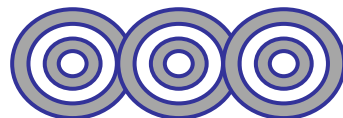




Chemistry, Raymond Chang
10th edition, 2010
McGraw-Hill



Chapter 6

Thermochemistry

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6.1

The nature of energy and types of energy

Every chemical reaction obeys two fundamental laws:

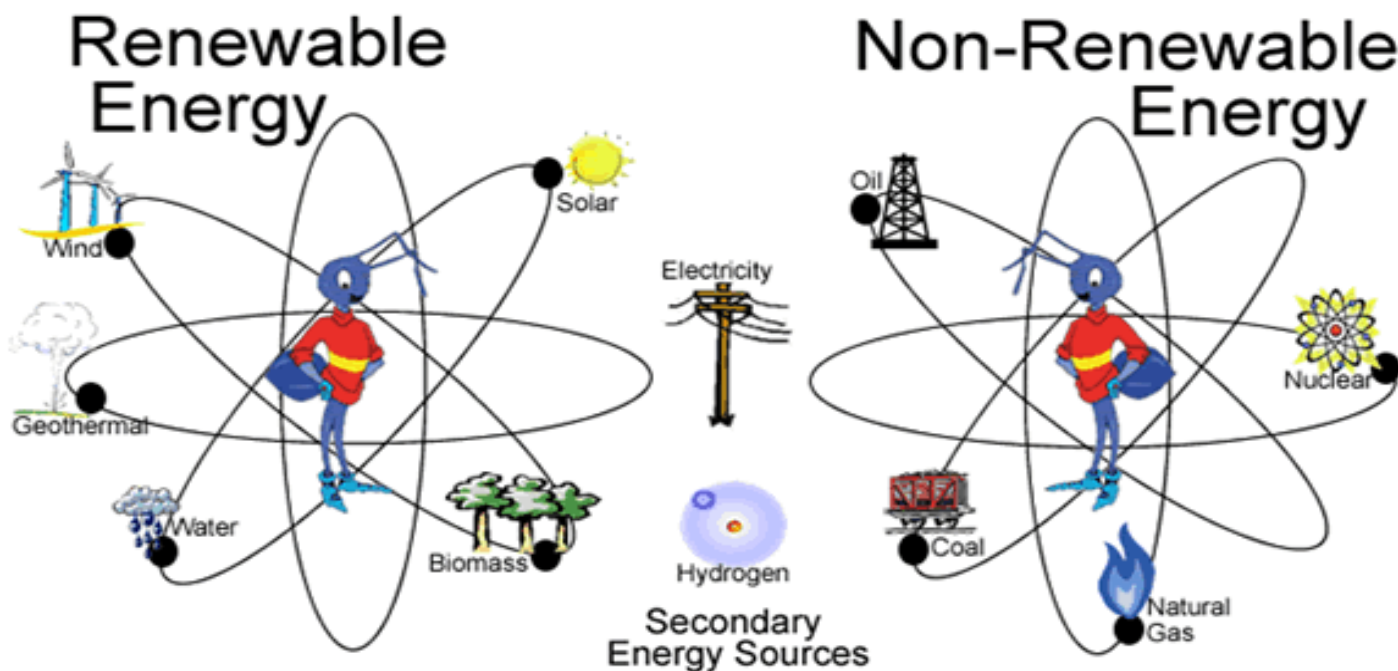
- the law of conservation of mass, and
- the law of conservation of energy.

Unlike matter, **energy** is known and recognized by its effects. It cannot be seen, touched, smelled or weighed.

Energy is usually defined as the capacity to do work or transfer heat.

All forms of energy are capable of doing work (that is, of exerting a force over a distance).

Chemists define work as directed energy change resulting from a process.





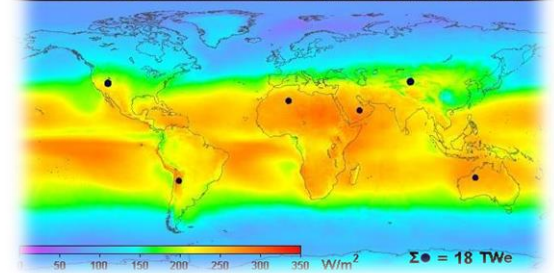
Kinetic energy

Radiant energy

Thermal energy

Chemical energy

Potential energy



All forms of energy can be converted (at least in principle) from one form to another. When one form of energy disappears, some other form of energy (of equal magnitude) must appear (law of conservation of energy: the total quantity of energy in the universe is assumed constant).



6.2

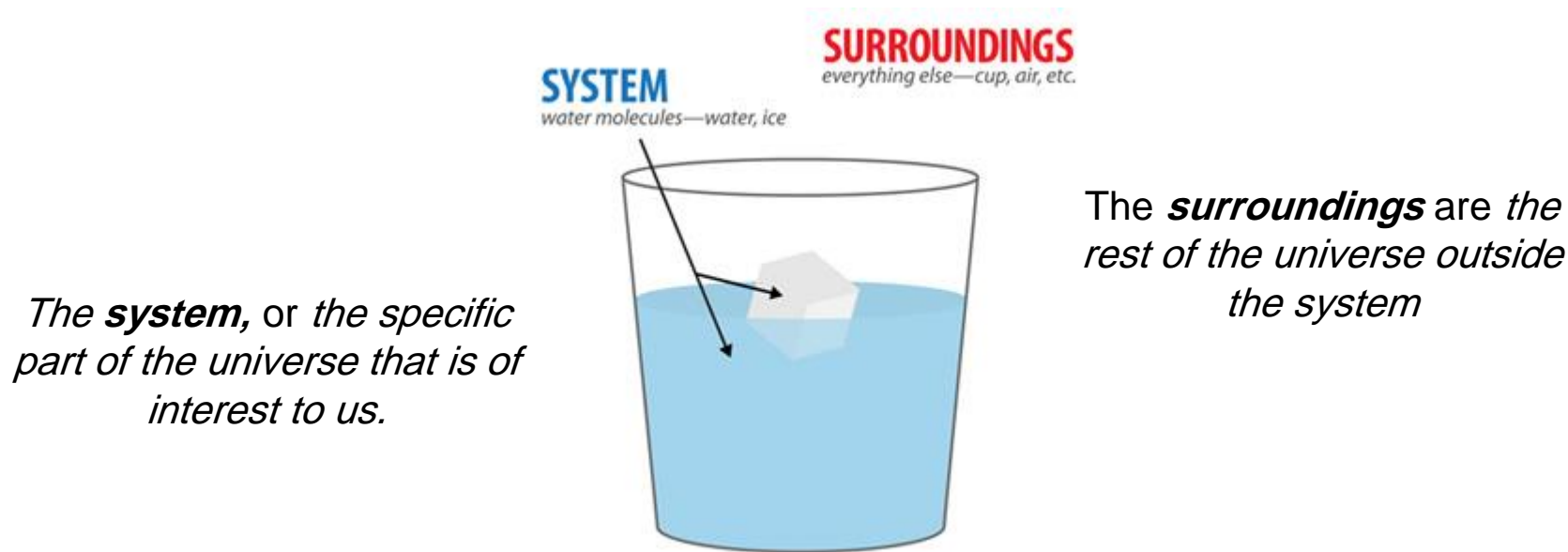
Energy changes in chemical reactions

Almost all chemical reactions **absorb** or **produce** (release) energy, generally in the form of heat.

Heat is the transfer of thermal energy between two bodies that are at different temperatures. Thus, we often speak of the “**heat flow**” from a hot object to a cold one.

We customarily talk of “**heat absorbed**” or “**heat released**” when describing the energy changes that occur during a process.

Thermochemistry is the study of heat change in chemical reactions.



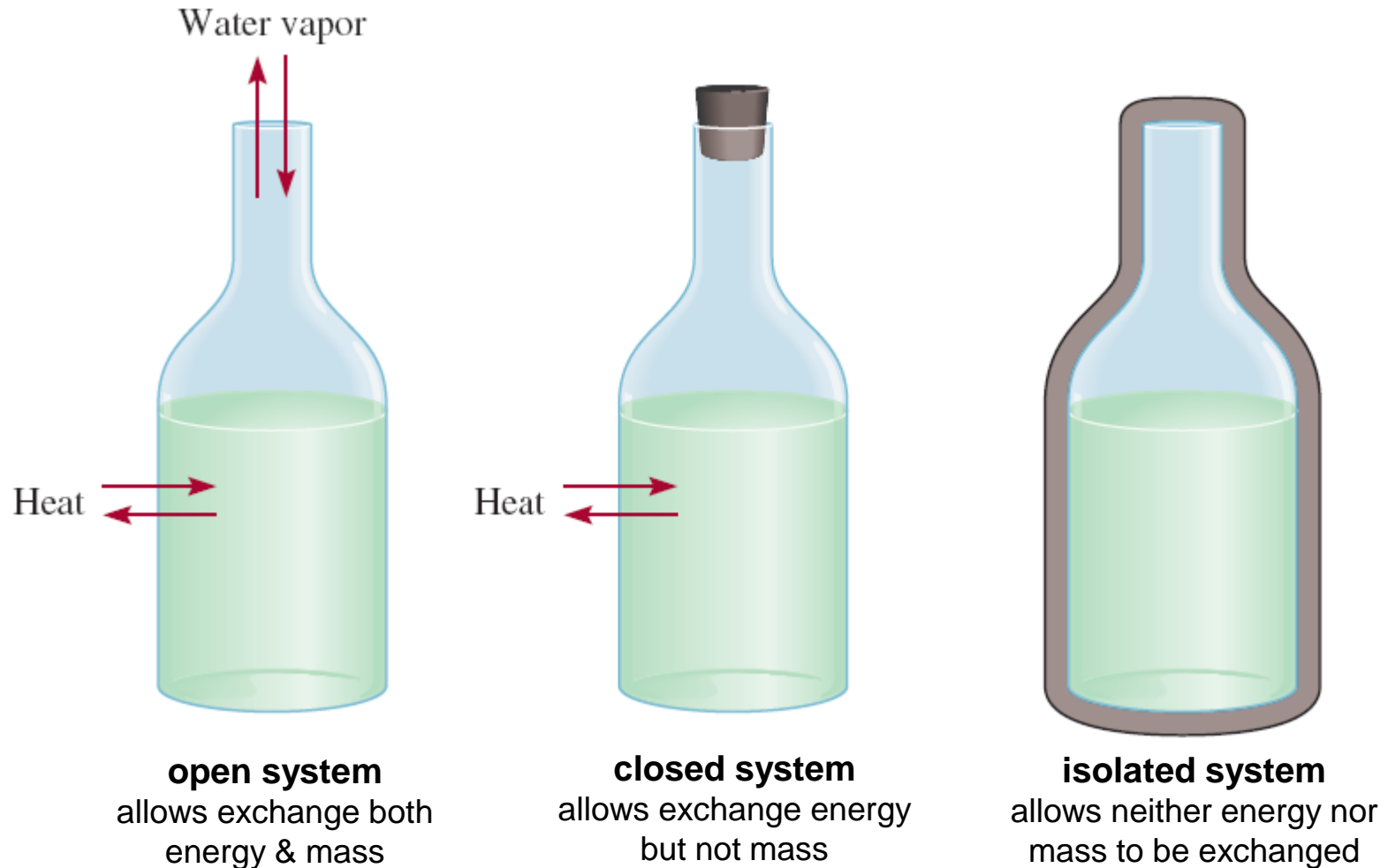
For chemists, systems usually include substances involved in chemical and physical changes.

There are three types of systems;

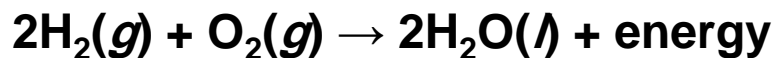
-An **open system** can exchange mass and energy, usually in the form of heat with its surroundings. e.g., an open system may consist of a quantity of water in an open container.

-If we close the flask, so that no water vapor can escape from or condense into the container, we create a **closed system**, which allows the transfer of energy (heat) but not mass.

-By placing the water in a totally insulated container, we can construct an **isolated system**, which does not allow the transfer of either mass or energy.



The combustion of hydrogen gas in oxygen is one of many chemical reactions that release considerable quantities of energy



The reacting mixture (H_2 , O_2 , and H_2O) the system and the rest of the universe the surroundings.

The heat generated by the combustion process is transferred from the system to its surroundings. This reaction is an example of an **exothermic process**, which gives off heat; transfers thermal energy to the surroundings.



The decomposition of mercury(II) oxide (HgO) at high temperatures:

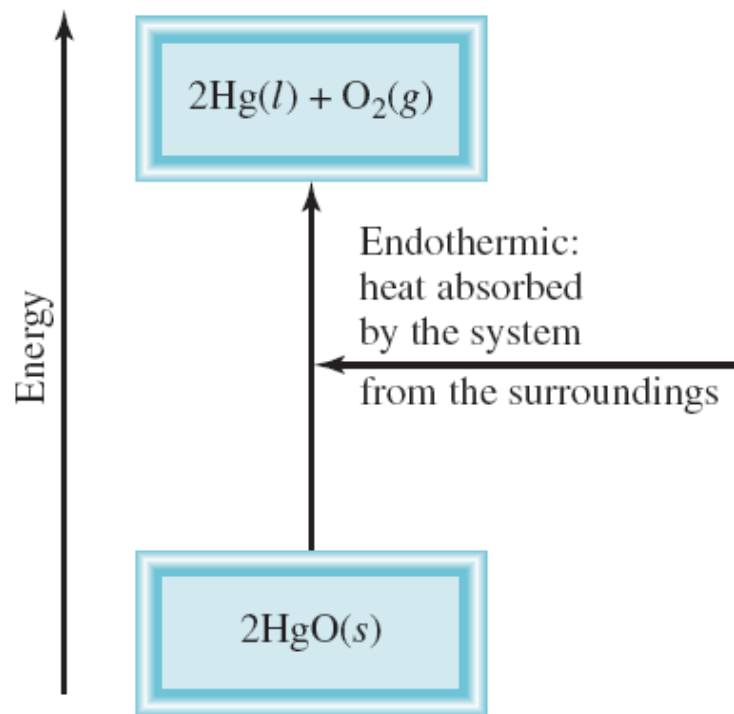
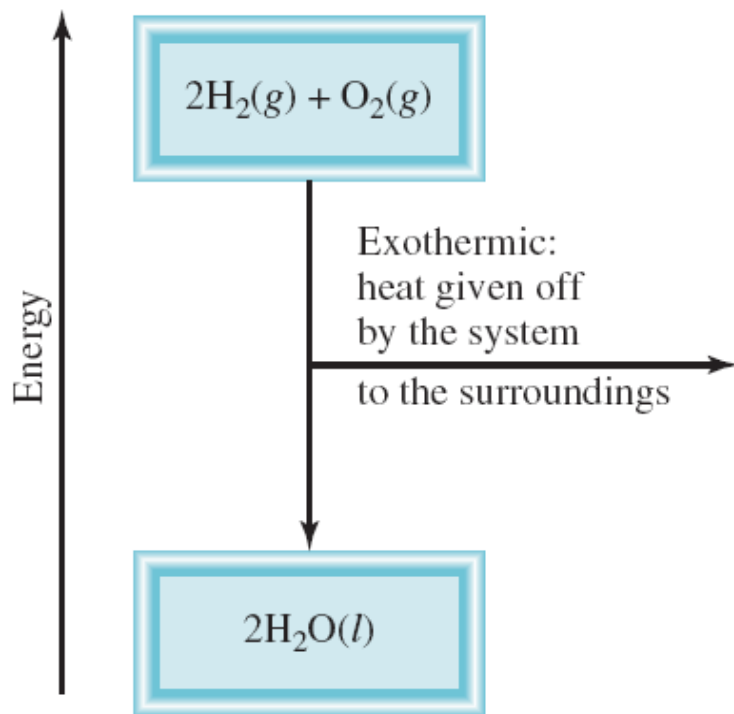


This reaction is an **endothermic process**, in which heat has to be supplied to the system (that is, to HgO) by the surroundings

Exo- comes from the Greek word meaning “outside”; **Endo-** means “within.”

-In **exothermic** reactions, the total energy of the products is less than the total energy of the reactants. The difference is the heat supplied by the system to the surroundings.

-In **endothermic** reactions, the difference between the energy of the products and the energy of the reactants is equal to the heat supplied to the system by the surroundings.



6.3

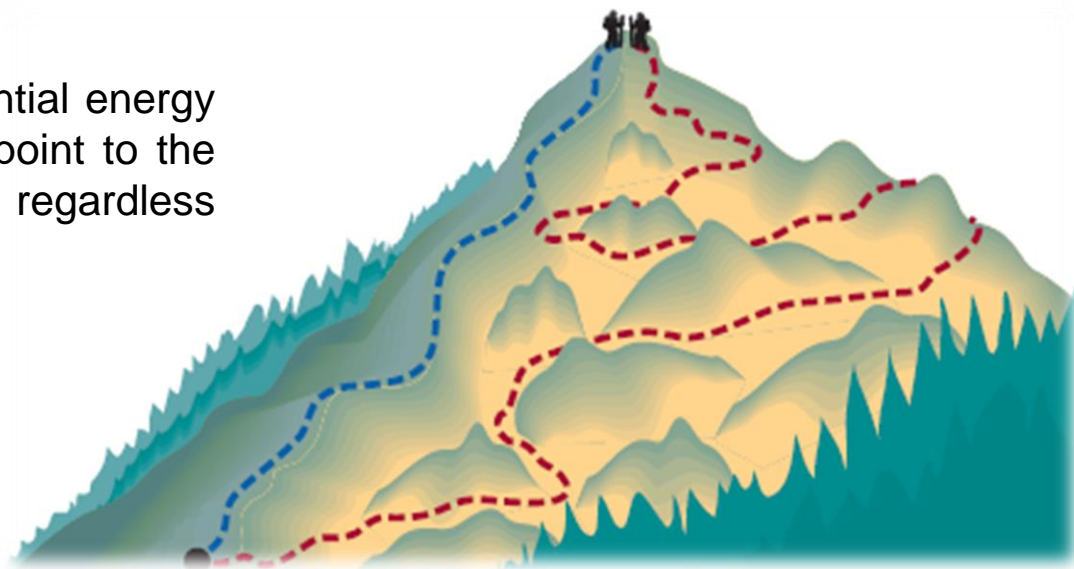
Introduction to thermodynamics

Thermochemistry is part of a broader subject called **thermodynamics**, which is the scientific study of the interconversion of heat and other kinds of energy.

In thermodynamics, we study changes in the **state of a system**, which is defined by the values of all relevant macroscopic properties, e.g., composition, energy, temperature, pressure and volume. Energy, pressure, volume and temperature are said to be **state functions** — properties that are determined by the state of the system, regardless of how that condition was achieved.

$\Delta V = V_f - V_i$ where V_i and V_f denote the initial and final volume.

The net increase in gravitational potential energy when we go from the same starting point to the top of a mountain is always the same, regardless of how we get there.

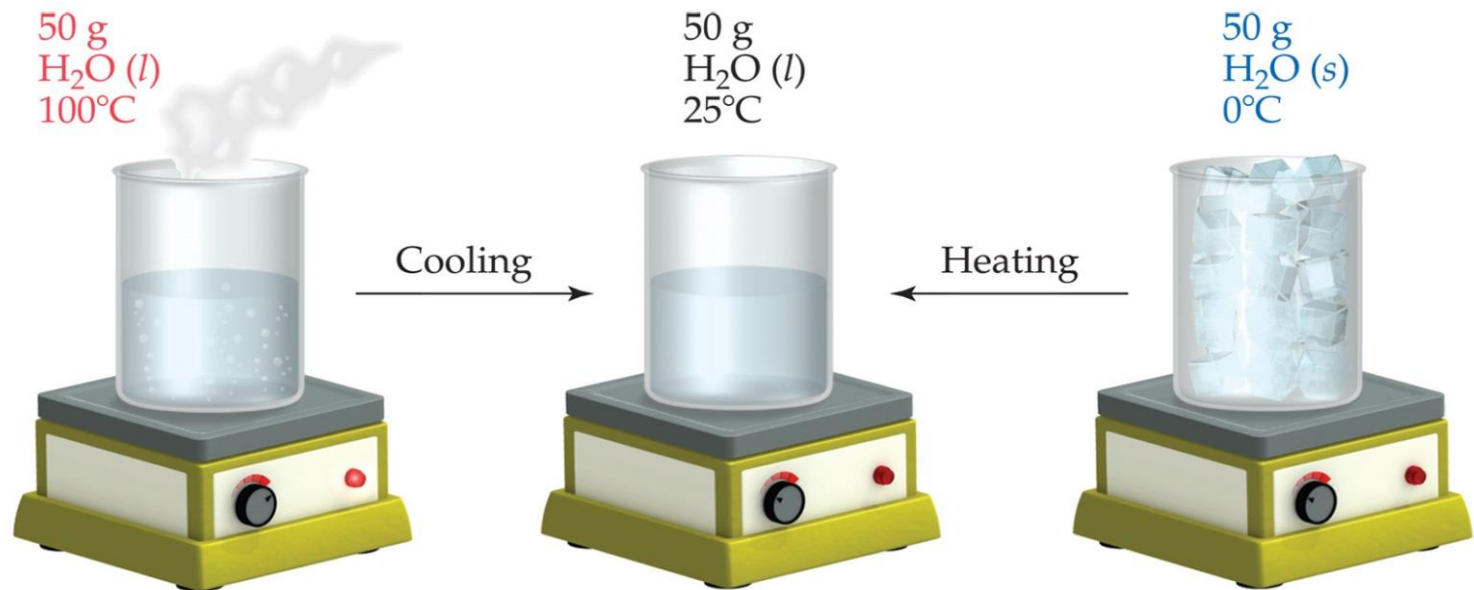


Changes in state functions do not depend on the pathway, but only on the initial and final state.

The water could have reached room temperature from either direction. Therefore, internal energy is a state function. It depends only on the present state of the system, not on the path by which the system arrived at that state.

And so, ΔE depends only on E_{initial} and E_{final} .

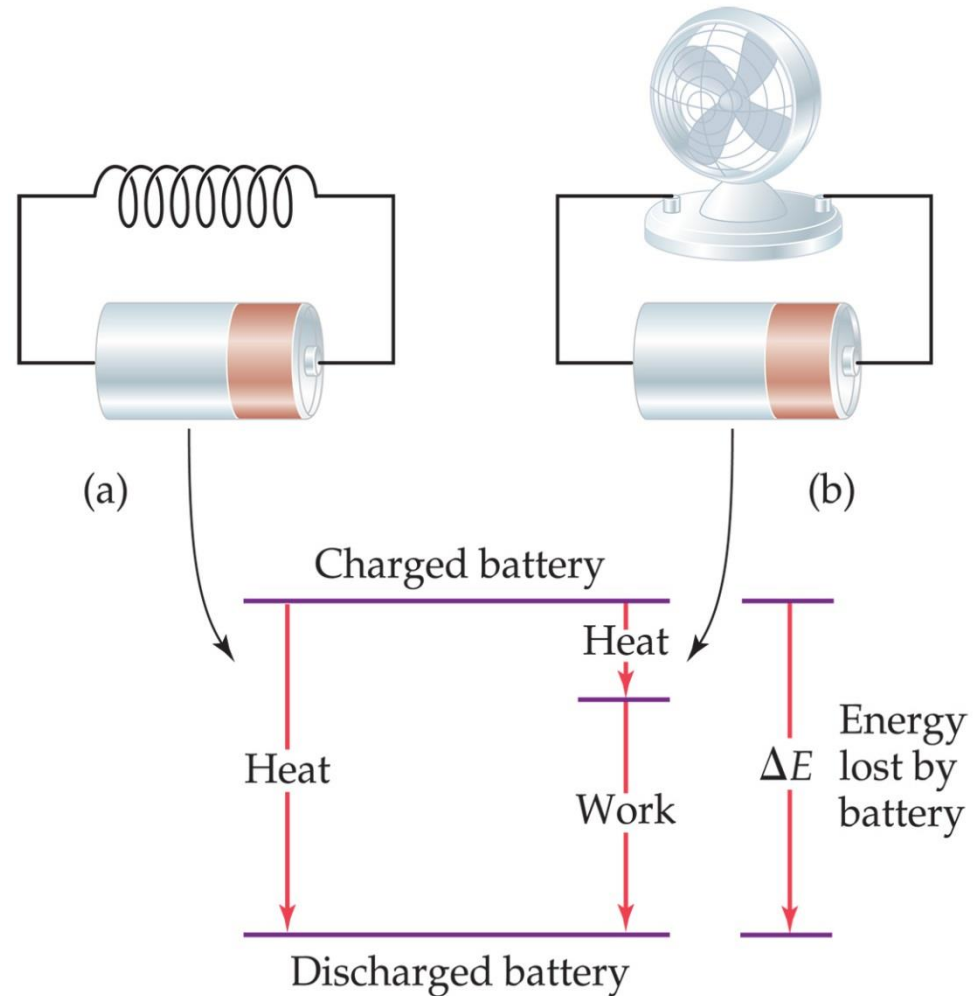
The conditions that influence internal energy include the temperature, pressure and the total quantity of matter in the system because energy is an extensive property.



State function: depends only on the initial and final states of system, not on how the internal energy is used.

However, q and w are *not* state functions.

Whether the battery is shorted out or is discharged by running the fan, its ΔE is the same. But q and w are different in the two cases.



(a) A battery shorted out by a wire (resistance) loses energy to the surroundings only as heat; no work is performed by the system. (b) A battery discharged through a motor loses energy as work (to make the fan turn) with small amount of heat. w and h are different in two cases but E is same.

First Law of Thermodynamics

The first law of thermodynamics, which is based on the law of conservation of energy, states that energy can be converted from one form to another, but cannot be created or destroyed.

-Energy is neither created nor destroyed.

-Energy is conserved.

-The total energy of the universe is a constant; if the system loses energy, it must be gained by the surroundings, and vice versa.

-Total energy lost by a system equals the total energy gained by a surrounding.

Thermodynamic quantities have three:

(1) a number, and (2) a unit, that together give the magnitude of the change, and (3) a sign that gives the direction.

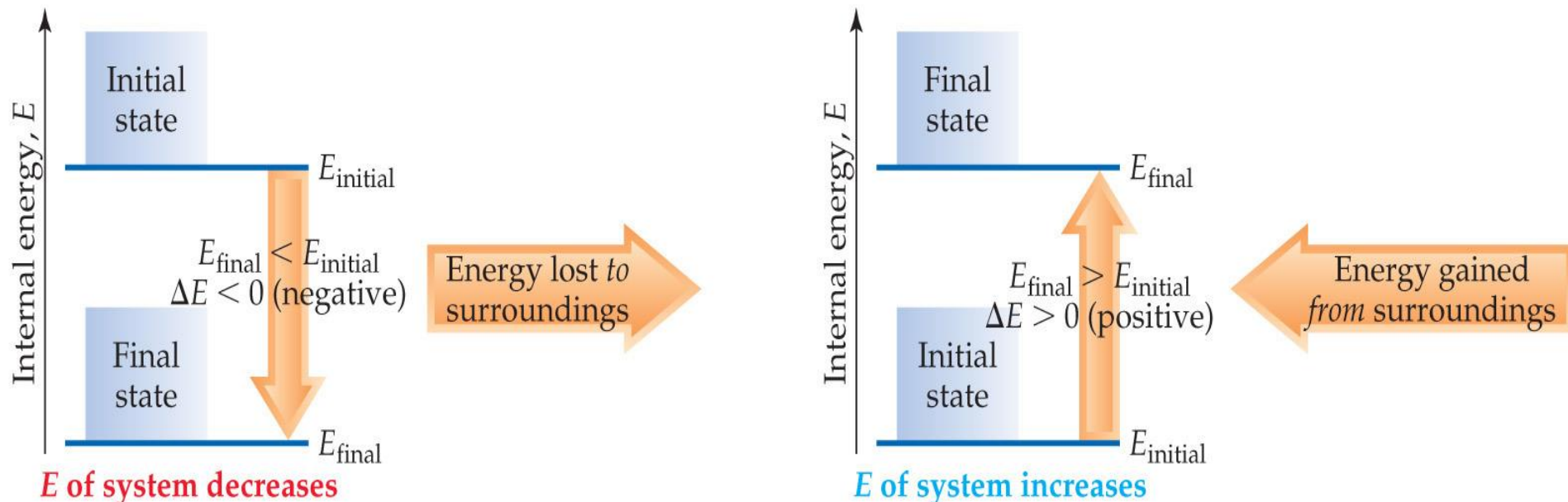
Internal Energy

The internal energy of a system is the sum of all **kinetic** and **potential** energies of all components of the system; we call it E .

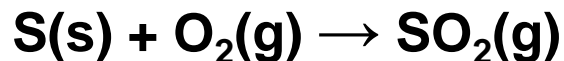
Cannot measure **absolute** internal energy.

By definition, the change in internal energy, ΔE , is the final energy of the system minus the initial energy of the system:

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



Consider the reaction between 1 mole of sulfur and 1 mole of oxygen gas to produce 1 mole of sulfur dioxide:



Our system is composed of

- the reactant molecules S and O₂ (the initial state), and
- the product molecules SO₂ (the final state).

We do not know the internal energy content of either the reactant molecules or the product molecules, but we can accurately measure the change in energy content, $\Delta\mathbf{E}$, given by

$$\Delta\mathbf{E} = \mathbf{E}_{(\text{product})} - \mathbf{E}_{(\text{reactants})}$$

$$= \text{energy content of 1 mol SO}_2(\text{g}) - \text{energy content of [1 mol S(s) + 1 mol O}_2(\text{g})]$$

We find that this reaction gives off heat. Therefore, the energy of the product is less than that of the reactants, and $\Delta\mathbf{E}$ is negative.

The transfer of energy from the system to the surroundings does not change the total energy of the universe. That is, the sum of the energy changes must be zero:

$$\Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0$$

or

$$\Delta E_{\text{sys}} = - \Delta E_{\text{surr}}$$

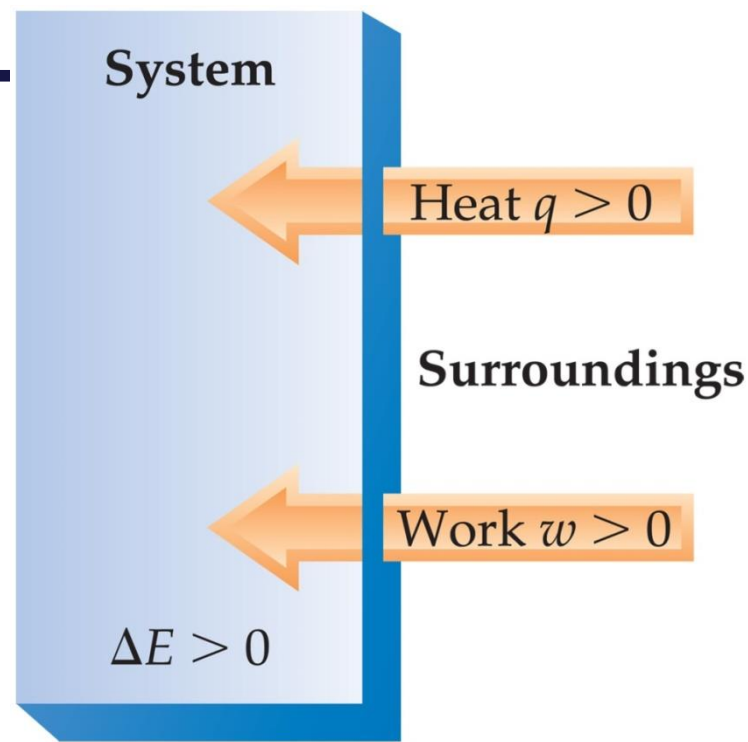
where the subscripts “sys” and “surr” denote system and surroundings, respectively.

When energy is exchanged between the system and the surroundings, it is exchanged as either heat (q) or work (w).

When a system undergoes any physical or chemical change, the change in internal energy (magnitude and sign) is given by the heat added to or absorbed by the system plus the work done on or by the system:

$$\Delta E = q + w$$

When heat is added to a system or work is done on a system, its internal energy increases.



Heat gained by a system and work done on a system are both +ve quantities. Both increase the internal energy of the system. ΔE +ve quantity.

The sign conventions for q and w are as follows:

- q is +ve for an endothermic process and -ve for an exothermic process,
- w is +ve for work done on the system by the surroundings and -ve for work done by the system on the surroundings.

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)	–

ΔE , q , w , and their **Signs**

For q	+ means system <i>gains</i> heat	– means system <i>loses</i> heat
For w	+ means work done <i>on</i> system	– means work done <i>by</i> system
For ΔE	+ means <i>net gain</i> of energy by system	– means <i>net loss</i> of energy by system

Work

The work can be defined as force F multiplied by distance d :

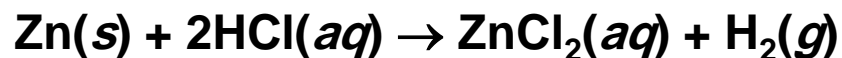
$$w = F \times d$$

In thermodynamics, work has a broader meaning that includes;

- Mechanical work (e.g., a crane lifting a steel beam),
- Electrical work (e.g., a battery supplying electrons to light the bulb of a flashlight),
- Surface work (e.g., blowing up a soap bubble).

One way to illustrate mechanical work is to study the expansion or compression of a gas. Many chemical and biological processes involve gas volume changes.

-e.g., when a gas is produced, then the gas produced can be used to push a piston, thus doing work.

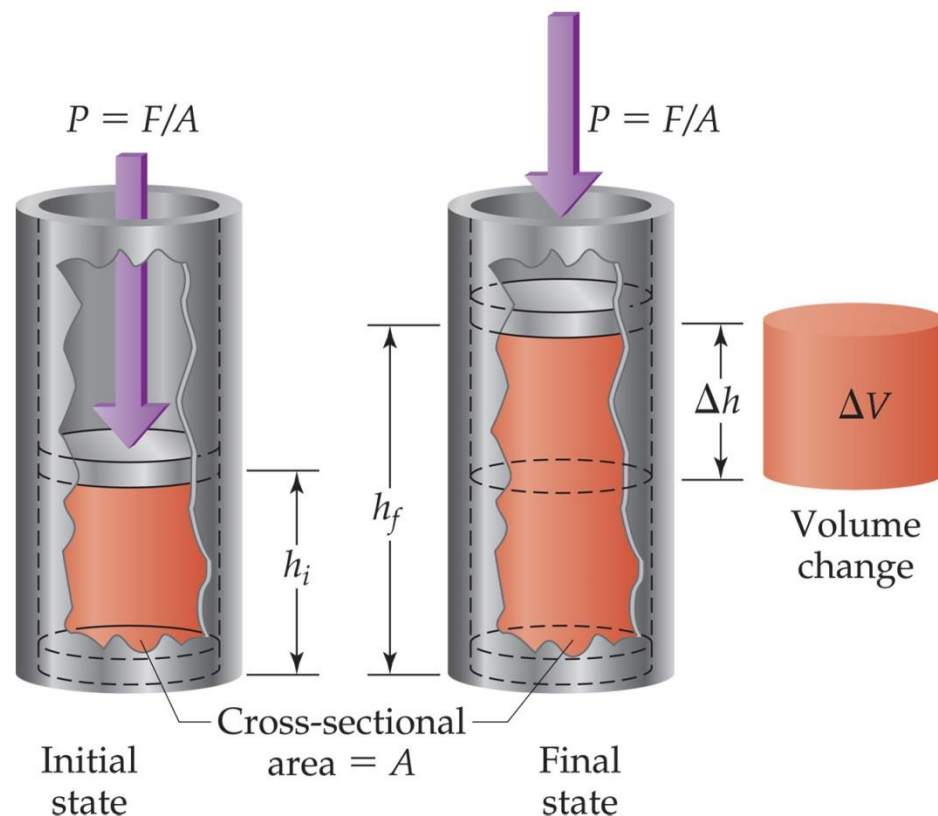


The work performed by the above reaction is called **pressure-volume work**. When the pressure is constant, then

$$w = -P \Delta V$$

where: P is pressure and ΔV is the change in volume of the system:

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



Why the negative sign in the Equation ???

-For gas expansion (work done *by* the system), $\Delta V > 0$, so $-P\Delta V$ is a -ve quantity.

-For gas compression (work done *on* the system), $\Delta V < 0$, and $-P\Delta V$ is a +ve quantity.

EXAMPLE

A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature.

Calculate the work done by the gas if it expands

(a) against a vacuum and

(b) against a constant pressure of 1.2 atm.

(a) Because the external pressure is zero, no work is done in the expansion.

$$\begin{aligned}w &= -P\Delta V \\ &= -(0)(6.0 - 2.0) \text{ L} \\ &= 0\end{aligned}$$

(b) The external, opposing pressure is 1.2 atm, so

$$\begin{aligned}w &= -P\Delta V \\ &= -(1.2 \text{ atm})(6.0 - 2.0) \text{ L} \\ &= -4.8 \text{ L}\cdot\text{atm}\end{aligned}$$

To convert the answer to joules, we write

$$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$$

$$w = -4.8 \times 101.3 = -4.9 \times 10^2 \text{ J}$$

Practice Exercise

A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 4.00 atm.

$$\Delta E = q + w$$

Heat and work are **not** state functions because they are not properties of a system. They manifest themselves only during a process (during a change). Thus, their values depend on the path of the process and vary accordingly.

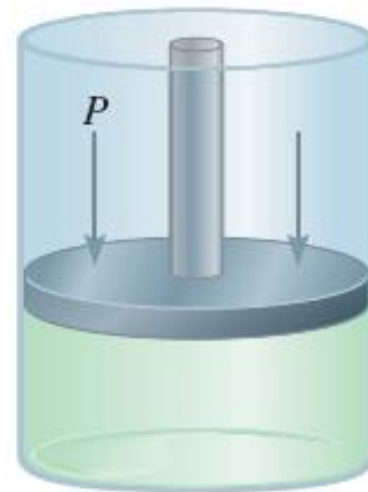
But,,

ΔE is a state function

It is important to note that regardless of which procedure is taken, the change in internal energy of the system, ΔE , depends on the sum of ($q + w$). If changing the path from the initial state to the final state increases the value of q , then it will decrease the value of w by the same amount and vice versa, so that ΔE remains unchanged.

EXAMPLE

The work done when a gas is compressed in a cylinder like that shown in the Figure is 462 J. During this process, there is a heat transfer of 128 J from the gas to the surroundings. Calculate the energy change for this process.



$$\begin{aligned}\Delta E &= q + w \\ &= -128 \text{ J} + 462 \text{ J} \\ &= 334 \text{ J}\end{aligned}$$

As a result, the energy of the gas increases by 334 J.

Practice Exercise

A gas expands and does P - V work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?

EXAMPLE

Two gases, A and B, are confined in a cylinder-and-piston. Substances A and B react to form a solid product: $A(g) + B(g) \rightarrow C(s)$. As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

Heat is transferred from the system to the surroundings, and work is done on the system by the surroundings, so q is negative and w is positive: $q = -1150 \text{ J}$ and $w = 480 \text{ J}$. Thus,

$$\Delta E = q + w = (-1150 \text{ J}) + (480 \text{ J}) = -670 \text{ J}$$

The negative value of ΔE tells us that a net quantity of 670 J of energy has been transferred from the system to the surroundings.

6.4

Enthalpy of chemical reactions

Constant Volume Processes

If a chemical reaction is run at constant volume, then $\Delta V = 0$ and no P-V work will result from this change.

$$w = -P \Delta V$$

$$\Delta E = q + w$$

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

at constant volume; $\Delta V=0$, so $w=0$

$$\Delta E = q_v$$

the subscript “ v ” means that this process carried out at constant-volume.

Constant Pressure Processes

In general, for a constant-pressure process we write

$$\begin{aligned}\Delta E &= q + w \\ &= q_p - P\Delta V\end{aligned}$$

or

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

where the subscript “p” denotes constant-pressure condition.

This thermodynamic function of a system called ***enthalpy (H)***, which is defined by the equation;

$$H = E + PV$$

where E is the internal energy of the system and P and V are the pressure and volume of the system, respectively.

$$**H = E + PV**$$

Because E and PV have energy units, enthalpy also has energy units.

E , P , and V are all state functions, that is, the changes in $(E + PV)$ depend only on the initial and final states. It follows, therefore, that the change in H , or ΔH , also depends only on the initial and final states. Thus, H is a state function.

For any process, the change in enthalpy is given by;

$$**\Delta H = \Delta E + \Delta(PV)**$$

If the pressure is held constant, then

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

Enthalpy of Reactions

Because most reactions are constant-pressure processes, we can equate the heat change in these cases to the change in enthalpy. For any reaction of the type

Reactants → Products

we define the change in enthalpy, called the enthalpy of reaction, ΔH , as the difference between the enthalpies of the products and the enthalpies of the reactants:

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

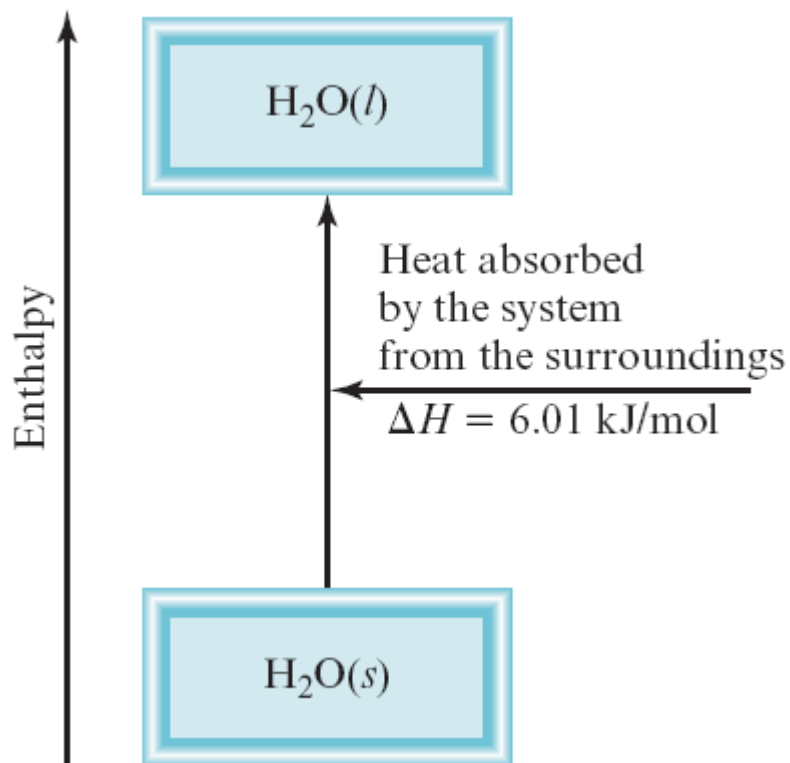
The enthalpy of reaction can be positive or negative, depending on the process.

-For an **endothermic** process (heat absorbed by the system from the surroundings), ΔH is positive (that is, $\Delta H > 0$).

-For an **exothermic** process (heat released by the system to the surroundings), ΔH is negative (that is, $\Delta H < 0$).

Thermochemical Equations

Physical change ...

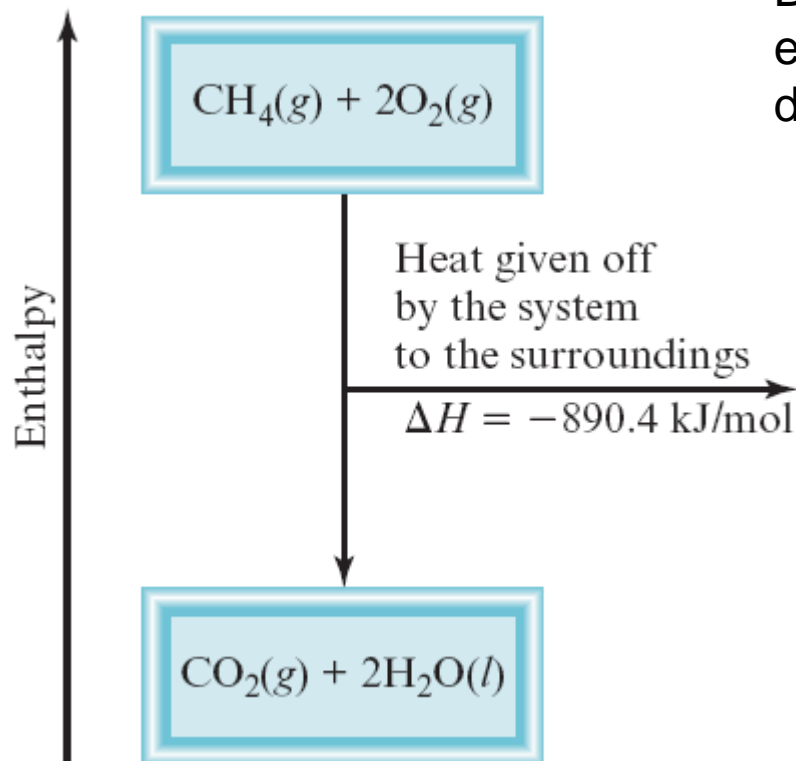


Melting 1 mole of ice at 0°C (an endothermic process) results in an enthalpy increase in the system of 6.01 kJ.

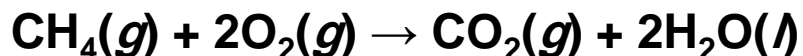


Thermochemical Equations

Chemical change ...



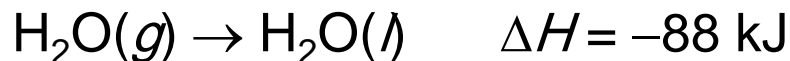
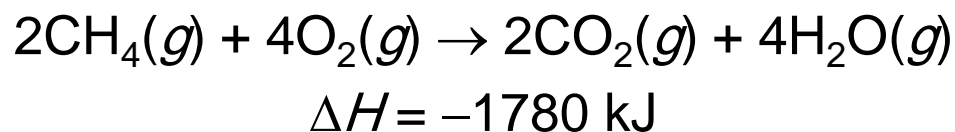
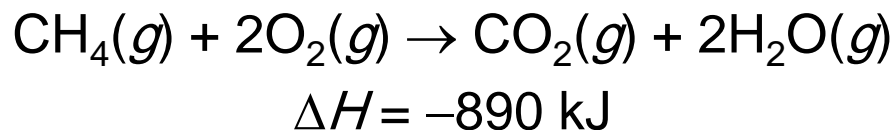
Burning 1 mole of methane in oxygen gas (an exothermic process) results in an enthalpy decrease in the system of 890.4 kJ.



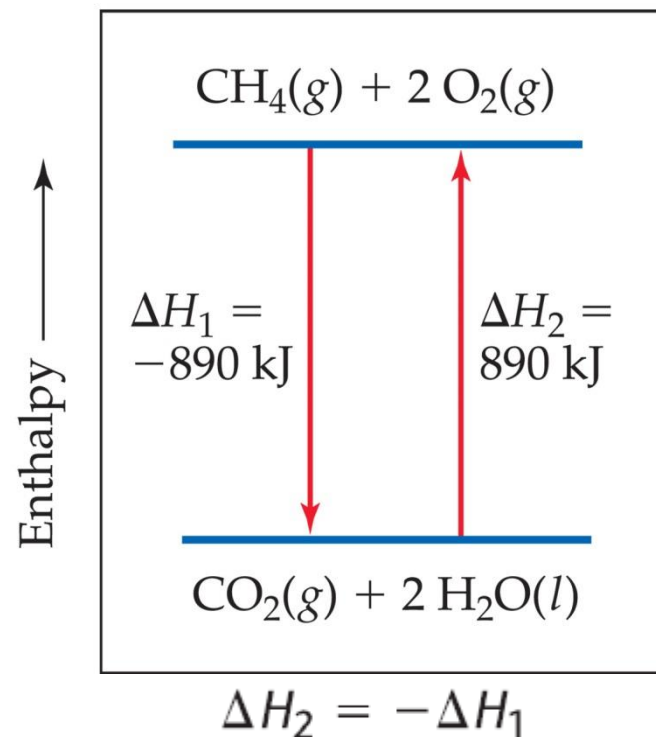
$$\Delta H = -890.4 \text{ kJ/mol}$$

Enthalpy Guidelines

1. Enthalpy is an extensive property. The magnitude of ΔH , therefore, is directly proportional to the amount of reactant consumed in the process.
2. ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction.
3. ΔH for a reaction depends on the state of the products and the state of the reactants.

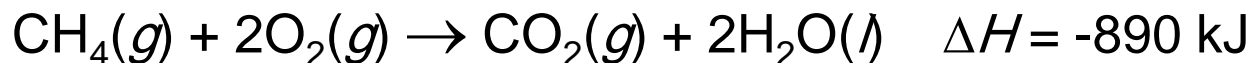


Condensation of gaseous water to form liquid water



Example

How much heat is released when 4.50 g of methane gas is burned in a constant pressure system?



Solution

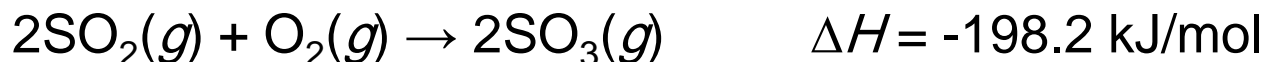
By adding the atomic weights of C and 4 H, we have 1 mol CH₄ = 16.0 g CH₄. We can use the appropriate conversion factors to convert grams of CH₄ to moles of CH₄ to kilojoules:

$$\text{Heat} = (4.50 \text{ g CH}_4) \left(\frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} \right) \left(\frac{-890 \text{ kJ}}{1 \text{ mol CH}_4} \right) = -250 \text{ kJ}$$

The negative sign indicates that the system released 250 kJ into the surroundings.

EXAMPLE

Given the thermochemical equation

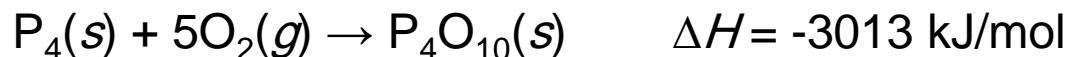


calculate the heat evolved when 87.9 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3 .

$$\Delta H = 87.9 \text{ g } \cancel{\text{SO}_2} \times \frac{1 \cancel{\text{ mol SO}_2}}{64.07 \text{ g } \cancel{\text{SO}_2}} \times \frac{-198.2 \text{ kJ}}{2 \cancel{\text{ mol SO}_2}} = -136 \text{ kJ}$$

Practice Exercise

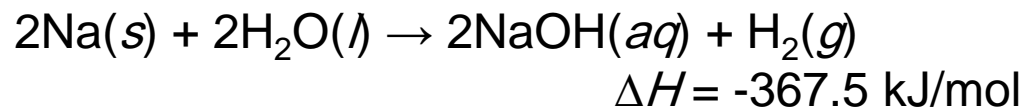
Calculate the heat evolved when 266 g of white phosphorus (P_4) burns in air according to the equation



A Comparison of ΔH and ΔE

What is the relationship between ΔH and ΔE for a process?

Let us consider the reaction between sodium metal and water:



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

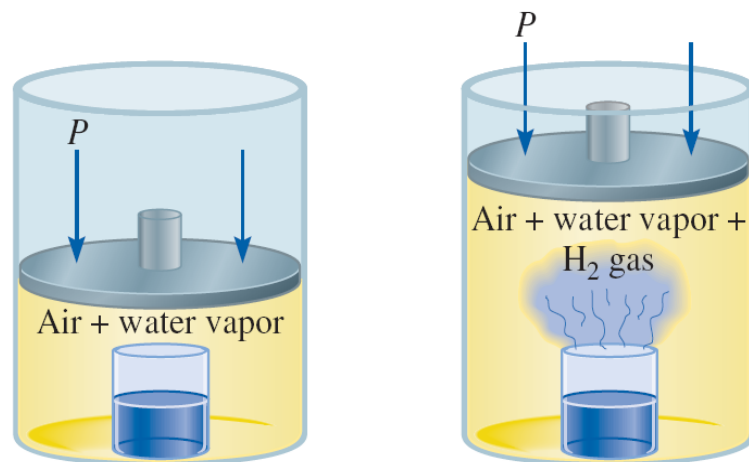
at 25°C (298 K) and 1 atm, 1 mole of H_2 has

$PV = 1 \times 0.0821 \times 298 = 24.5 \text{ L}\cdot\text{atm}$, so;

$-P \Delta V = -24.5 \text{ L}\cdot\text{atm} = -2.5 \text{ kJ}$. Finally;

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

This calculation shows that ΔE and ΔH are approximately the same.



A beaker of water inside a cylinder fitted with a movable piston. The pressure inside is equal to the atmospheric pressure. As the Na metal reacts with water, the H_2 gas generated pushes the piston upward (doing work on the surroundings) until the pressure inside is again equal to the pressure outside.

Recall that;

$$PV = nRT$$

$$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J} = 0.1013 \text{ kJ}$$

Another way to calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature. In this case,

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

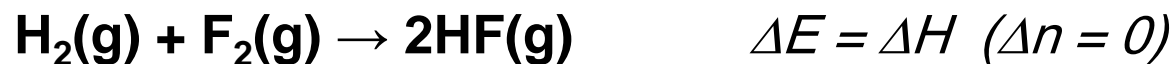
$$\Delta E = \Delta H - RT \Delta n$$

where Δn is defined as

$\Delta n =$ (number of moles of product gases – number of moles of reactant gases)

For reactions that do not result in a change in the number of moles of gases from reactants to products,

e.g.,



EXAMPLE

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO₂ at 1 atm and 25°C:



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

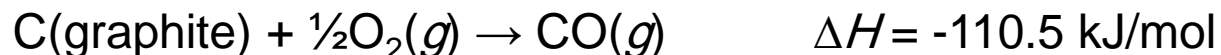
$$R = 8.314 \text{ J/K}\cdot\text{mol}, \quad T = 298 \text{ K}$$

$$\Delta E = \Delta H - RT \Delta n$$

$$= -566000 - (8.314 \times 298 \times -1) = -563522 \text{ J/mol} = -563.5 \text{ kJ/mol}$$

Practice Exercise

What is ΔE for the formation of 1 mole of CO at 1 atm and 25°C?



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

$$= -110500 - (8.314 \times 298 \times \frac{1}{2}) = -111739 \text{ J/mol} = -111.74 \text{ kJ/mol}$$

6.5

Calorimetry

In the laboratory, heat changes in physical and chemical processes are measured with a calorimeter; a closed container designed specifically for this purpose. Calorimetry; the measurement of **heat changes**.

- **Calorimetry**: the measurement of heat flow.
- **Calorimeter**: a device used measure heat flow.

Specific Heat and Heat Capacity

The **specific heat** (s) of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius. It has the units $\text{J/g}\cdot^{\circ}\text{C}$.

The **heat capacity** (C) of a substance is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius. Its units are J°C .

Specific heat is an intensive property whereas heat capacity is an extensive property.

The relationship between the heat capacity and specific heat of a substance is

$$C = m s$$

where m is the mass of the substance in grams. e.g., the specific heat of water is $4.184 \text{ J/g}^{\circ}\text{C}$, and the heat capacity of 60.0 g of water is $(60.0 \text{ g})(4.184 \text{ J/g}^{\circ}\text{C}) = 251 \text{ J}^{\circ}\text{C}$

The equations for calculating the heat change are given by

$$q = m s \Delta t$$

$$q = C \Delta t$$

where:

q: the amount of heat that has been absorbed or released in a particular process.

Δt : is the temperature change; $\Delta t = t_{final} - t_{initial}$

The sign convention for q is the same as that for enthalpy change;

q is - positive for endothermic processes, and

- negative for exothermic processes.

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 ₂ O	4.184
CH ₃ CH ₂ OH	2.460

Notice that the specific heat of liquid water is higher than those of the other substances listed. The high specific heat of water affects Earth's climate because it makes the temperatures of the oceans relatively resistant to change. It also is very important in maintaining a constant temperature in our bodies.

EXAMPLE

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.

$$\begin{aligned}q &= m s \Delta t \\&= (466 \text{ g}) (4.184 \text{ J/g } ^\circ\text{C}) (74.60^\circ\text{C} - 8.50^\circ\text{C}) \\&= 1.29 \times 10^5 \text{ J} = 129 \text{ kJ.}\end{aligned}$$

Practice Exercise

An iron bar of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

6.6

Standard enthalpy of formation and reaction

The reference point for all enthalpy expressions is called the standard enthalpy of formation (ΔH_f°).

Substances are said to be in the standard state at 1 atm and 25°C, hence the term “standard enthalpy.” The superscript ° represents standard-state conditions (1 atm), and the subscript “f” stands for formation.

The **standard enthalpy of formation** of a compound is the heat change that results when **1 mole** of the compound is formed from its elements at **1 atm** and **25°C**.



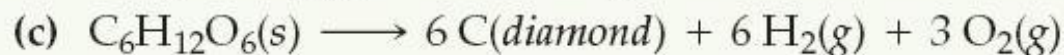
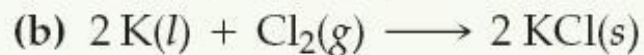
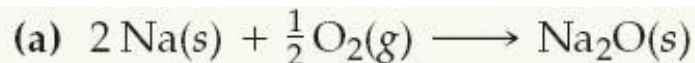
Example



- The elemental source of oxygen is O_2 , not O or O_3 , because O_2 is the stable form of oxygen at standard conditions.
- Similarly, the elemental source of carbon is graphite and not diamond, because graphite is the more stable (lower energy).
- Likewise, the most stable form of hydrogen under standard conditions is $\text{H}_2(\text{g})$.

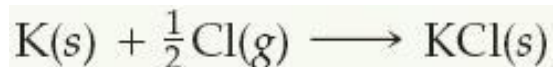
Example

For which of the following reactions at 25 °C would the enthalpy change represent a standard enthalpy of formation? For each that does not, what changes are needed to make it an equation whose ΔH is an enthalpy of formation?

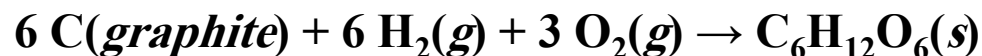


(a) 1 mol Na_2O is formed from the elements sodium and oxygen in their proper states, solid Na and O_2 gas, respectively. Therefore, the enthalpy change for reaction (a) corresponds to a standard enthalpy of formation.

(b) Potassium is given as a liquid. It must be changed to the solid form, its standard state at 25°C. Furthermore, two moles of product are formed, so the enthalpy change for the reaction as written is twice the standard enthalpy of formation of $\text{KCl}(s)$. The equation for the formation reaction of 1 mol of $\text{KCl}(s)$ is



(c) The reaction does not form a substance from its elements. Instead, a substance decomposes to its elements, so this reaction must be reversed. Next, the element carbon is given as diamond, whereas graphite is the standard state of carbon at 25°C and 1 atm. The correct equation should be



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

-e.g., Molecular oxygen (O_2) is more stable than the other allotropic form of oxygen, ozone (O_3), at 1 atm and 25°C . Thus, we can write $\Delta H^\circ_f(O_2) = 0$, but $\Delta H^\circ_f(O_3) = 142.2 \text{ kJ/mol}$.

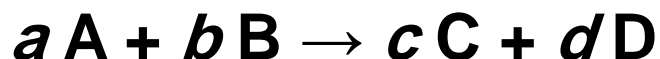
-e.g., graphite is a more stable allotropic form of carbon than diamond at 1 atm and 25°C , so we have $\Delta H^\circ_f(\text{C, graphite}) = 0$ and $\Delta H^\circ_f(\text{C, diamond}) = 1.90 \text{ kJ/mol}$.

Standard enthalpies of formation of some substances at 25°C

Substance	ΔH°_f (kJ/mol)	Substance	ΔH°_f (kJ/mol)
$O(g)$	249.4	$C_2H_2(g)$ acetylene	226.7
$O_2(g)$	0	$C_6H_6(l)$ benzene	49.0
$O_3(g)$	142.2	$C_6H_{12}O_6(s)$ glucose	-1273
$Cl_2(g)$	0	$C_{12}H_{22}O_{11}(s)$ sucrose	-2221
$H_2O_2(l)$	-187.6	NH_3 ammonia	-46.19
$H_2O(g)$	-241.8	$HF(g)$	-268.6
$H_2O(l)$	-285.8	$HCl(g)$	-92.3
$CO(g)$	-110.5	$HBr(g)$	-36.23
$CO_2(g)$	-393.5	$HI(g)$	25.9
$CH_4(g)$ methane	-74.8	$NaCl(s)$	-410.9
$C_2H_6(g)$ ethane	-84.68	$AgCl(s)$	-127
$C_3H_8(g)$ propane	-103.85	$NaHCO_3(s)$ sodium bicarbonate	-947.7
$CH_3OH(l)$ methanol	-238.6	$Na_2CO_3(s)$ sodium carbonate	-1130.9
$C_2H_5OH(l)$ ethanol	-277.7	$CaCO_3(s)$ calcium carbonate	-1207.1

The importance of the standard enthalpies of formation is that once we know their values, we can readily calculate the **standard enthalpy of reaction**, $\Delta H_{\text{rxn}}^{\circ}$, defined as the enthalpy of a reaction carried out at 1 atm.

e.g., consider the hypothetical reaction



where a , b , c , and d are stoichiometric coefficients. For this reaction

$$\Delta H_{\text{rxn}}^{\circ} = [c\Delta H_{\text{f}}^{\circ}(\text{C}) + d\Delta H_{\text{f}}^{\circ}(\text{D})] - [a\Delta H_{\text{f}}^{\circ}(\text{A}) + b\Delta H_{\text{f}}^{\circ}(\text{B})]$$

We can generalize this Equation as

$$\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_{\text{f}}^{\circ}(\text{products}) - \sum m\Delta H_{\text{f}}^{\circ}(\text{reactants})$$

where m and n denote the stoichiometric coefficients for the reactants and products,

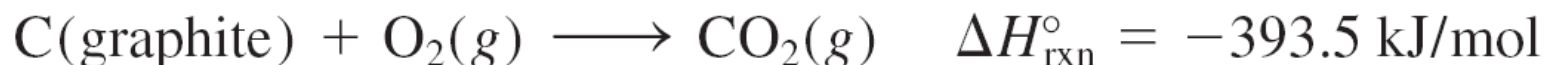
To use this Equation to calculate $\Delta H_{\text{rxn}}^{\circ}$, we must know the $\Delta H_{\text{f}}^{\circ}$ values of the compounds that take part in the reaction. These values can be determined by applying direct method or indirect method.

The Direct Method

This method of measuring ΔH_f° works for compounds that can be readily synthesized from their elements.

Example,,,

Calculate the enthalpy of formation of carbon dioxide $\text{CO}_2(\text{g})$.



$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \Delta H_f^\circ(\text{CO}_2, \text{g}) - [\Delta H_f^\circ(\text{C, graphite}) + \Delta H_f^\circ(\text{O}_2, \text{g})] \\ &= -393.5 \text{ kJ/mol}\end{aligned}$$

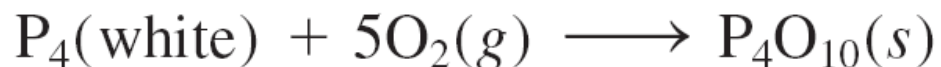
Because both graphite and O_2 are stable allotropic forms of the elements,

$\Delta H_f^\circ(\text{C, graphite})$ and $\Delta H_f^\circ(\text{O}_2, \text{g}) = \text{zero}$

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$$

Other compounds that can be studied by the direct method are; **SF₆**, **P₄O₁₀** and **CS₂**. The equations representing their syntheses are



Note that S(rhombic), P(white), C(graphite) are the most stable allotropes of sulfur, phosphorus and carbon, respectively, at 1 atm and 25°C, so their ΔH_f° values = 0.

Substance	ΔH_f° (kJ/mol)
S(rhombic)	0
S(monoclinic)	0.30
C(graphite)	0
C(diamond)	1.9
P(white)	0
O ₂ (g)	0
F ₂ (g)	0

The Indirect Method

Many compounds cannot be directly synthesized from their elements. In these cases, ΔH_f can be determined by Hess's law.

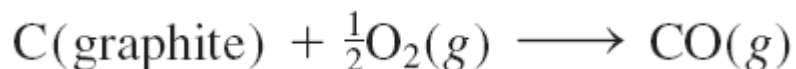
Hess's law stated that; *when reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.*

In other words, if a reaction is carried out in a number of steps, ΔH for the overall reaction is the sum of ΔH for each individual step.

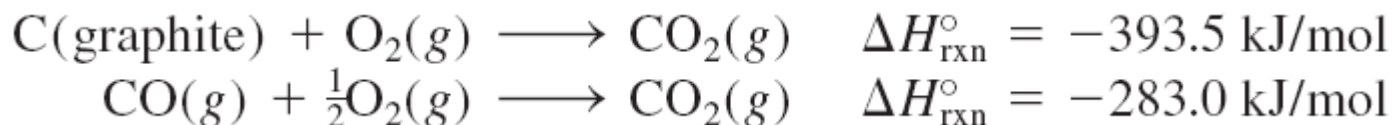
Enthalpy change is a state function, its independent on the number of steps or the nature of the path by which the reaction is carried out.

Example

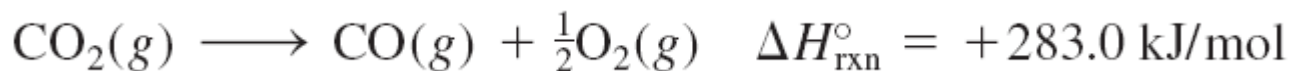
Let's say we are interested in the standard enthalpy of formation of carbon monoxide (CO). We might represent the reaction as



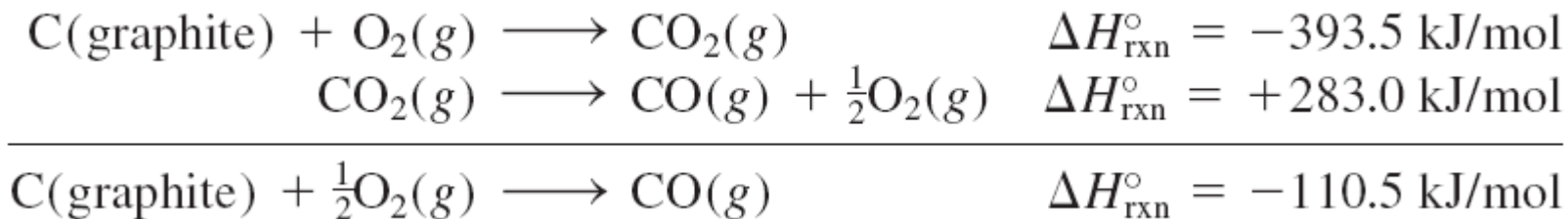
However, burning graphite also produces some CO_2 , so we cannot measure the enthalpy change for CO directly as shown. Instead, we must employ an indirect route, based on Hess's law. It is possible to carry out the following two separate reactions, which do go to completion:



First, we reverse the second Equation

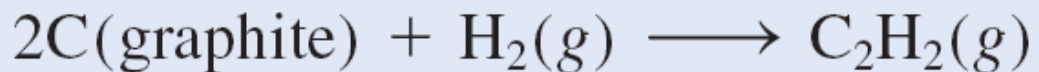


Because chemical equations can be added and subtracted just like algebraic equations,

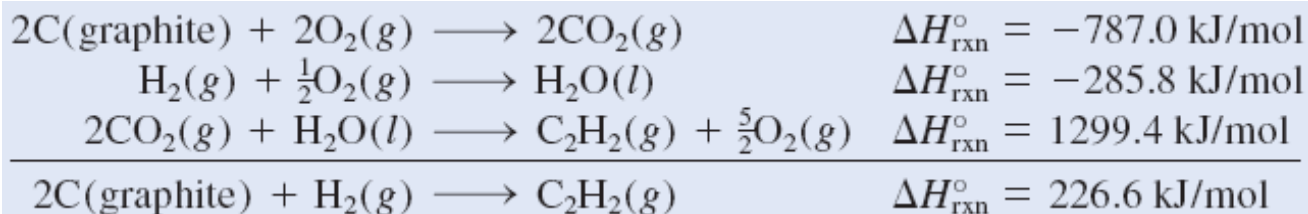
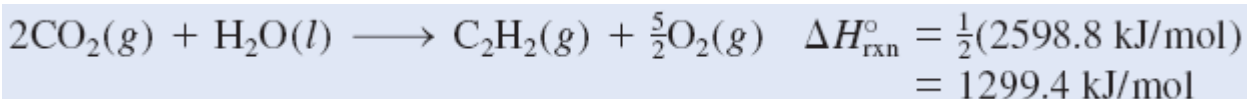
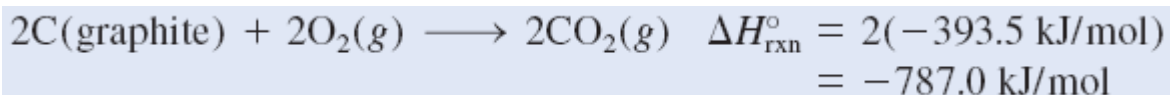
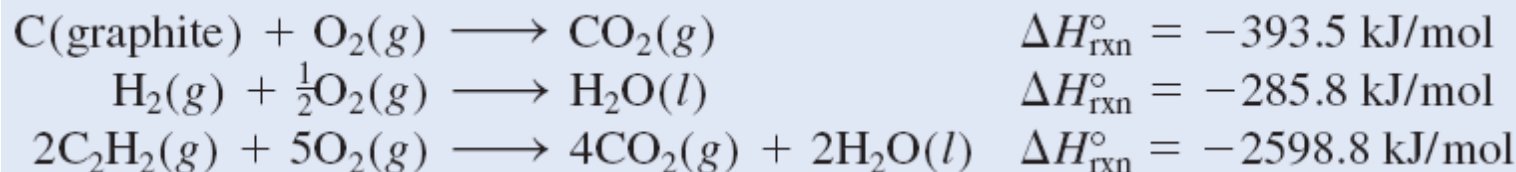


EXAMPLE

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:



The equations for each step and the corresponding enthalpy changes are



EXAMPLE

The thermite reaction involves aluminum and iron(III) oxide



This reaction is highly exothermic and the liquid iron formed is used to weld metals. Calculate the heat released in kJ/g of Al reacted with Fe_2O_3 .

$\Delta H_f^\circ(\text{Fe}(l)) = 12.40 \text{ kJ/mol}$, $\Delta H_f^\circ(\text{Al}_2\text{O}_3(s)) = -1669.8 \text{ kJ/mol}$, $\Delta H_f^\circ(\text{Fe}_2\text{O}_3(s)) = -822.2 \text{ kJ/mol}$.

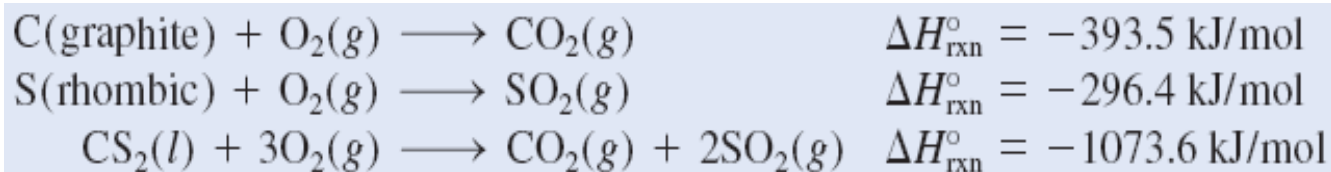
$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= [\Delta H_f^\circ(\text{Al}_2\text{O}_3) + 2\Delta H_f^\circ(\text{Fe})] - [2\Delta H_f^\circ(\text{Al}) + \Delta H_f^\circ(\text{Fe}_2\text{O}_3)] \\ &= [(-1669.8 \text{ kJ/mol}) + 2(12.40 \text{ kJ/mol})] - [2(0) + (-822.2 \text{ kJ/mol})] \\ &= -822.8 \text{ kJ/mol}\end{aligned}$$

This is the amount of heat released for two moles of Al reacted. to convert to kJ/g Al. The molar mass of Al is 26.98 g, so

$$\begin{aligned}\text{heat released per gram of Al} &= \frac{-822.8 \text{ kJ}}{2 \text{ mol Al}} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \\ &= -15.25 \text{ kJ/g}\end{aligned}$$

Practice Exercise

Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that



Practice Exercise

Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. Calculate the heat released (in kilojoules) per gram of the compound reacted with oxygen. The standard enthalpy of formation of benzene is 49.04 kJ/mol.

