacts with 1.00 mole of NaOH is

$$\text{heat of neutralization} = \frac{-2.81\ \text{kJ}}{0.0500\ \text{mol}} = -56.2\ \text{kJ/mol}$$

Enthalpy of Solution

The ***enthalpy of solution*** (**ΔH_{soln}**) is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

$$\Delta H_{soln} = \Delta H_{soln} - H_{components}$$

Table 6.5 Heats of Solution of Some Ionic Compounds

Compound	ΔH_{soln} (kJ / mol)
LiCl	–37.1
$CaCl_2$	–82.8
NaCl	4.0
KCl	17.2
NH_4Cl	15.2
NH_4NO_3	26.6

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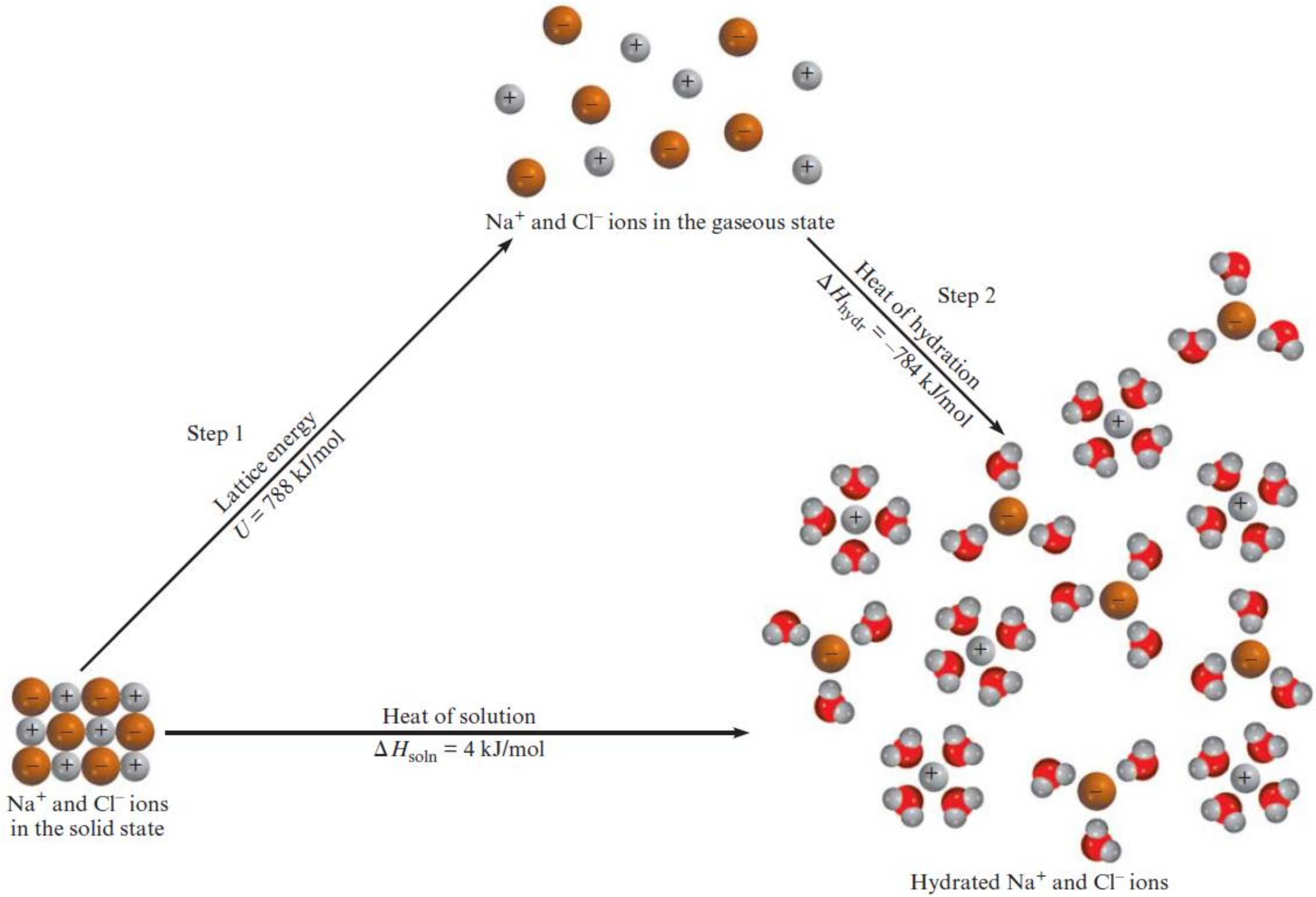
The Solution Process for NaCl



$$\Delta \boldsymbol{H}_{\text{sol}} = \text{step 1} + \text{step 2} = 788 - 784 = 4 \text{ kJ} / \text{mol}$$

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