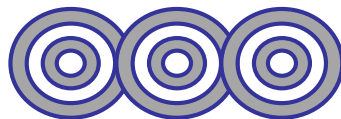***Chemistry, The Central Science*, 11th edition**
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Chapter 5
Thermochemistry

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Energy is necessary for all life. The study of energy and its transformations is known as **thermodynamics** (Greek: therme, ''heat'', dynamis, ''power'').

Thermodynamic aspects that involve the relationships between chemical reactions and energy changes involving heat. Is called **thermochemistry**.

5.1
The Nature of Energy

Energy

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

- **Work** is the energy used to cause an object with mass to move against a force.

- **Heat** is the energy used to cause the temperature of an object to increase.

Kinetic energy

is energy an object possesses by virtue of its motion.

$$E_k = \tfrac{1}{2}\, mv^2$$

Where E_k: is the kinetic energy, m: is the mass of the object, υ: is the object speed.

Potential Energy

is energy an object possesses by virtue of its position relative to other objects or chemical composition.

$$E_p = mgh$$

Where E_p: is the potential energy, m: is the mass of the object, h is the height of the object relative to some reference height (relative to its being on the Earth's surface), and g is the gravitational constant, 9.8 m/s^2.

Electrostatic potential energy is one of the most important forms of potential energy in chemistry, which arises from the interactions between charged particles.

Electrostatic potential energy, E_d, is the attraction between two oppositely charged particles, a apart: E_d, is proportional to the electrical charges on the two interacting objects, Q_1 and Q_2, and is inversely proportional to the distance d separating them.

$$E_d = \frac{\kappa Q_1 Q_2}{d}$$

The constant, $\kappa = 8.99 \times 10^9$ J-m/C^2.

When the two particles have the same sign, the two charges repel one another, pushing them apart; E_{el} is positive. When they have opposite signs, they attract one another, pulling them toward each other; E_{el} is negative. The lower the energy of a system, the more stable it is. Thus, the more strongly opposite charges interact, the more stable the system.

Units of Energy

The SI unit of energy is the **joule (J)**.

$$1\,J = 1\,kg\text{-}m^2/s^2$$

An older, non-SI unit is still in widespread use: the **calorie (cal)**.
1 cal = 4.184 J

A nutritional Calorie:
1 Cal = 1000 cal = 1 kcal

A calorie was originally defined as the amount of energy required to raise the temperature of 1 g of water from 14.5 to 15.5 ^{o}C. Its now defined in terms of the joule.

System and Surroundings

The portion we single out for study is called the **system**. The system includes the molecules we want to study. (part of the universe we are interested in). Here, the hydrogen and oxygen gas molecules.

The **surroundings** are everything else (the rest of the universe). Here, the cylinder, piston and everything beyond (including us).

- System may be open, closed, or isolated.
- An **open** system is one in which matter and energy can be exchanged with the surroundings.
- A **closed** system can exchange energy but not matter (like this example).
- An **isolated** system is one in which neither energy nor matter can exchange with the surroundings.

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) + energy$$

Work

Energy is transferred between systems and surroundings in two general ways, as **work** or **heat**.

Energy used to move an object over some distance is **work**.

$$w = F \times d$$

where w is work, F is the force, and d is the distance over which the force is exerted.

Heat

Energy can also be transferred as **heat**.

Heat is the energy transferred from a hotter object to a colder one.

Heat is the energy transferred between a system and its surroundings because of their difference in temperature.

Conversion of Energy

Energy can be converted from one type to another.

For example, the cyclist above has potential energy as she sits on top of the hill. As she coasts down the hill, her potential energy is converted to kinetic energy. At the bottom, all the potential energy she had at the top of the hill is now kinetic energy (**energy does not disappear**).

Sample Exercise: Describing and Calculating Energy Changes

A bowler lifts a 5.4-kg bowling ball from ground level to a height of 1.6 m and then drops the ball back to the ground. **(a)** What happens to the potential energy of the bowling ball as it is raised from the ground? **(b)** What quantity of work, in J, is used to raise the ball? **(c)** After the ball is dropped, it gains kinetic energy. If we assume that all of the work done in part (b) has been converted to kinetic energy by the time the ball strikes the ground, what is the speed of the ball at the instant just before it hits the ground?

Solution

(a) Because the bowling ball is raised to a greater height above the ground, its potential energy increases.
(b) $w = F \times d$, while $F = m \times g$:

$$w = F \times d = m \times g \times d = (5.4 \text{ kg})(9.8 \text{ m/s}^2)(1.6 \text{ m}) = 85 \text{ kg-m}^2/\text{s}^2 = 85 \text{ J}$$

Thus, the bowler has done 85 J of work to lift the ball to a height of 1.6 m.

(c) When the ball is dropped, its potential energy is converted to kinetic energy. At the instant just before the ball hits the ground, we assume that the kinetic energy is equal to the work done in part (b), 85 J:

$$E_k = \tfrac{1}{2} mv^2 = 85 \text{ J} = 85 \text{ kg-m}^2/\text{s}^2$$

$$v^2 = \left(\frac{2E_k}{m}\right) = \left(\frac{2(85 \text{ kg-m}^2/\text{s}^2)}{5.4 \text{ kg}}\right) = 31.5 \text{ m}^2/\text{s}^2$$

$$v = \sqrt{31.5 \text{ m}^2/\text{s}^2} = 5.6 \text{ m/s}$$

5.2
The First Law of Thermodynamics

First Law of Thermodynamics

- 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.
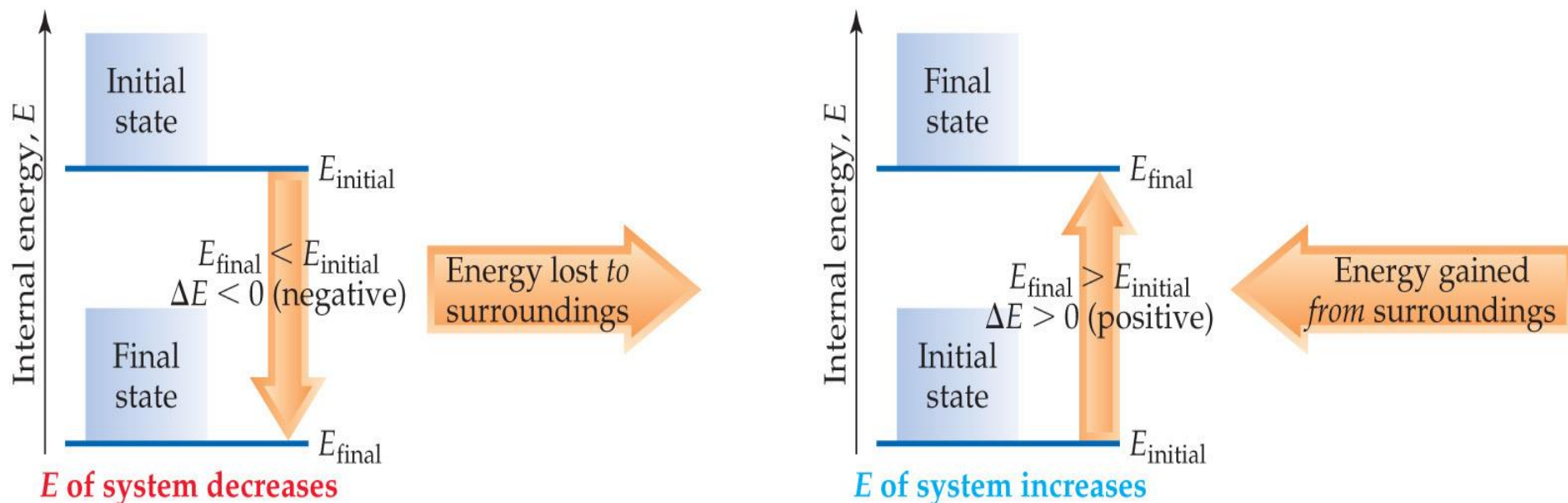
Internal Energy

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, Δ**E**, is the final energy of the system minus the initial energy of the system:

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

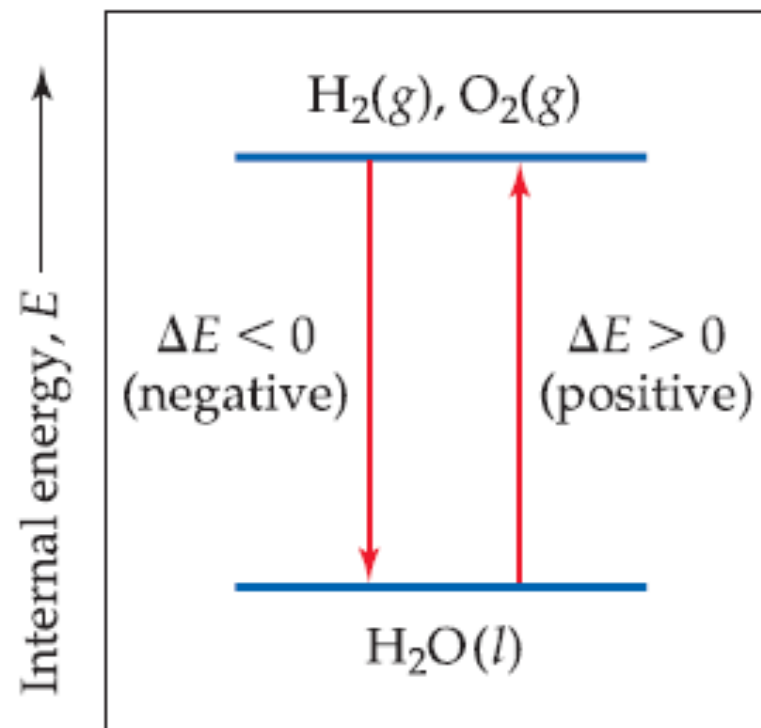Internal energy, E

Initial state

E_{initial}

$E_{\text{final}} < E_{\text{initial}}$
$\Delta E < 0$ (negative)

Final state

E_{final}

E of system decreases

Energy lost *to* surroundings

Internal energy, E

Final state

E_{final}

$E_{\text{final}} > E_{\text{initial}}$
$\Delta E > 0$ (positive)

Initial state

E_{initial}

E of system increases

Energy gained *from* surroundings

Changes in Internal Energy

If $\Delta E > 0$, $E_{final} > E_{initial}$
- Therefore, the system *absorbed* energy from the surroundings.
- This energy change is called **endergonic**.

If $\Delta E < 0$, $E_{final} < E_{initial}$
- Therefore, the system *released* energy to the surroundings.
- This energy change is called **exergonic**.

Energy diagram, shows that the internal energy of the H_2 and O_2 mixture is greater than that of H_2O.

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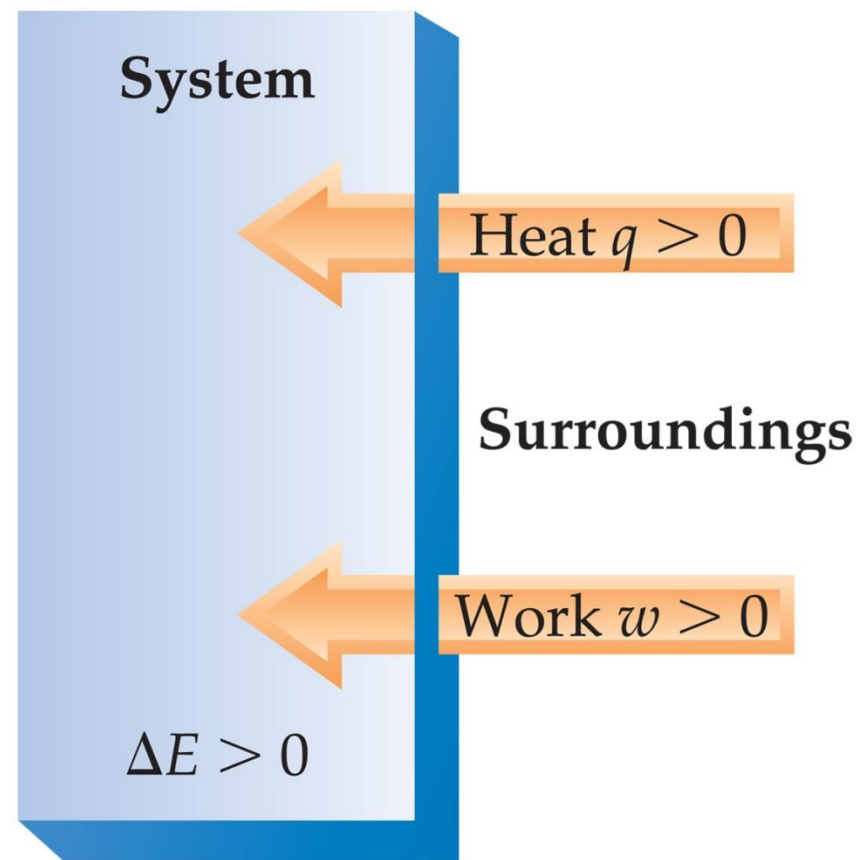
Heat gained by a system and work done on a system are both +ve quantities. Both increase the internal energy of the system. ΔE +ve quantity.

ΔE, q, w, and their **Signs**

TABLE 5.1 ■ Sign Conventions for q, w, and ΔE

For q	+ means system *gains* heat	− means system *loses* heat
For w	+ means work done *on* system	− means work done *by* system
For ΔE	+ means *net gain* of energy by system	− means *net loss* of energy by system

Sign Convention for q:

$q > 0$: Heat is transferred from the surroundings to the system

$q < 0$: Heat is transferred from the system to the surroundings

Sign Convention for w:

$w > 0$: Work is done by the surroundings on the system

$w < 0$: Work is done by the system on the surroundings

Sign of $\Delta E = q + w$

$q > 0$ and $w > 0$: $\Delta E > 0$

$q > 0$ and $w < 0$: The sign of ΔE depends on the magnitudes of q and w

$q < 0$ and $w > 0$: The sign of ΔE depends on the magnitudes of q and w

$q < 0$ and $w < 0$: $\Delta E < 0$

Sample Exercise: Relating Heat and Work to Changes of Internal Energy

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?

Solution

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 J and w = 480 kJ. Thus,

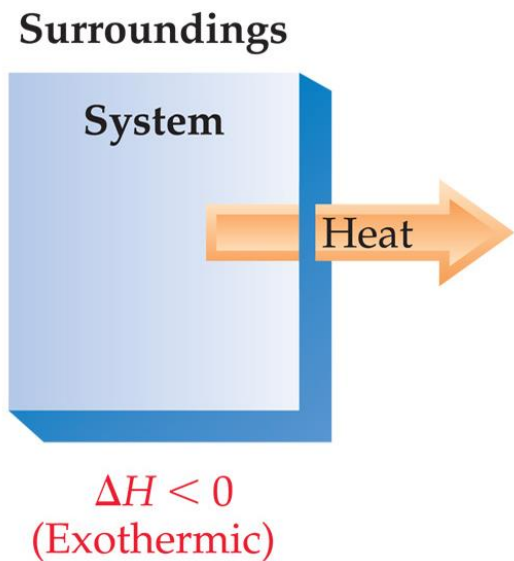$$\Delta E = q + w = (-1150 \text{ J}) + (480 \text{ J}) = -670 \text{ J}$$

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.
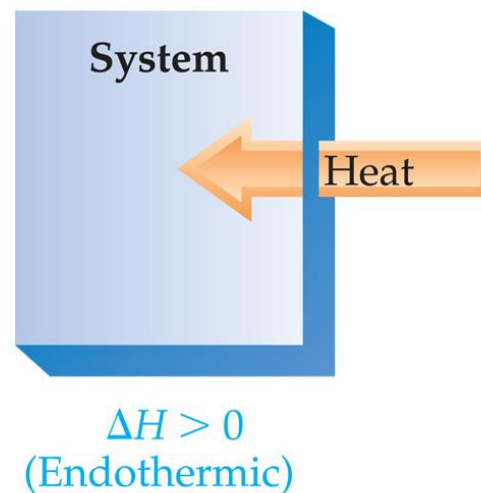
Exchange of Heat between System and Surroundings

When heat is absorbed by the system from the surroundings, the process is **endothermic**.
Endo- is a prefix meaning ''into''.
An endothermic reaction feels cold.

Surroundings

System

Heat

$\Delta H > 0$
(Endothermic)

Surroundings
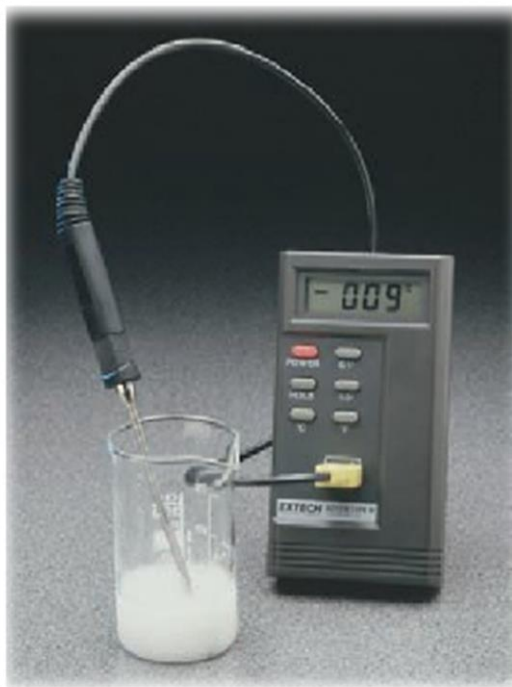
System

Heat

$\Delta H < 0$
(Exothermic)

When heat is released (lost) by the system into the surroundings, the process is **exothermic**.
Exo- is a prefix meaning ''out of''.
An exothermic reaction feels hot.

Examples of endothermic and exothermic reactions

When ammonium thiocyanate and barium hydroxide octahydrate are mixed at room temp., and endothermic reaction occurs:

$$2NH_4SCN(s) + Ba(OH)_2 \cdot 8H_2O(s) \longrightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

As a result, the temp. of the system drops from about $20°C$ to $-9°C$.

The reaction of powdered aluminum with Fe_2O_3 (the thermite reaction) is highly exothermic. The reaction proceeds vigorously to form Al_2O_3 and molten iron:

$$2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(l)$$

State Functions

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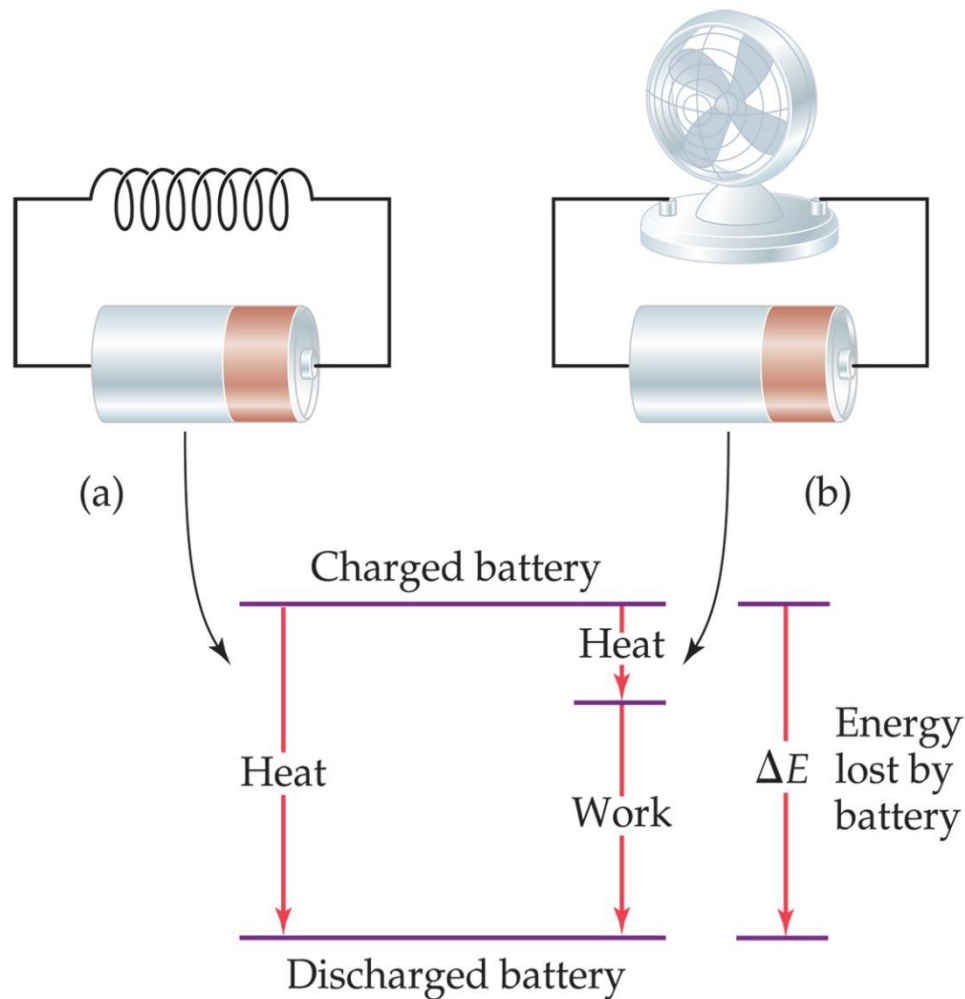
The conditions that influence internal energy include the temperature, pressure and the total quantity of matter in the system because energy in an extensive property.

50 g
H_2O (l)
100°C

50 g
H_2O (l)
25°C

50 g
H_2O (s)
0°C

Cooling

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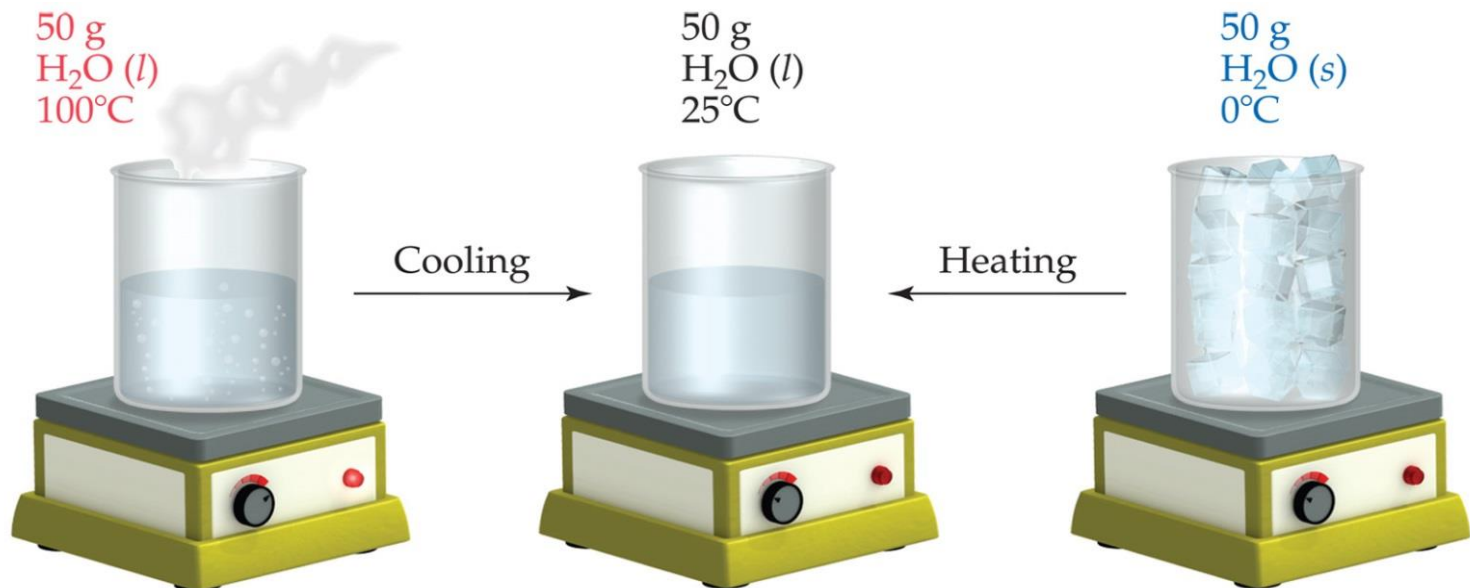
State function: depends only on the initial and final states of system, not on how the internal energy is used.

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)

(b)

Charged battery

Heat

Heat

Work

ΔE Energy lost by battery

Discharged battery

(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.
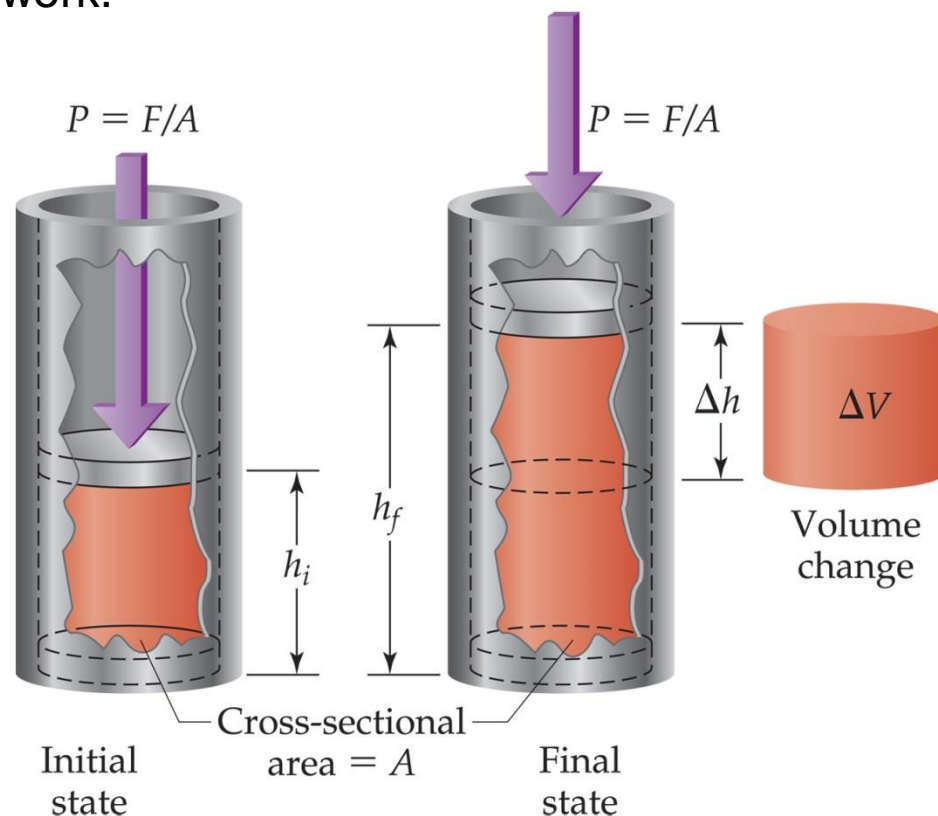
5.3
Enthalpy

Work

- Chemical reactions can absorb or release heat.
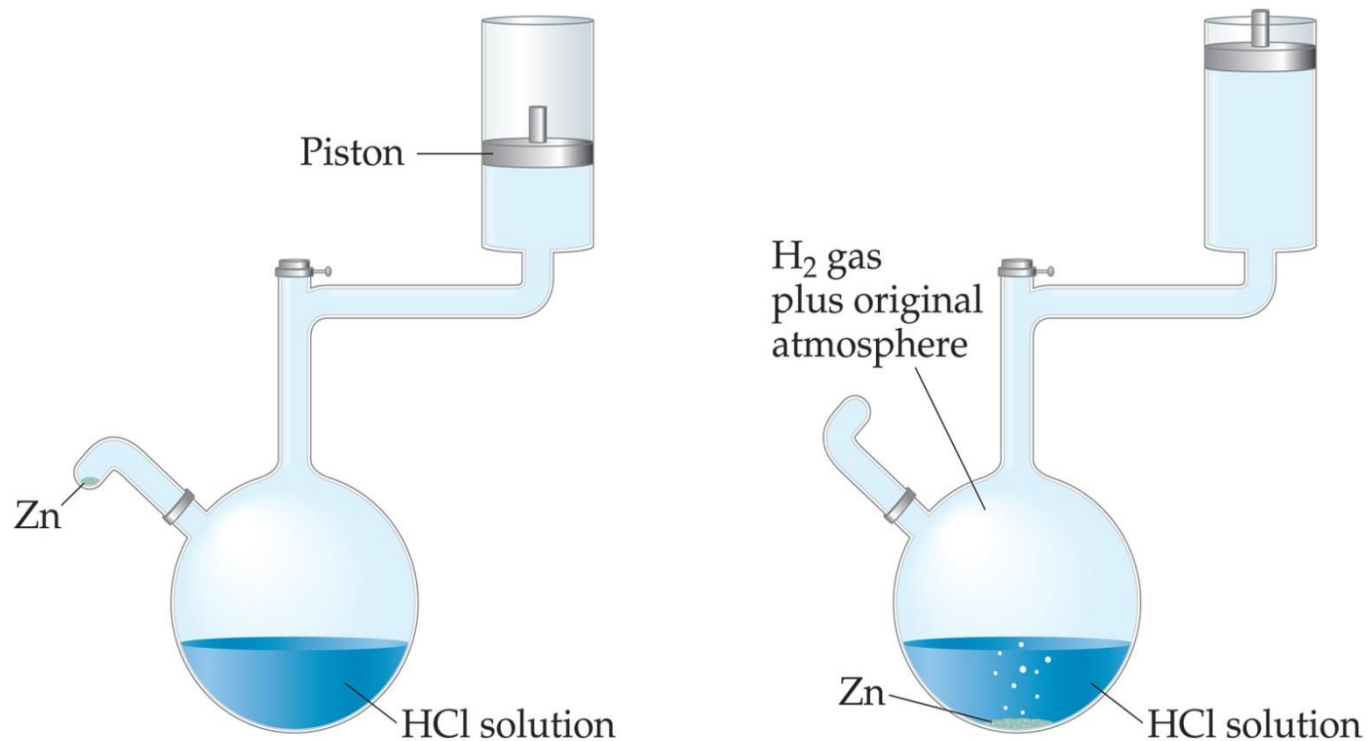- However, they also have the ability to do work.

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

  Zn(s) + 2H$^+$(aq) → Zn^{2+}(aq) + H$_2$(g)

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

$$w = -P\,\Delta V$$

$P = F/A$

$P = F/A$

h_i

h_f

Δh

ΔV

Volume change

Initial state

Cross-sectional area = A

Final state

A system that does work on its surroundings. Reaction of zinc metal with HCl at constant pressure. The piston is free to move up and down in its cylinder to maintain a constant pressure equal to atmospheric pressure inside the apparatus. When zinc is added to the acid solution, hydrogen (H_2) gas is evolved. The H_2 gas does work on the surroundings, raising the piston against atmospheric pressure to maintain constant pressure inside the reaction vessel.

$$w = -P\,\Delta V$$

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

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

Why the negative sign in the Equation ???

When the volume expands ΔV is positive and w is a negative quantities. That is, energy leaves the system as work, indicating that work is done by the system on the surroundings. On the other hand, when a gas is compressed, ΔV is a negative quantity.

Enthalpy

If a process takes place at constant pressure and the only work done is this pressure-volume work, we can account for heat flow during the process by measuring the **enthalpy** of the system.

Enthalpy, H: heat transferred between the system and surroundings carried out under constant pressure (Greek word enthalpein, meaning ''to worm'').

Enthalpy is the internal energy plus the product of pressure and volume:

$$H = E + PV$$

Enthalpy is a state function.

If the process occurs at constant pressure,

$$\Delta H = \Delta(E + PV)$$
$$= \Delta E + P\,\Delta V$$

Since $\Delta E = q + w$ and $w = -P\Delta V$, we can substitute these into the enthalpy expression:

$$\Delta H = \Delta E + P\Delta V$$
$$\Delta H = (q + w) - w$$

$$\Delta H = q_p$$

So, at constant pressure, the change in enthalpy is the heat gained or lost.

Because q_p is something we can either measure or readily calculate, and because so many physical and chemical changes of interest to us occur at constant pressure, enthalpy is a more useful function than internal energy.

For most reactions the difference in ΔH and ΔE is small because $P\Delta V$ is small.

Endothermicity and Exothermicity

When ΔH, is positive (+ve), the system gains heat from the surroundings. **A process is endothermic.**

When ΔH, is negative (-ve), the surroundings gain heat from the system. **A process is exothermic.**

$\Delta H > 0$
Endothermic

$\Delta H < 0$
Exothermic
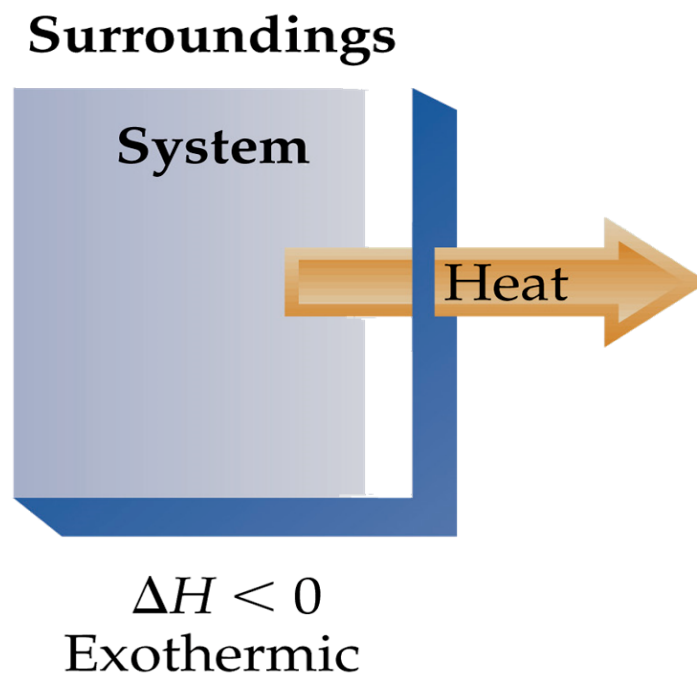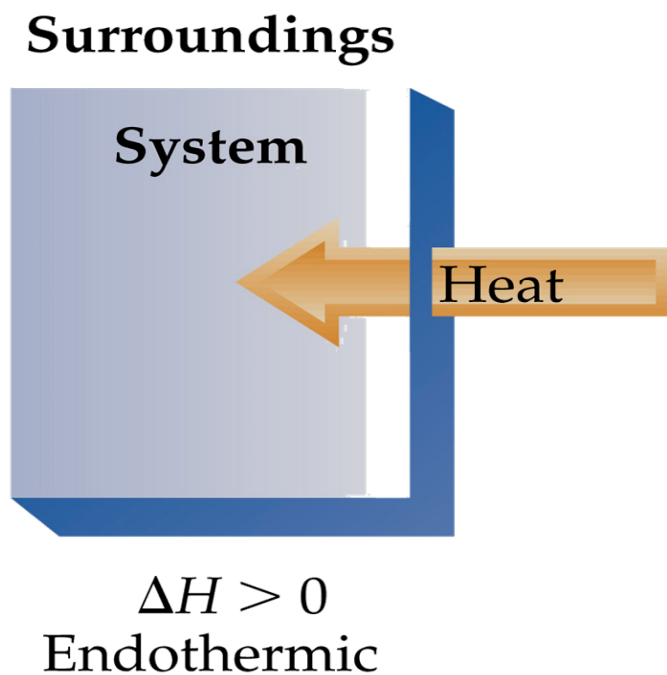
$$P = F/A$$

Magnitude of work = force × distance = $F \times \Delta h$

Magnitude of work = $F \times \Delta h = P \times A \times \Delta h$

$$= P \times \Delta V$$

Because the system (the confined gas) is doing work on the surroundings, the work is a negative quantity:

$$w = -P \, \Delta V$$

If **P-V** work is the only work that can be done, we can substitute the above equation to give:

$$\Delta E = q + w = q - P \, \Delta V$$

When a reaction is carried out in a constant volume container ($\Delta V = 0$), the heat transferred equals the change in internal energy:

$$\boxed{\Delta E = q_V} \qquad \text{(constant volume)}$$

Most reactions are run under constant pressure conditions. In this case the equation becomes:

$$\Delta E = q_P - P \, \Delta V \text{ or}$$

$$q_P = \Delta E + P \, \Delta V \qquad \text{(constant pressure)} \qquad \boxed{\Delta H = q_P}$$

Sample Exercise: Determining the Sign of ΔH

Indicate the sign of the enthalpy change, ΔH, in each of the following processes carried out under atmospheric pressure, and indicate whether the process is endothermic or exothermic:

(a) An ice cube melts;

(b) 1 g of butane (C_4H_{10}) is combusted in sufficient oxygen to give complete combustion to CO_2 and H_2O.

Solution

In (a) the water that makes up the ice cube is the system. The ice cube absorbs heat from the surroundings as it melts, so ΔH is positive and the process is endothermic.

In (b) the system is the 1 g of butane and the oxygen required to combust it. The combustion of butane in oxygen gives off heat, so ΔH is negative and the process is exothermic.
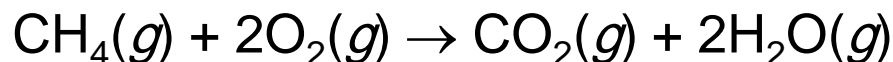
5.4
Enthalpies of Reaction

Enthalpy of Reaction

The change in enthalpy, *ΔH*, is the enthalpy of the products minus the enthalpy of the reactants:

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$
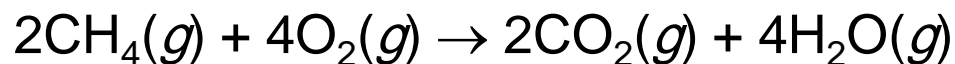
$$= H_{\text{products}} - H_{\text{reactants}}$$

This quantity, Δ*H*, is called the **enthalpy of reaction**, or the **heat of reaction**.
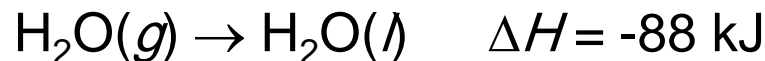
Enthalpy Guidelines

1. **E**nthalpy 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.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$
$$\Delta H = -890 \text{ kJ}$$

$$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$
$$\Delta H = -1780 \text{ kJ}$$

$$H_2O(g) \rightarrow H_2O(l) \quad \Delta H = -88 \text{ kJ}$$

Condensation of gaseous water to form liquid water

CH$_4$(g) + 2 O$_2$(g)

Enthalpy

$\Delta H_1 = -890$ kJ

$\Delta H_2 = 890$ kJ

CO$_2$(g) + 2 H$_2$O(l)

$\Delta H_2 = -\Delta H_1$
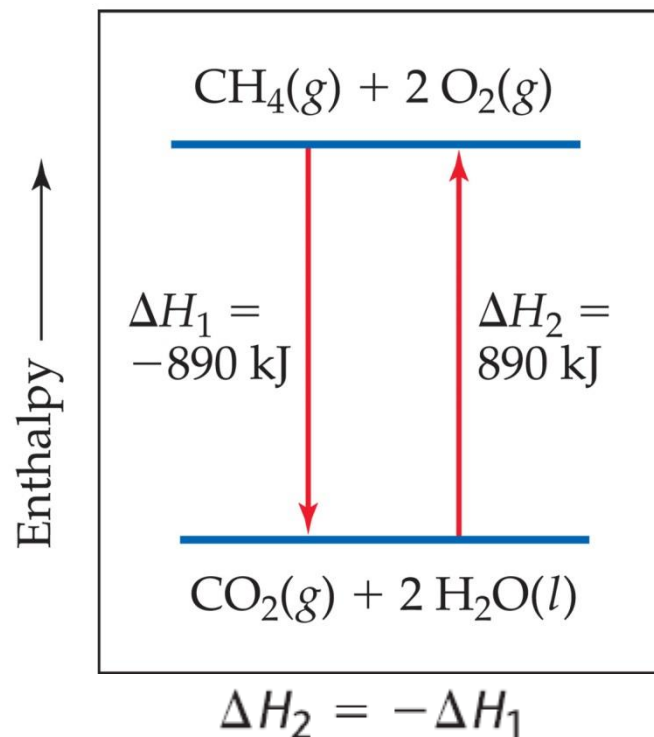
Sample Exercise: Relating ΔH to Quantities of Reactants and Products

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

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = \text{-890 kJ}$$
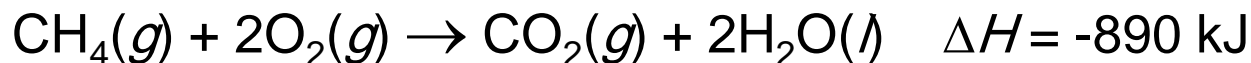
Solution

By adding the atomic weights of C and 4 H, we have 1 mol CH_4 = 16.0 g CH_4. We can use the appropriate conversion factors to convert grams of CH_4 to moles of CH_4 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.

5.5
Calorimetry

Since we cannot know the exact enthalpy of the reactants and products experimentally, we measure ΔH through **calorimetry**, by measuring the heat flow accompanying a reaction at constant pressure.

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

Heat Capacity and Specific Heat

- The amount of energy required to raise the temperature of a substance by 1 K (or 1°C) is its **heat capacity**, C.

- Molar heat capacity, C_m is the heat capacity of 1 mol of a substance.

- **Specific heat capacity** (**specific heat, C_s**) is the amount of energy required to raise the temperature of 1 g of a substance by 1 K.

q is the quantity of heat that a substance has gained or lost.

$$\text{Specific heat} = \frac{(\text{quantity of heat transferred})}{(\text{grams of substance}) \times (\text{temperature change})}$$

$$C_s = \frac{q}{m \times \Delta T} \qquad \boxed{q = C_s \times m \times \Delta T}$$

e.g., 209 J is required to increase the temperature of 50.0 g of water by 1.00 K. thus, the specific heat of water is:

$$C_s = \frac{209 \text{ J}}{(50.0 \text{ g})(1.00 \text{ K})} = 4.18 \frac{\text{J}}{\text{g-K}}$$

TABLE 5.2 ■ **Specific Heats of Some Substances at 298 K**

Elements		Compounds	
Substance	**Specific Heat (J/g-K)**	**Substance**	**Specific Heat (J/g-K)**
$N_2(g)$	1.04	$H_2O(l)$	4.18
$Al(s)$	0.90	$CH_4(g)$	2.20
$Fe(s)$	0.45	$CO_2(g)$	0.84
$Hg(l)$	0.14	$CaCO_3(s)$	0.82

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.

Sample Exercise: Relating Heat, Temperature Change, and Heat Capacity

How much heat is needed to warm 250 g of water (about 1 cup) from 22 °C to near its boiling point, 98 °C? The specific heat of water is 4.18 J/g-K.

Solution

$$\Delta T = 98\,°C - 22\,°C = 76\,°C = 76\,K$$

$$q = C_s \times m \times \Delta T$$

$$= (4.18\,\text{J/g-K})(250\,\text{g})(76\,\text{K}) = 7.9 \times 10^4\,\text{J}$$

What is the molar heat capacity of water?

The molar heat capacity is the heat capacity of one mole of substance.

For 1.0 g, $C_s = 4.18$ J
For 18 g, $C_s = 4.18 \times 18 = 75.2$ J

$$1\,\text{mol}\,H_2O = 18.0\,\text{g}\,H_2O$$

$$C_m = \left(4.18\,\frac{\text{J}}{\text{g-K}}\right)\left(\frac{18.0\,\text{g}}{1\,\text{mol}}\right) = 75.2\,\text{J/mol-K}$$

Constant Pressure Calorimetry

For many reactions, such as those occurring in solution, it is easy to control pressure so that ΔH is measured directly.
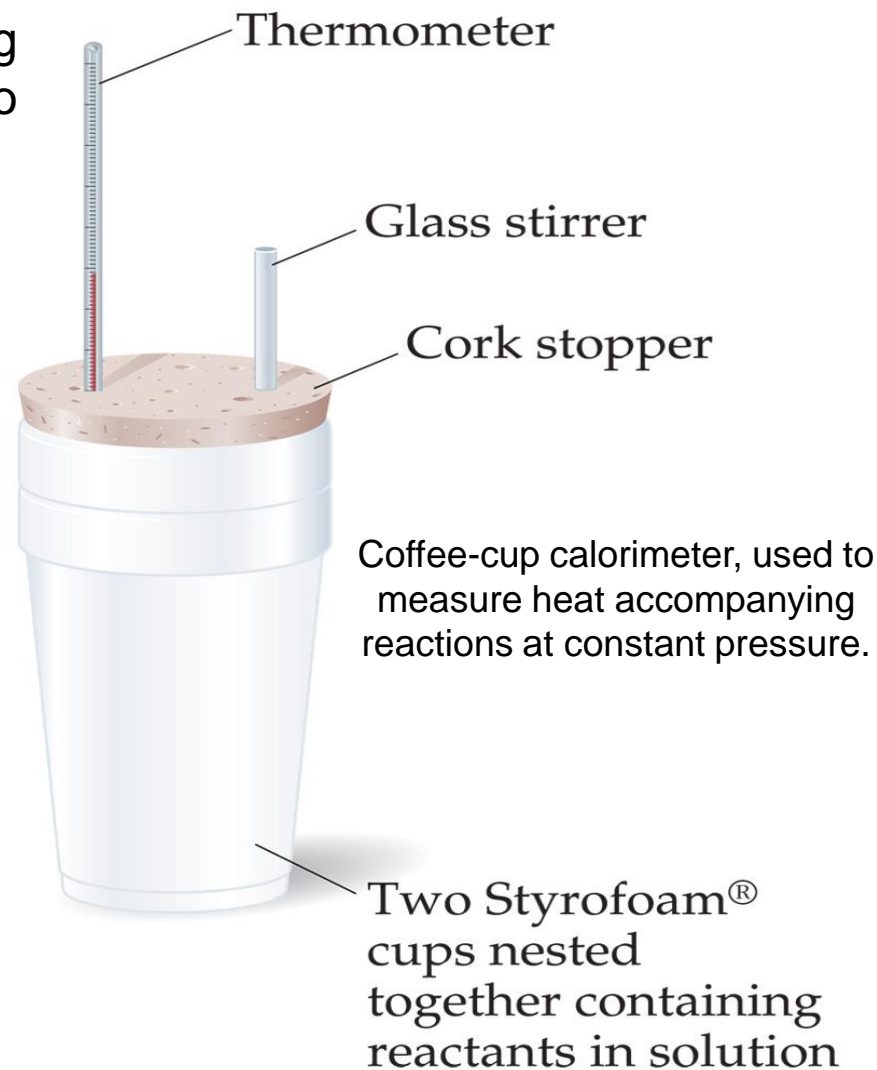
$$q_p = \Delta H$$

By carrying out a reaction in aqueous solution in a simple calorimeter such as **Coffee-cup**, one can indirectly measure the heat change for the system by measuring the heat change for the water in the calorimeter.

Because the specific heat for water is well known (4.184 J/g-K), we can measure ΔH for the reaction with this equation:

$$q_{soln} = -\, q_{rxn}$$

$$q_{soln} = grams\ of\ soln. \times specific\ heat\ of\ soln. \times \Delta T = -\, q_{rxn}$$

Thermometer

Glass stirrer

Cork stopper

Coffee-cup calorimeter, used to measure heat accompanying reactions at constant pressure.

Two Styrofoam® cups nested together containing reactants in solution

Sample Exercise: Measuring ΔH Using a Coffee-Cup Calorimeter

When a student mixes 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 °C to 27.5 °C. Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming that the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100 mL, that its density is 1.0 g/mL, and that its specific heat is 4.18 J/g-K.

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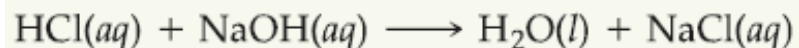
Solution

$$(100 \text{ mL})(1.0 \text{ g/mL}) = 100 \text{ g}$$

$$\Delta T = 27.5\,°C - 21.0\,°C = 6.5\,°C = 6.5 \text{ K}$$

$$q_{rxn} = -C_s \times m \times \Delta T$$

$$= -(4.18 \text{ J/g-K})(100 \text{ g})(6.5 \text{ K}) = -2.7 \times 10^3 \text{ J} = -2.7 \text{ kJ}$$

$$\Delta H = q_P = -2.7 \text{ kJ}$$

Because the process occurs at constant pressure,

To express the enthalpy change on a molar basis, we use the fact that the number of moles of HCl is given by the product of the respective solution volumes 50 mL = 0.050 L) and concentrations (1.0 M = 1.0 mol/L):

$$(0.050 \text{ L})(1.0 \text{ mol/L}) = 0.050 \text{ mol}$$

$$\Delta H = -2.7 \text{ kJ}/0.050 \text{ mol} = -54 \text{ kJ/mol}$$
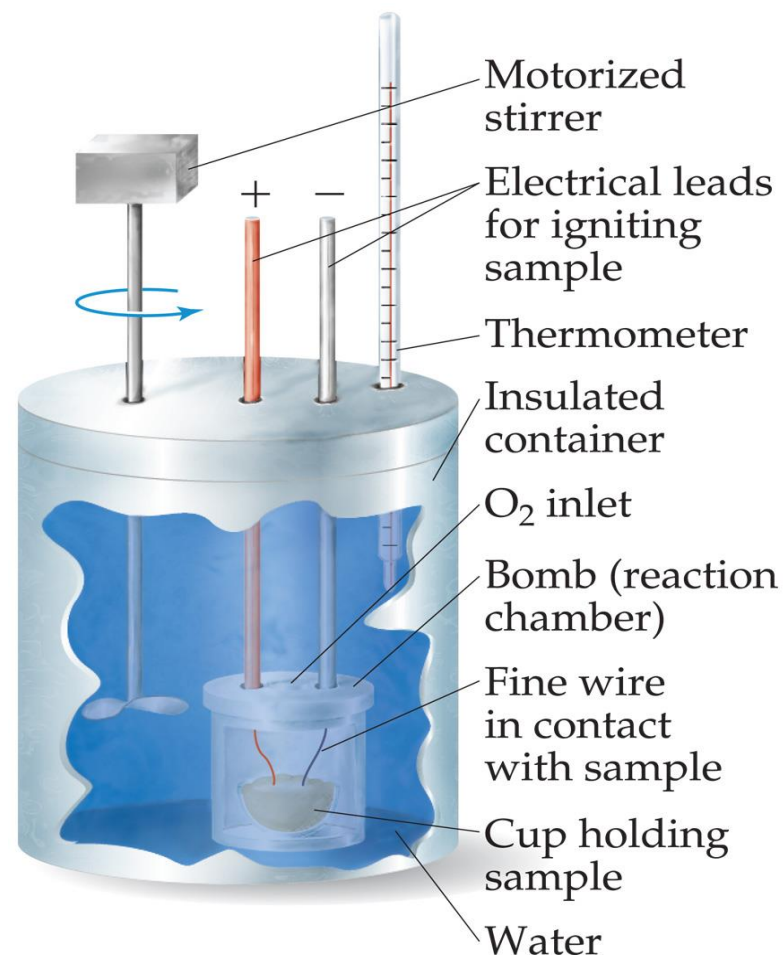
Bomb Calorimetry (Constant Volume Calorimetry)

Reactions can be carried out in a sealed "bomb" such as this one.

Usually study combustion, usually organic compounds react with excess oxygen.

The heat absorbed (or released) by the water is a very good approximation of the enthalpy change for the reaction.

Because the volume in the bomb calorimeter is constant, what is measured is really the change in internal energy, ΔE, not ΔH. For most reactions, the difference is very small.

$$q_{rxn} = -C_{cal} \times \Delta T$$

- Motorized stirrer
- Electrical leads for igniting sample
- Thermometer
- Insulated container
- O_2 inlet
- Bomb (reaction chamber)
- Fine wire in contact with sample
- Cup holding sample
- Water

Bomb calorimeter used to measure heat accompanying combustion reactions at constant volume.

Sample Exercise: Measuring q_{rxn} Using a Bomb Calorimeter

Methylhydrazine (CH_6N_2) is used as a liquid rocket fuel. The combustion of methylhydrazine with oxygen produces $N_2(g)$, $CO_2(g)$, and $H_2O(l)$:

$$2\ CH_6N_2(l) + 5\ O_2(g) \rightarrow 2\ N_2(g) + 2\ CO_2(g) + 6\ H_2O(l)$$

When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 °C to 39.50 °C. In a separate experiment the heat capacity of the calorimeter is measured to be 7.794 kJ/°C. Calculate the heat of reaction for the combustion of a mole of CH_6N_2.

Solution

$$\Delta T = (39.50\ °C - 25.00\ °C) = 14.50\ °C$$

$$q_{rxn} = -C_{cal} \times \Delta T = -(7.794\ kJ/°C)(14.50\ °C) = -113.0\ kJ$$

$$\left(\frac{-113.0\ kJ}{4.00\ g\ CH_6N_2}\right) \times \left(\frac{46.1\ g\ CH_6N_2}{1\ mol\ CH_6N_2}\right) = -1.30 \times 10^3\ kJ/mol\ CH_6N_2$$
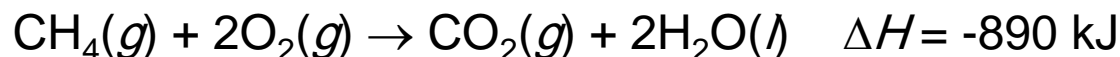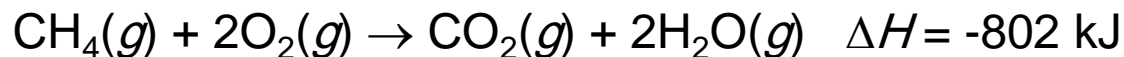
5.6
Hess's Law

Many enthalpies of reaction have been measure and tabulated. It is often possible to calculate the ΔH for a reaction from the tabulated ΔH values of other reactions. Thus, its not necessary to make calorimetric measurements for all reactions.
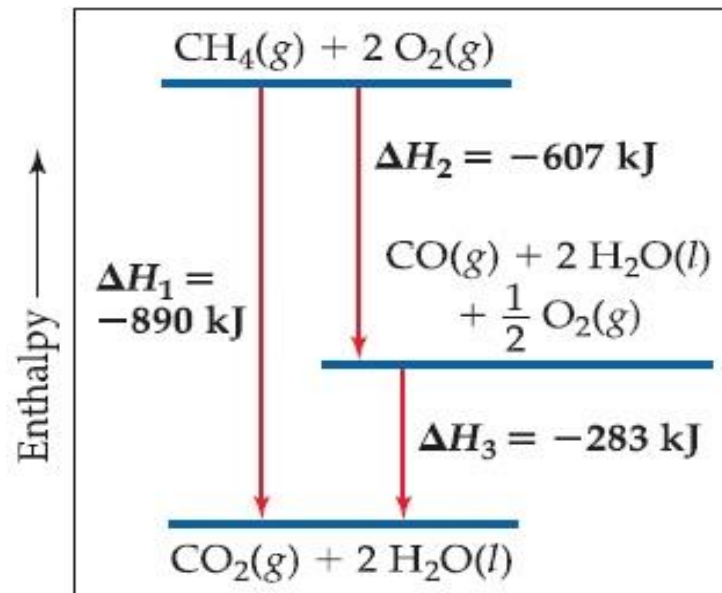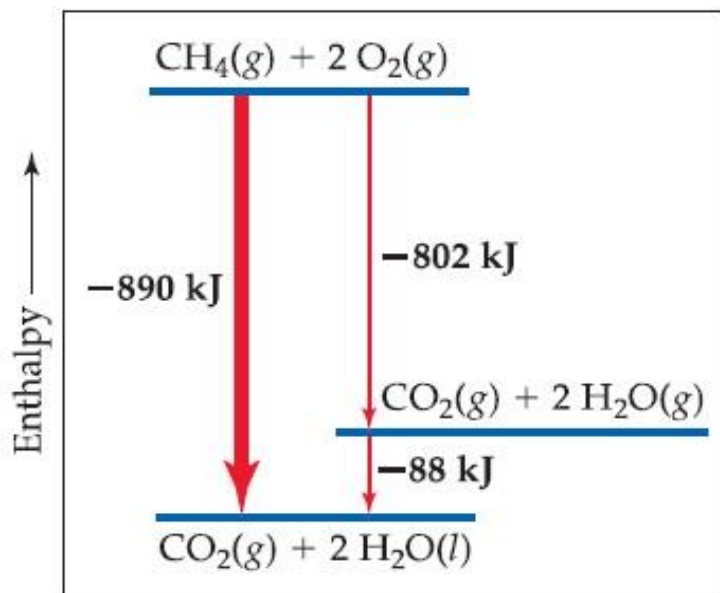
Enthalpy change is a state function, its independent on the number of steps or the nature of the path by which the reaction is carried out.

Hess's law: 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.

- **For example:**

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H = -802 \text{ kJ}$$
$$2H_2O(g) \rightarrow 2H_2O(l) \qquad\qquad\qquad\qquad \Delta H = -88 \text{ kJ}$$
$$\overline{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890 \text{ kJ}}$$
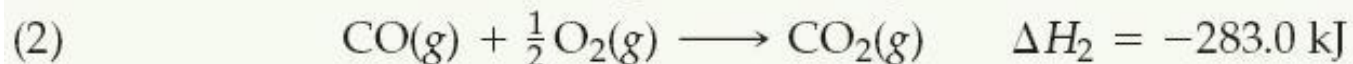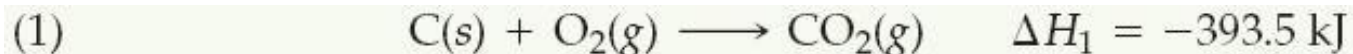
Enthalpy diagrams

Because ΔH is a state function, the total enthalpy change depends only on the initial state of the reactants and the final state of the products. ΔH is a same whether the reaction takes place in one step or in a series of steps.
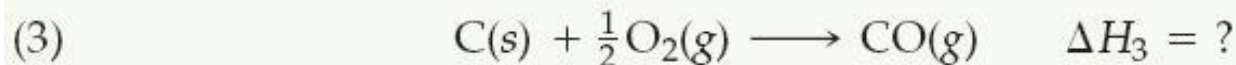
Sample Exercise: Using Hess's Law to Calculate ΔH

The enthalpy of reaction for the combustion of C to CO_2 is –393.5 kJ/mol C, and the enthalpy for the combustion of CO to CO_2 is –283.0 kJ/mol CO:

(1) $\qquad\qquad\qquad C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_1 = -393.5 \text{ kJ}$

(2) $\qquad\qquad\qquad CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_2 = -283.0 \text{ kJ}$

Using these data, calculate the enthalpy for the combustion of C to CO:

(3) $\qquad\qquad\qquad C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H_3 = ?$

Solution

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad\qquad \Delta H_1 = -393.5 \text{ kJ}$$
$$CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g) \qquad -\Delta H_2 = 283.0 \text{ kJ}$$
$$\overline{C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad\qquad\qquad \Delta H_3 = -110.5 \text{ kJ}}$$
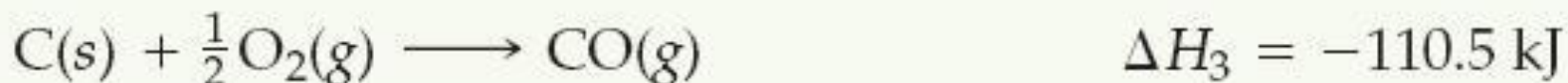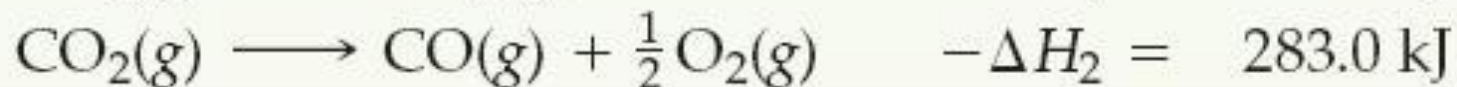
Sample Exercise: Using Three Equations with Hess's Law to Calculate ΔH

Calculate ΔH for the reaction

$$2\,C(s) + H_2(g) \rightarrow C_2H_2(g)$$

given the following chemical equations and their respective enthalpy changes

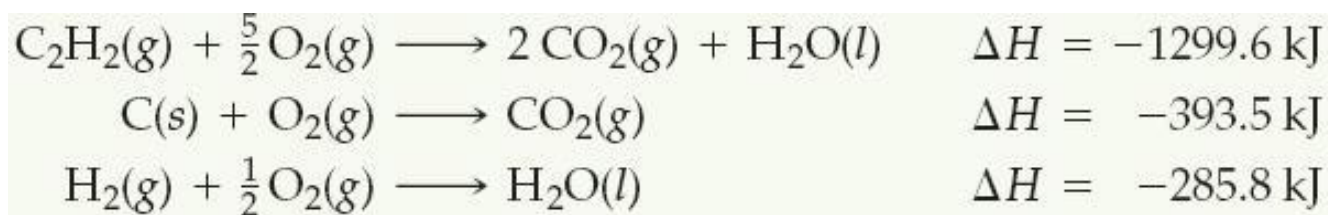$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l) \qquad \Delta H = -1299.6 \text{ kJ}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8 \text{ kJ}$$

Solution

$$2\,CO_2(g) + H_2O(l) \longrightarrow C_2H_2(g) + \tfrac{5}{2}O_2(g) \qquad \Delta H = 1299.6 \text{ kJ}$$
$$2\,C(s) + 2\,O_2(g) \longrightarrow 2\,CO_2(g) \qquad \Delta H = -787.0 \text{ kJ}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8 \text{ kJ}$$
$$\overline{2\,C(s) + H_2(g) \longrightarrow C_2H_2(g) \qquad \Delta H = 226.8 \text{ kJ}}$$
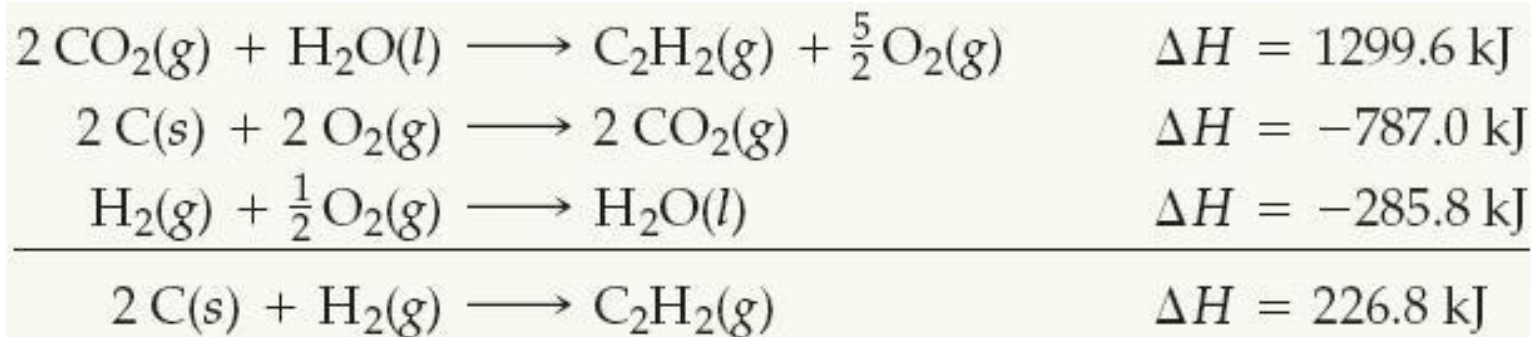
5.7
Enthalpies of Formation

If 1 mol of compound is formed from its constituent elements, then the enthalpy change for the reaction is called the **enthalpy of formation**, ΔH_f.

An **enthalpy of formation**, ΔH_f, or heat of formation is defined as the enthalpy change for the reaction in which a compound is made from its constituent elements.

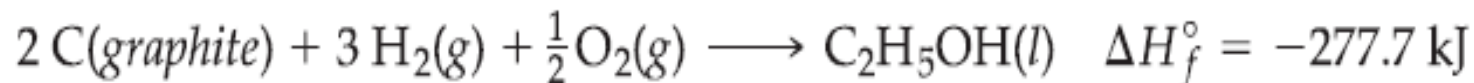$$\text{elements} \longrightarrow \text{compound} \qquad \Delta H_f$$
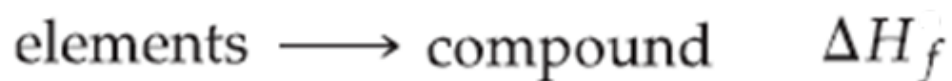
To compare the enthalpies of different reactions, we must define a set of conditions, called a **standard state**, at which most enthalpies are tabulated.

The standard state of a substance is its pure form at atmospheric pressure (1.00 atm) and 25 °C.

Standard enthalpy of formation, ΔH_f°, is the enthalpy measured under standard conditions (when everything is in its standard state).

$$\text{elements (in standard states)} \longrightarrow \text{compound (in standard state)} \qquad \Delta H_f^\circ$$

e.g.,

$$2\,C(\textit{graphite}) + 3\,H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l) \quad \Delta H_f^\circ = -277.7\ kJ$$

-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 $H_2(g)$.

If there is more than one state for a substance under standard conditions, the more stable one is used.

By definition, the standard enthalpy of formation of the most stable form of any element is zero, because there is no formation reaction needed when the element is already in its standard state.
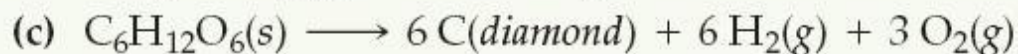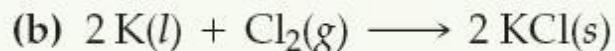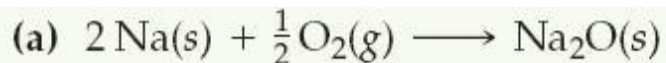
Thus, the values of ΔH_f° for C(graphite), $H_2(g)$. $O_2(g)$, and the standard states of other elements are zero by definition.

Standard Enthalpies of Formation, ΔH_f°, at 298 K

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

Sample Exercise: Identifying Equations Associates with Enthalpies of Formation

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) $2\,Na(s) + \frac{1}{2}O_2(g) \longrightarrow Na_2O(s)$

(b) $2\,K(l) + Cl_2(g) \longrightarrow 2\,KCl(s)$

(c) $C_6H_{12}O_6(s) \longrightarrow 6\,C(diamond) + 6\,H_2(g) + 3\,O_2(g)$

Solution

(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 room temperature. Furthermore, two moles of product are formed, so the enthalpy change for the reaction as written is twice the standard enthalpy of formation of $KCl(s)$. The equation for the formation reaction of 1 mol of $KCl(s)$ is

$$K(s) + \frac{1}{2}Cl(g) \longrightarrow KCl(s)$$
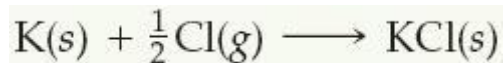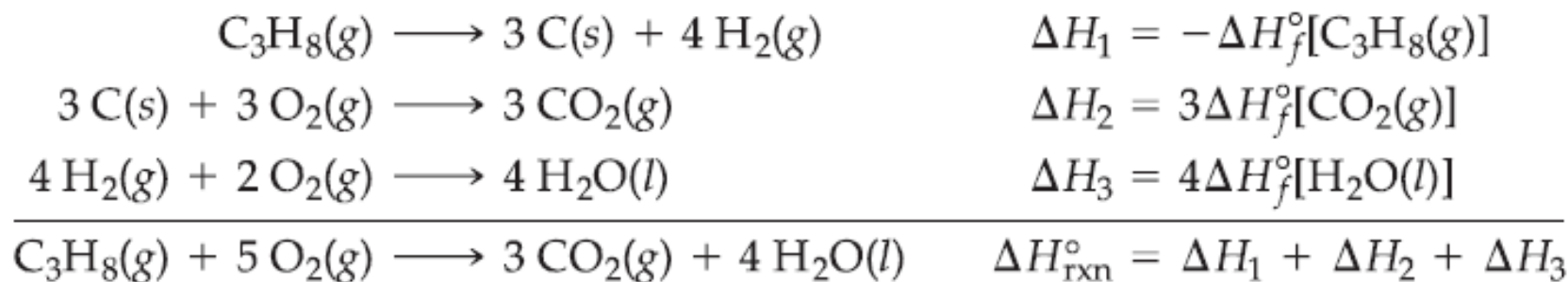
(c) The reaction does not form a substance from its elements. Instead, a substance decomposes to its elements, so this reaction must be reversed. Next, the element carbon is given as diamond, whereas graphite is the standard state of carbon at room temperature and 1 atm pressure. The correct equation should be

$$6\,C(\boldsymbol{graphite}) + 6\,H_2(g) + 3\,O_2(g) \rightarrow C_6H_{12}O_6(s)$$
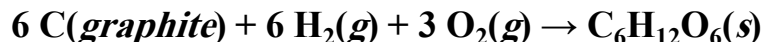
Using Enthalpies of Formation to Calculate Enthalpies of Reaction

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

We can write this equation as the sum of three formation reactions:

$$C_3H_8(g) \longrightarrow 3\,C(s) + 4\,H_2(g) \qquad \Delta H_1 = -\Delta H^\circ_f[C_3H_8(g)]$$

$$3\,C(s) + 3\,O_2(g) \longrightarrow 3\,CO_2(g) \qquad \Delta H_2 = 3\Delta H^\circ_f[CO_2(g)]$$

$$4\,H_2(g) + 2\,O_2(g) \longrightarrow 4\,H_2O(l) \qquad \Delta H_3 = 4\Delta H^\circ_f[H_2O(l)]$$

$$\overline{C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H^\circ_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3}$$

$$= -\Delta H^\circ_f[C_3H_8(g)] + 3\Delta H^\circ_f[CO_2(g)] + 4\Delta H^\circ_f[H_2O(l)]$$

$$= -(-103.85\ \text{kJ}) + 3(-393.5\ \text{kJ}) + 4(-285.8\ \text{kJ}) = -2219.9\ \text{kJ}$$

We can break down any reaction into formation reactions. Then the standard enthalpy change of a reaction is the sum of the standard enthalpies of formation of the products minus the standard enthalpies of formation of the reactants.
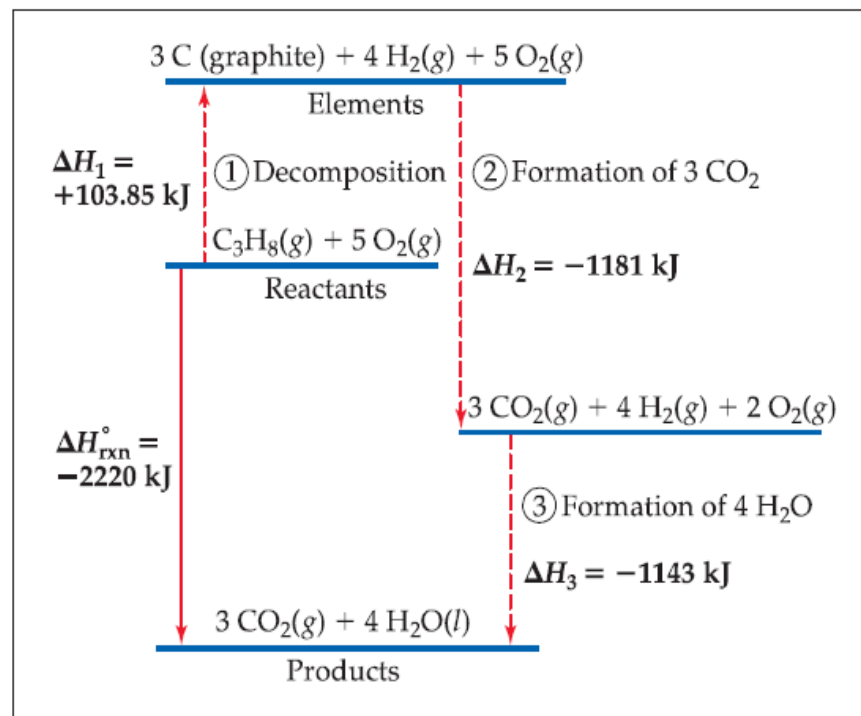
e.g.,

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

We use Hess's Law to calculate enthalpies of a reaction from enthalpies of formation.

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

where n and m are the stoichiometric coefficients.

Enthalpy

3 C (graphite) + 4 H$_2$(g) + 5 O$_2$(g) — Elements

$\Delta H_1 = +103.85$ kJ ① Decomposition   ② Formation of 3 CO$_2$

C$_3$H$_8$(g) + 5 O$_2$(g) — Reactants $\Delta H_2 = -1181$ kJ

3 CO$_2$(g) + 4 H$_2$(g) + 2 O$_2$(g)

$\Delta H^{\circ}_{rxn} = -2220$ kJ   ③ Formation of 4 H$_2$O $\Delta H_3 = -1143$ kJ

3 CO$_2$(g) + 4 H$_2$O(l) — Products

$$\Delta H = [3(-393.5 \text{ kJ}) + 4(-285.8 \text{ kJ})] - [1(-103.85 \text{ kJ}) + 5(0 \text{ kJ})]$$
$$= [(-1180.5 \text{ kJ}) + (-1143.2 \text{ kJ})] - [(-103.85 \text{ kJ}) + (0 \text{ kJ})]$$
$$= (-2323.7 \text{ kJ}) - (-103.85 \text{ kJ}) = -2219.9 \text{ kJ}$$

Sample Exercise: Calculating an Enthalpy of Reaction from Enthalpies of Formation

(a) Calculate the standard enthalpy change for the combustion of 1 mol of benzene, $C_6H_6(l)$, to form $CO_2(g)$ and $H_2O(l)$.
(b) Compare the quantity of heat produced by combustion of 1.00 g propane to that produced by 1.00 g benzene.

Solution

(a)
The balanced equation for the combustion reaction of
1 mol $C_6H_6(l)$ is

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

$\Delta H^\circ_f = 0$ for any element in its most stable form under standard
conditions, so $\Delta H^\circ_f [O_2(g)] = 0$

$$
\begin{aligned}
\Delta H^\circ_{rxn} &= [6\Delta H^\circ_f(CO_2) + 3\Delta H^\circ_f(H_2O)] - [\Delta H^\circ_f(C_6H_6) + \tfrac{15}{2}\Delta H^\circ_f(O_2)] \\
&= [6(-393.5\ \text{kJ}) + 3(-285.8\ \text{kJ})] - \left[(49.0\ \text{kJ}) + \tfrac{15}{2}(0\ \text{kJ})\right] \\
&= (-2361 - 857.4 - 49.0)\ \text{kJ} \\
&= -3267\ \text{kJ}
\end{aligned}
$$

(b)
$\Delta H^\circ = -2220$ kJ for the combustion of 1 mol of propane. In part (a) we
determined that $\Delta H^\circ = -3267$ kJ for the combustion of 1 mol benzene. To
determine the heat of combustion per gram of each substance, we use the
molar masses to convert moles to grams:

$$C_3H_8(g): \quad (-2220\ \text{kJ/mol})(1\ \text{mol}/44.1\ \text{g}) = -50.3\ \text{kJ/g}$$

$$C_6H_6(l): \quad (-3267\ \text{kJ/mol})(1\ \text{mol}/78.1\ \text{g}) = -41.8\ \text{kJ/g}$$

Sample Exercise: Calculating an Enthalpy of Formation Using an Enthalpy of Reaction

The standard enthalpy change for the reaction

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

is 178.1 kJ. From the values for the standard enthalpies of formation of CaO(s) and $CO_2(g)$ given in the Table, calculate the standard enthalpy of formation of $CaCO_3(s)$.

Solution

Inserting the ΔH°_{rxn} given and the known ΔH°_{f} values from previous Table

$$\Delta H^{\circ}_{rxn} = [\Delta H^{\circ}_{f}(CaO) + \Delta H^{\circ}_{f}(CO_2)] - \Delta H^{\circ}_{f}(CaCO_3)$$

Solving for $\Delta H^{\circ}_{f}(CaCO_3)$ gives

$$178.1 \text{ kJ} = -635.5 \text{ kJ} - 393.5 \text{ kJ} - \Delta H^{\circ}_{f}(CaCO_3)$$

$$\Delta H^{\circ}_{f}(CaCO_3) = -1207.1 \text{ kJ/mol}$$

Q & A

A moving racquetball has _____ energy.

a. kinetic
b. potential
c. work
d. heat

A motionless racquetball has _____ energy.

 a. kinetic

 b. potential

 c. work

 d. heat

A racquetball player perspires during the game, giving off _____ energy.

- a. kinetic
- b. potential
- c. work
- d. heat

The sum of all the kinetic and potential energies of a system's components is known as its:

    a. integral energy.

    b. dynamic energy.

    c. internal energy.

    d. work energy.

A system absorbs heat during an _____ process.

a. exothermic

b. isothermic

c. adiabatic

d. endothermic

When a hot piece of metal is placed into cool water, energy:

a. flows from the metal to the water.

b. flows from the water to the metal.

c. does not flow.

d. is not conserved.

By definition, the standard heat of formation of carbon in its graphite form is _____ kilojoules/mole.

a. 100

b. 1000

c. 1

d. 0

The standard heat of formation of carbon in its diamond form is +1.88 kJ/mole. This means that diamond is _____ graphite.

a. as stable as

b. more stable than

c. less stable than

d. an isotope of

Which of the following is NOT a source of renewable energy?

a. nuclear energy

b. solar energy

c. geothermal energy

d. hydroelectric energy

Which of the following is NOT a state function?

    a. internal energy

    b. temperature

    c. enthalpy

    d. work

What is the kinetic energy, in J, of (a) an Ar atom moving with a speed of 650 m/s, (b) a mole of Ar atoms moving with a speed of 650 m/s.
(Hint: 1 amu = 1.66×10^{-27} kg)

***Answers:* (a)** 1.4×10^{-20} J, **(b)** 8.4×10^{3} J

Which metal will undergo the greatest temperature change if an equal amount of heat is added to each?

- Fe, $s = 0.45$ J/g K
- Al, $s = 0.90$ J/g K
- Cu, $s = 0.38$ J/g K
- Pb, $s = 0.13$ J/g K
- Sn, $s = 0.22$ J/g K

If a piece of metal at 85°C is added to water at 25°C, the final temperature of the system is 30°C. Which of the following is true?

- Heat lost by the metal > heat gained by water.
- Heat gained by water > heat lost by the metal.
- Heat lost by metal > heat lost by the water.
- Heat lost by the metal = heat gained by water.
- More information is required.

Which reaction represents the ΔH_f reaction for $NaNO_3$?

1. $Na^+\,(aq) + NO_3^-\,(aq) \longrightarrow NaNO_3\,(aq)$

2. $Na^+\,(g) + NO_3^-\,(g) \longrightarrow NaNO_3\,(s)$

3. $Na\,(s) + NO_3\,(s) \longrightarrow NaNO_3\,(s)$

4. $2\,Na\,(s) + N_2\,(g) + 3\,O_2\,(g) \longrightarrow 2\,NaNO_3\,(s)$

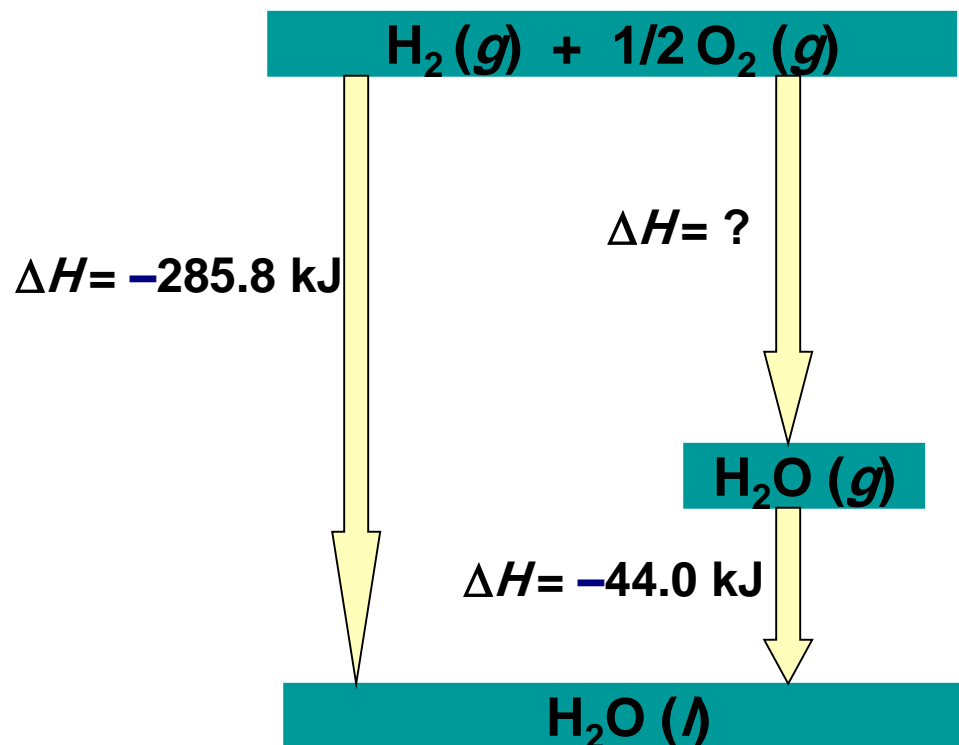5. $2\,Na\,(s) + 1/2\,N_2\,(g) + 3/2\,O_2\,(g) \longrightarrow NaNO_3\,(s)$
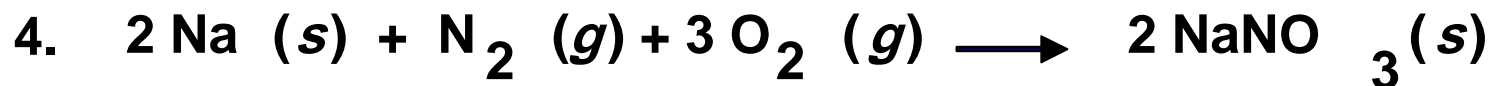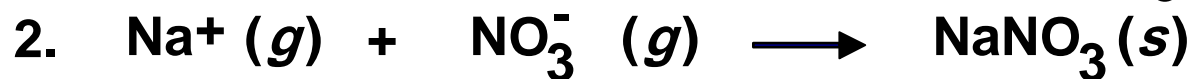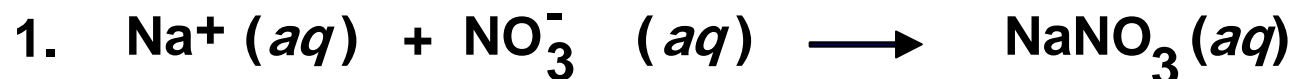
Which of the following statements is true for the diagram?

- Internal energy > 0
- Internal energy < 0
- Enthalpy > 0
- Enthalpy < 0
- Internal energy = enthalpy

System   **Surroundings**
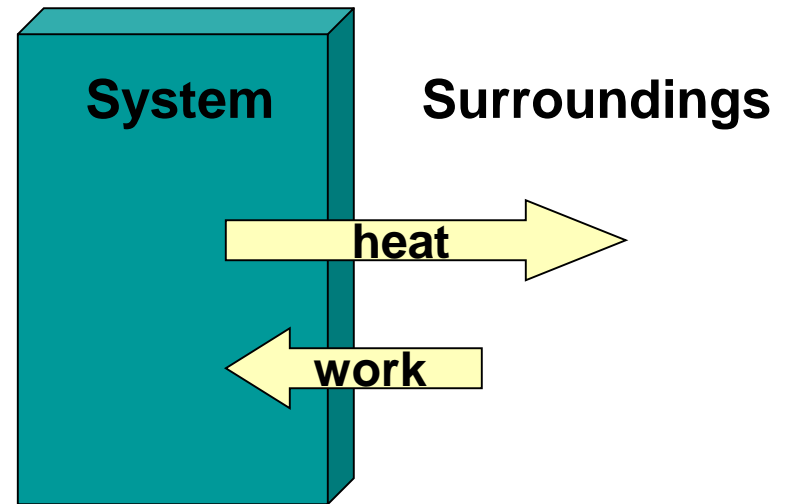
heat

work

What is the value of the unknown ΔH in the diagram?

- +329.5 kJ
- −329.5 kJ
- +285.8 kJ
- −241.8 kJ
- +241.8 kJ

$$H_2 (g) + 1/2\, O_2 (g)$$

$\Delta H = -285.8$ kJ

$\Delta H = ?$

$$H_2O (g)$$

$\Delta H = -44.0$ kJ

$$H_2O (l)$$

Calculate the change in the internal energy of the system for a process in which the system absorbs 140 J of heat from the surroundings and does 85 J of work on the surroundings.

Answer: **+55 J**

Suppose we confine 1 g of butane and sufficient oxygen to completely combust it in a cylinder like that in Figure 5.12. The cylinder is perfectly insulating, so no heat can escape to the surroundings. A spark initiates combustion of the butane, which forms carbon dioxide and water vapor. If we used this apparatus to measure the enthalpy change in the reaction, would the piston rise, fall, or stay the same?

Answer: The piston must move to maintain a constant pressure in the cylinder. The products contain more molecules of gas than the reactants, as shown by the balanced equation

$$2\ C_4H_{10}(g) + 13\ O_2(g) \longrightarrow 8\ CO_2(g) + 10\ H_2O(g)$$
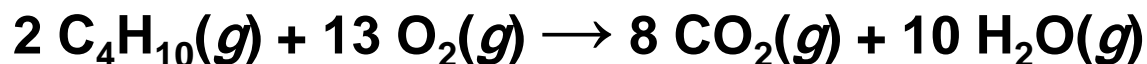
As a result, the piston would rise to make room for the additional molecules of gas. Heat is given off, so the piston would also rise an additional amount to accommodate the expansion of the gases because of the temperature increase.

Hydrogen peroxide can decompose to water and oxygen by the following reaction:

2 H$_2$O$_2$(l) $\longrightarrow$ 2 H$_2$O(l) + O$_2$(g) ΔH = –196 kJ

Calculate the value of q when 5.00 g of H$_2$O$_2$(l) decomposes at constant pressure.

Answer: –14.4 kJ

(a) Large beds of rocks are used in some solar-heated homes to store heat. Assume that the specific heat of the rocks is 0.82 J/g-K. Calculate the quantity of heat absorbed by 50.0 kg of rocks if their temperature increases by 12.0 °C. **(b)** What temperature change would these rocks undergo if they emitted 450 kJ of heat?

Answers: **(a)** 4.9×10^5 J, **(b)** 11 K decrease = 11 °C decrease.

When 50.0 mL of 0.100 M AgNO$_3$ and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30 °C to 23.11 °C. The temperature increase is caused by the following reaction:.

$$AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$$
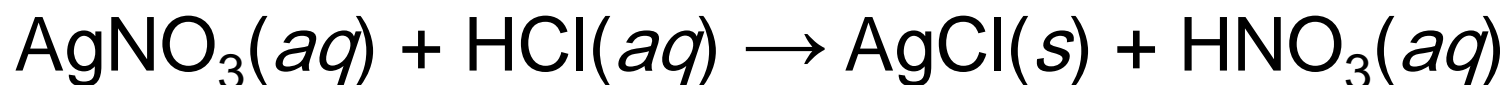
Calculate ΔH for this reaction in kJ/mol AgNO$_3$, assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g °C.
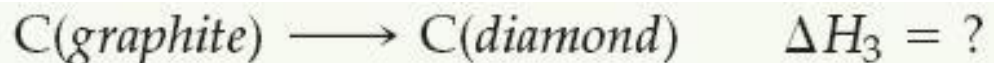
Answer: –68,000 J/mol = –68 kJ/mol

A 0.5865-g sample of lactic acid ($HC_3H_5O_3$) is burned in a calorimeter whose heat capacity is 4.812 kJ/°C. The temperature increases from 23.10 °C to 24.95 °C. Calculate the heat of combustion of lactic acid **(a)** per gram and **(b)** per mole.

Answers: **(a)** –15.2 kJ/g, **(b)** –1370 kJ/mol.

Carbon occurs in two forms, graphite and diamond. The enthalpy of the combustion of graphite is –393.5 kJ/mol and that of diamond is –395.4 kJ/mol:

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_1 = -393.5 \text{ kJ}$$

$$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_2 = -395.4 \text{ kJ}$$

Calculate for the conversion of graphite to diamond:

$$C(\text{graphite}) \longrightarrow C(\text{diamond}) \qquad \Delta H_3 = ?$$

Answer: ΔH_3 = +1.9 kJ

Calculate ΔH for the reaction

$$NO(g) + O(g) \longrightarrow NO_2(g)$$
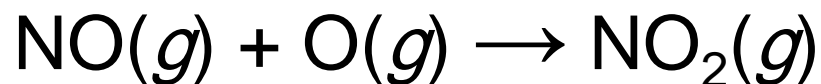
given the following information:

$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$	$\Delta H = -198.9$ kJ
$O_3(g) \longrightarrow \frac{3}{2}O_2(g)$	$\Delta H = -142.3$ kJ
$O_2(g) \longrightarrow 2\,O(g)$	$\Delta H = 495.0$ kJ
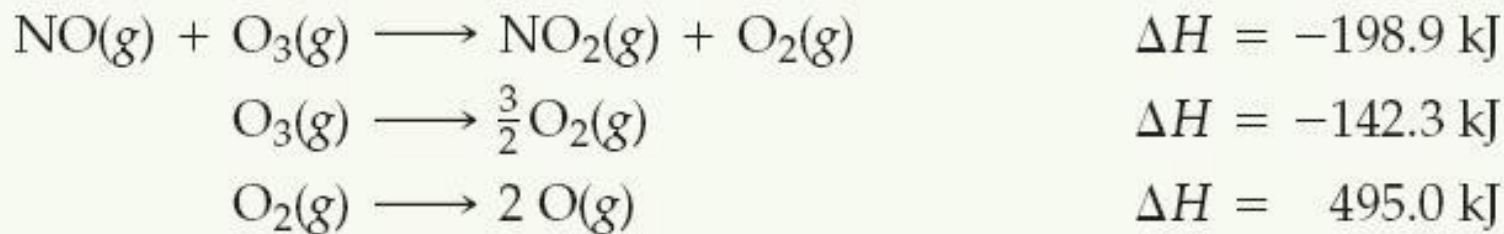
Answer: –304.1 kJ

Write the equation corresponding to the standard enthalpy of formation of liquid carbon tetrachloride (CCl_4).

Answer: $C(graphite) + 2\ Cl_2(g) \rightarrow CCl_4(l)$

Using the standard enthalpies of formation listed in Table 5.3, calculate the enthalpy change for the combustion of 1 mol of ethanol:

$$C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$$

Answer: −1367 kJ.

Given the following standard enthalpy change, use the standard enthalpies of formation in Table 5.3 to calculate the standard enthalpy of formation of CuO(s):

$$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l) \qquad \Delta H° = -129.7 \text{ kJ}$$

Answer: –156.1 kJ/mol