CHEM 103
CHEMISTRY I

CHAPTER 5

THERMOCHEMISTRY

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Energy

- **Energy** is the ability to do work or transfer heat.

  - Energy used to cause an object that has mass to move is called **work**.

  - Energy used to cause the temperature of an object to rise is called **heat**.

- This chapter is about **thermodynamics**, which is the study of energy transformations, and **thermochemistry**, which applies the field to chemical reactions, specifically.

Kinetic Energy

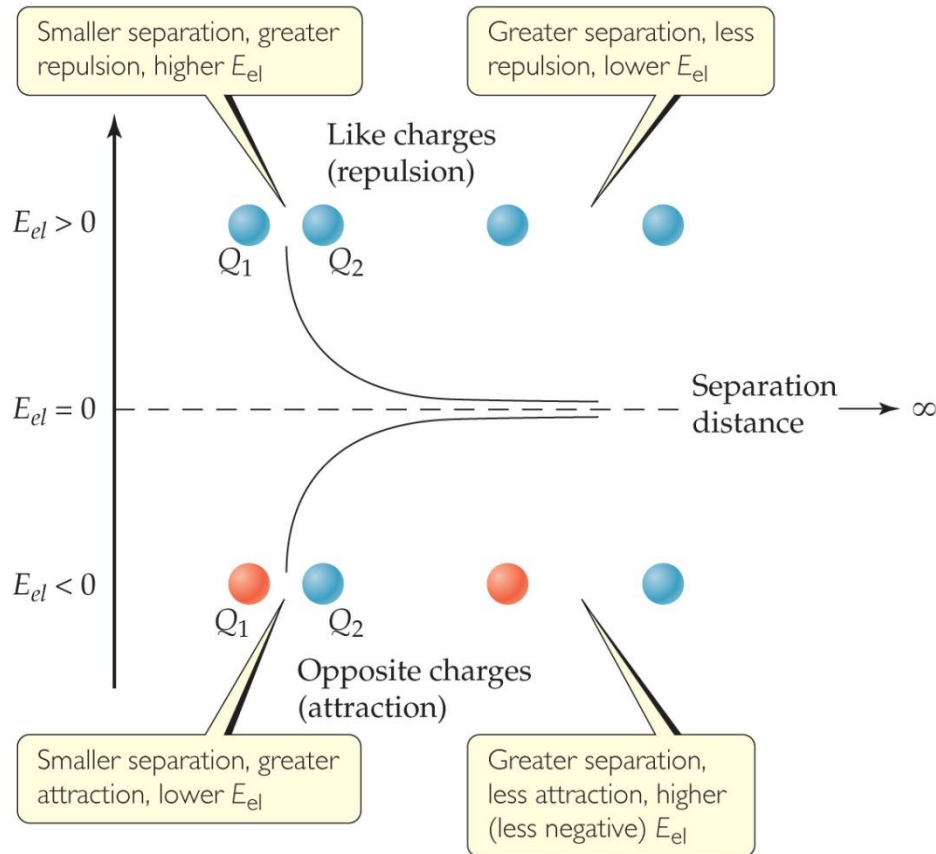**Kinetic energy** is energy an object possesses by virtue of its motion:

$$E_k = \frac{1}{2} mv^2$$
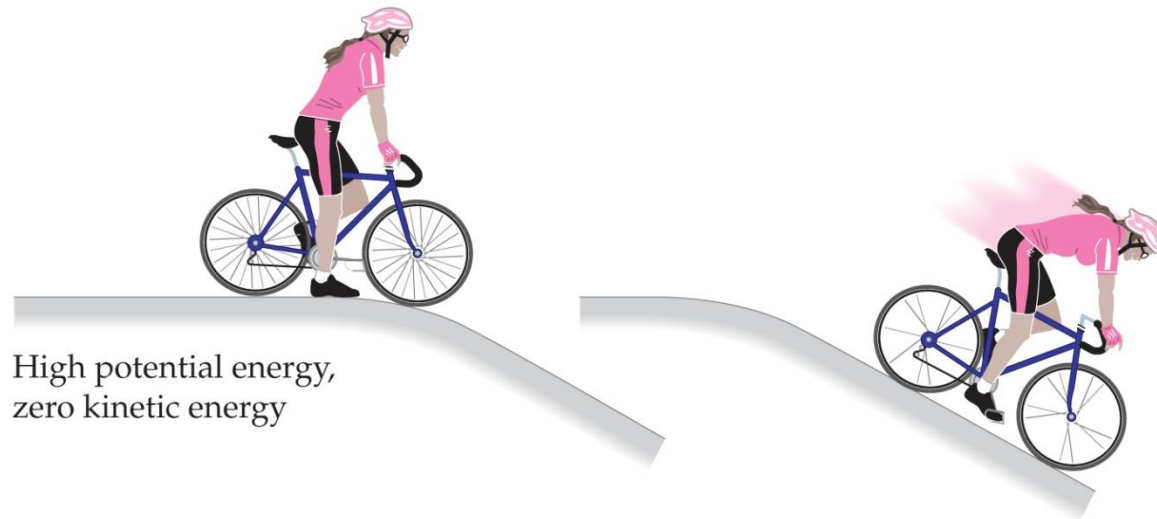
High potential energy,
zero kinetic energy

Decreasing potential energy,
increasing kinetic energy

Potential Energy

Smaller separation, greater repulsion, higher E_{el}

Greater separation, less repulsion, lower E_{el}

Like charges (repulsion)

$E_{el} > 0$

Q_1 Q_2

$E_{el} = 0$

Separation distance $\rightarrow$ ∞

$E_{el} < 0$

Q_1 Q_2

Opposite charges (attraction)

Smaller separation, greater attraction, lower E_{el}

Greater separation, less attraction, higher (less negative) E_{el}

- **Potential energy** is energy an object possesses by virtue of its position or chemical composition.

- The most important form of potential energy in molecules is electrostatic potential energy, E_{el}:

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

Units of Energy

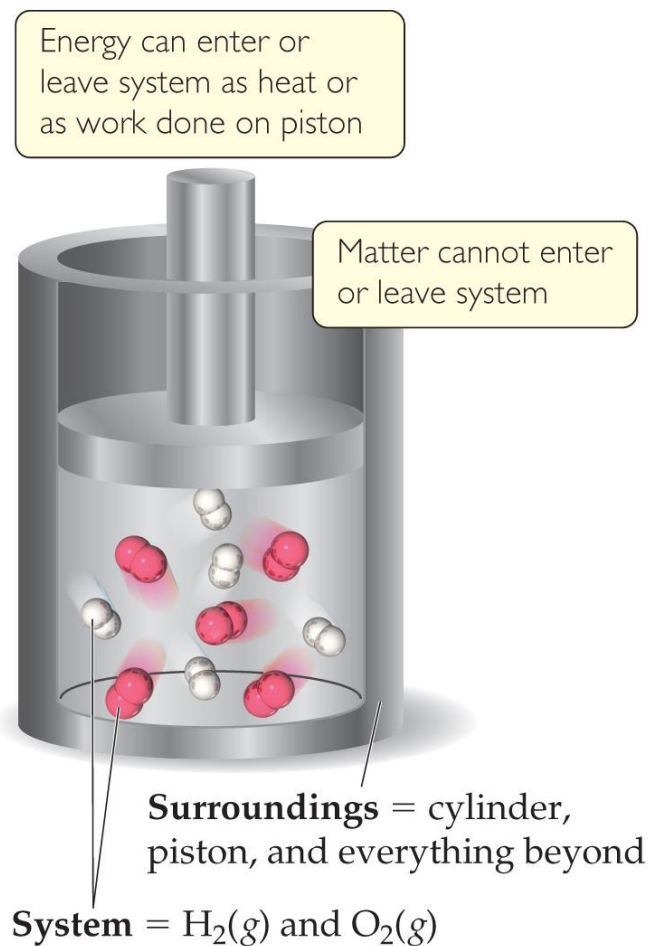- The SI unit of energy is the **joule (*J*)**:

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

- An older, non-SI unit is still in widespread use, the **calorie (*cal*)**:

$$1 \text{ cal} = 4.184 \text{ J}$$

(Note: this is *not* the same as the calorie of foods; the food calorie is 1 kcal!)

Definitions: System and Surroundings

Energy can enter or leave system as heat or as work done on piston

Matter cannot enter or leave system

Surroundings = cylinder, piston, and everything beyond

System = $H_2(g)$ and $O_2(g)$

- The **system** includes the molecules we want to study (here, the hydrogen and oxygen molecules).

- The **surroundings** are everything else (here, the cylinder and piston).

Definitions: Work

- 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.

Work done by pitcher on ball to make ball move

Heat

Heat added by burner to water makes water temperature rise

- Energy can also be transferred as heat.
- Heat flows from warmer objects to cooler objects.

Conversion of Energy

- Energy can be converted from one type to another.
- The cyclist 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 until the bottom, where the energy is converted to kinetic energy.

High potential energy, zero kinetic energy

Decreasing potential energy, increasing kinetic energy
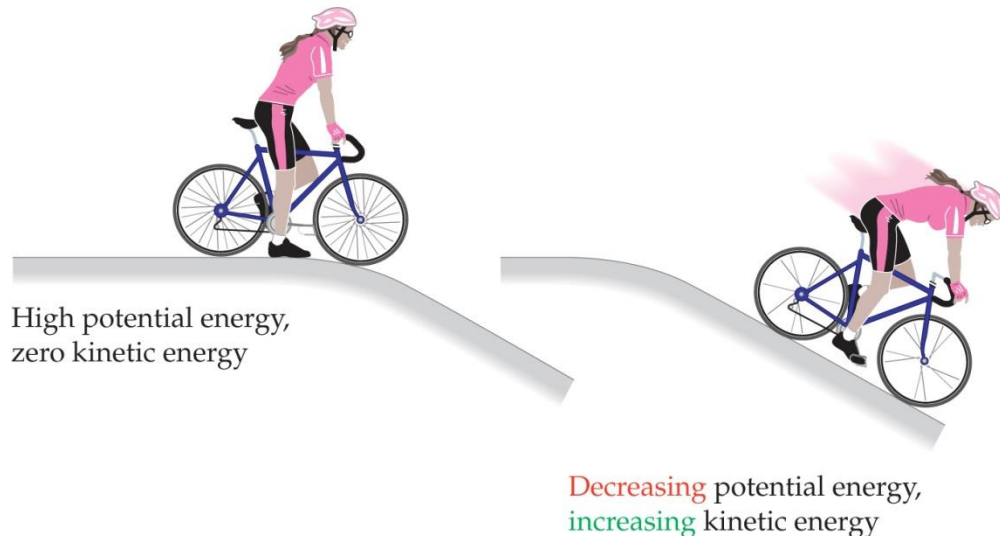
First Law of Thermodynamics

- Energy is neither created nor destroyed.

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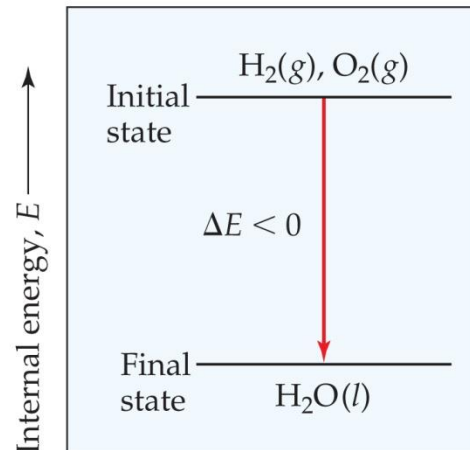
Internal Energy

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.*
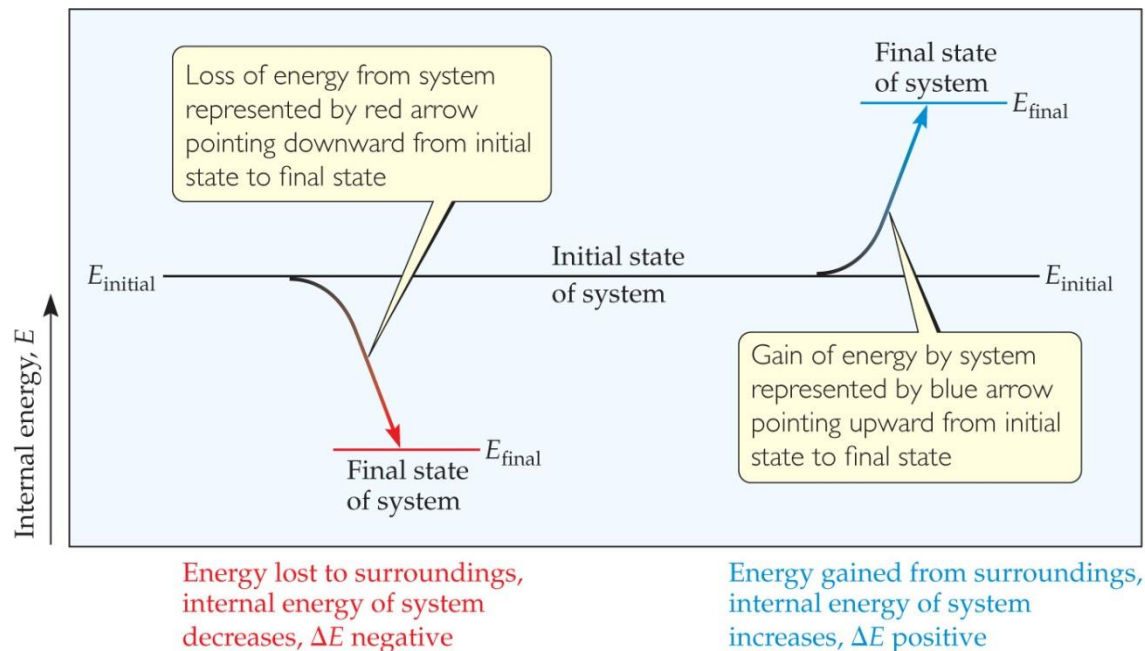
Internal Energy

By definition, the change in internal energy, ΔE, is the final energy of the system minus the initial energy of the system:
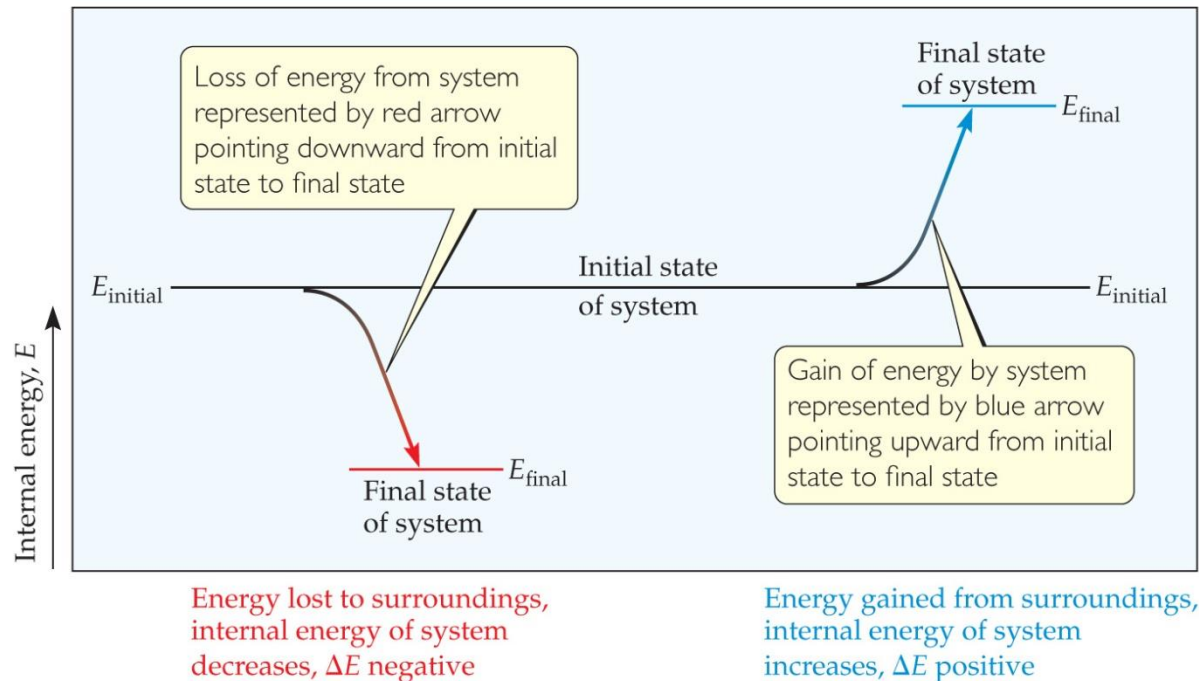
$$\Delta E = E_{final} - E_{initial}$$

Internal energy, E

Initial state — $H_2(g), O_2(g)$

$\Delta E < 0$

Final state — $H_2O(l)$

$E_{initial}$ greater than E_{final}; therefore, energy is released from system to surroundings during reaction and $\Delta E < 0$
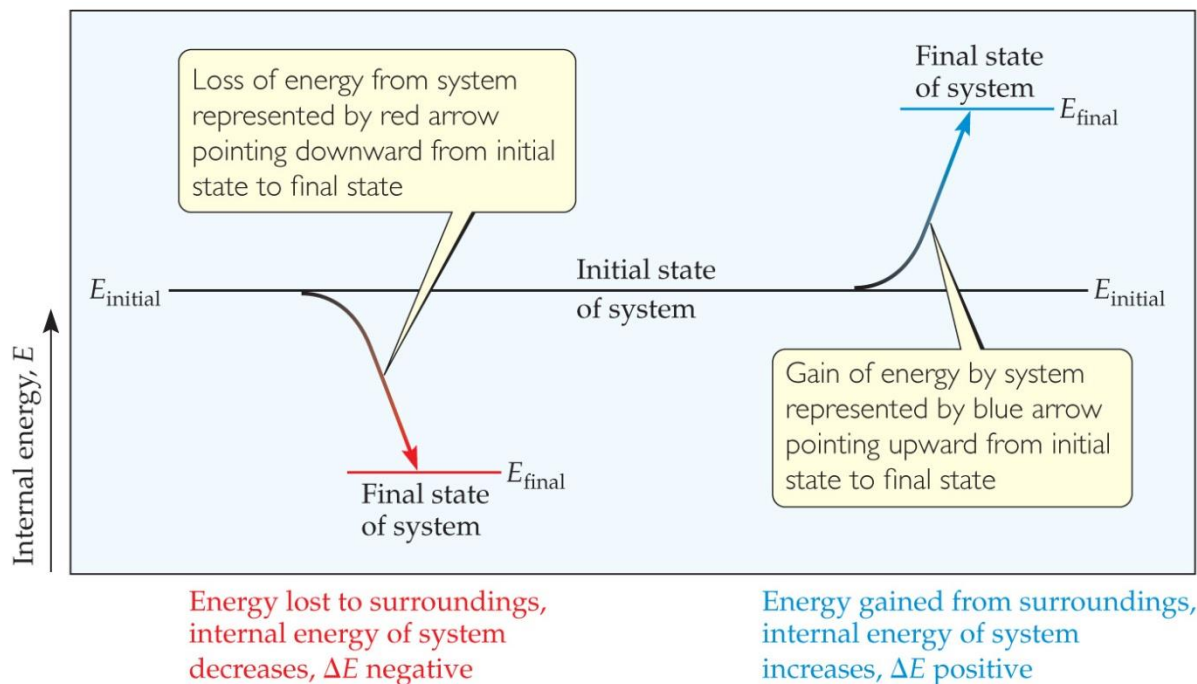
Changes in Internal Energy

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

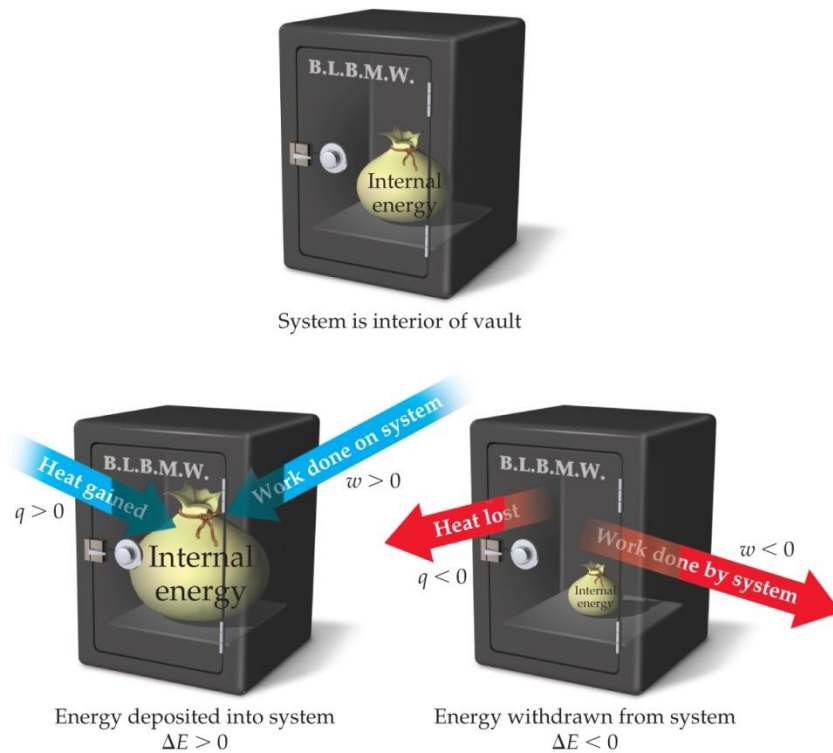Loss of energy from system represented by red arrow pointing downward from initial state to final state

$E_{initial}$

Initial state of system

E_{final}

Final state of system

Final state of system

E_{final}

$E_{initial}$

Gain of energy by system represented by blue arrow pointing upward from initial state to final state

Internal energy, E

Energy lost to surroundings, internal energy of system decreases, ΔE negative

Energy gained from surroundings, internal energy of system increases, ΔE positive

Changes in Internal Energy

- ## If $\Delta E < 0$, $E_{final} < E_{initial}$

  - Therefore, the system *released* energy to the surroundings.

  - This energy change is called **exergonic**.

Loss of energy from system represented by red arrow pointing downward from initial state to final state

Final state of system E_{final}

Initial state of system

$E_{initial}$

$E_{initial}$

Gain of energy by system represented by blue arrow pointing upward from initial state to final state

E_{final}

Final state of system

Internal energy, E

Energy lost to surroundings, internal energy of system decreases, ΔE negative

Energy gained from surroundings, internal energy of system increases, ΔE positive

Changes in Internal Energy

System is interior of vault

Energy deposited into system
$\Delta E > 0$

Energy withdrawn from system
$\Delta E < 0$

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

- That is, $\Delta E = q + w$.

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

Exchange of Heat between System and Surroundings

- When heat is absorbed by the system from the surroundings, the process is **endothermic**.

System: reactants + products

Surroundings: solvent, initially at room temperature
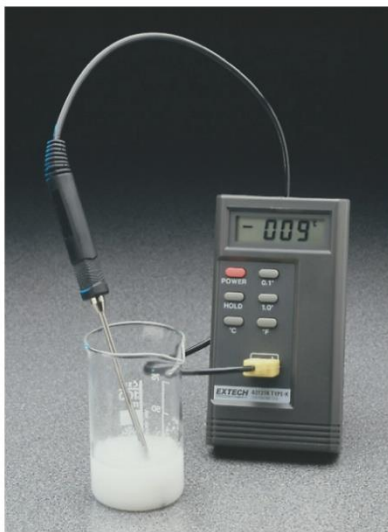
(a) An endothermic reaction

Heat flows from surroundings into system, temperature of surroundings drops, thermometer reads temperature well below room temperature

Exchange of Heat between System and Surroundings

- When heat is released by the system into the surroundings, the process is **exothermic**.

System: reactants + products
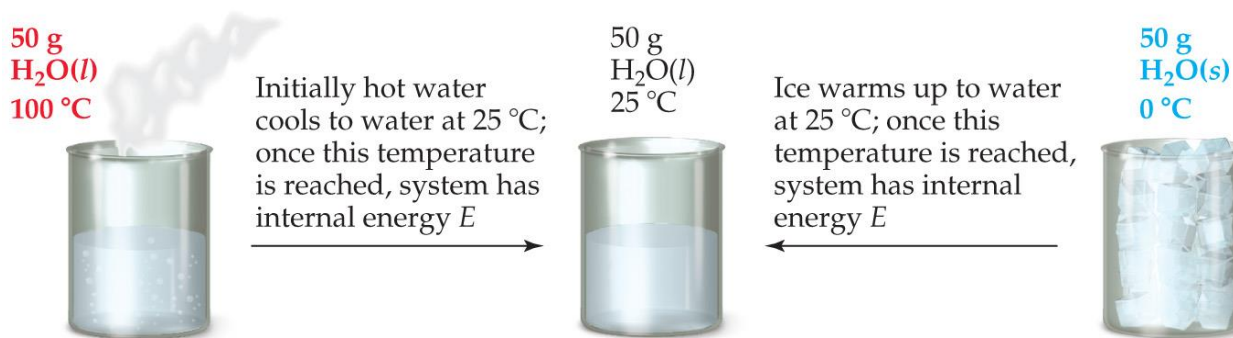
Surroundings:
air around reactants

(b) An exothermic reaction

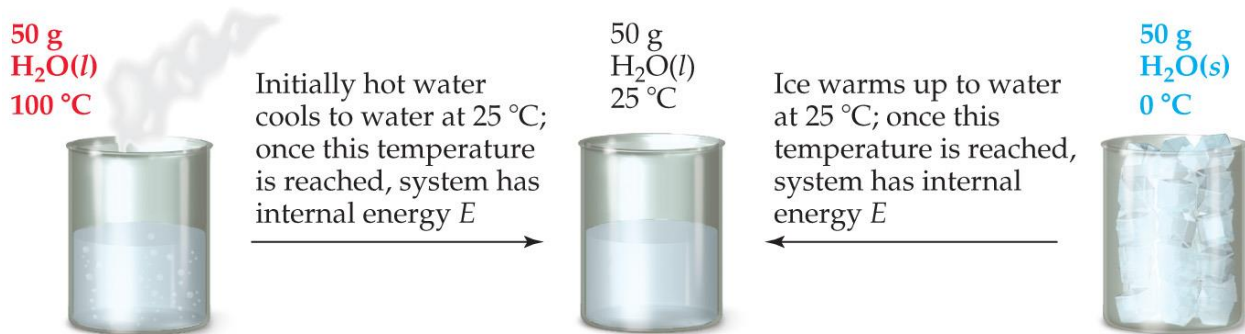Heat flows (violently) from system into surroundings, temperature of surroundings increases

State Functions

- Usually we have no way of knowing the internal energy of a system; finding that value is simply too complex a problem.

- However, we do know that the internal energy of a system is independent of the path by which the system achieved that state.

  – In the system below, the water could have reached room temperature from either direction.

50 g
$H_2O(l)$
100 °C

Initially hot water cools to water at 25 °C; once this temperature is reached, system has internal energy E

50 g
$H_2O(l)$
25 °C

Ice warms up to water at 25 °C; once this temperature is reached, system has internal energy E
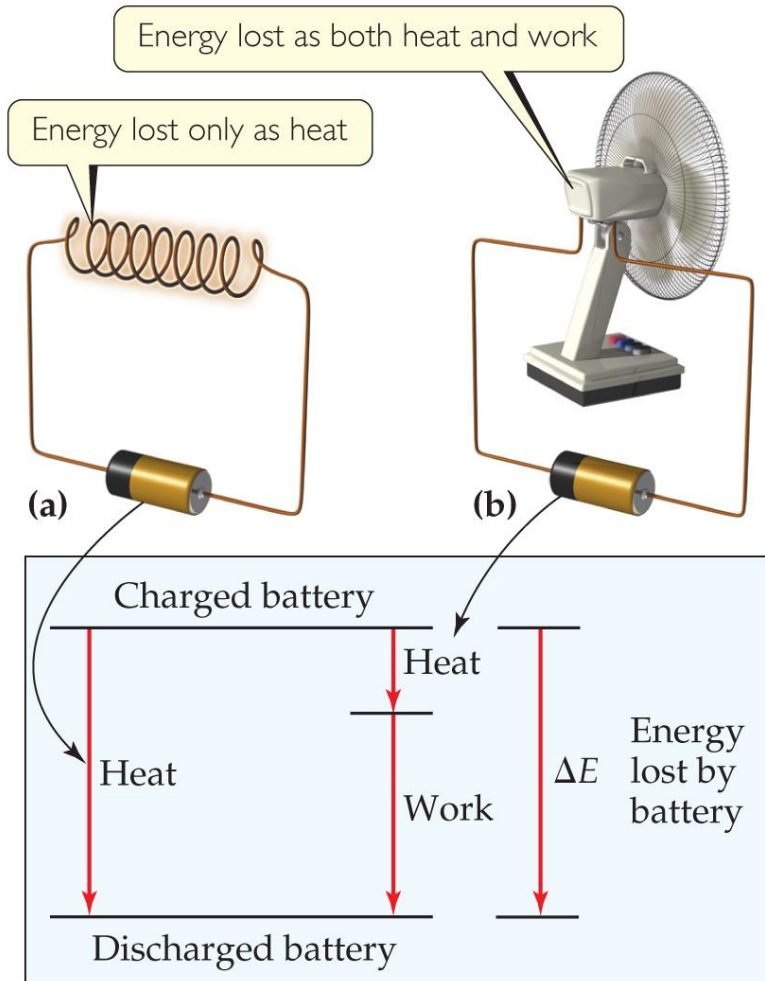
50 g
$H_2O(s)$
0 °C

State Functions

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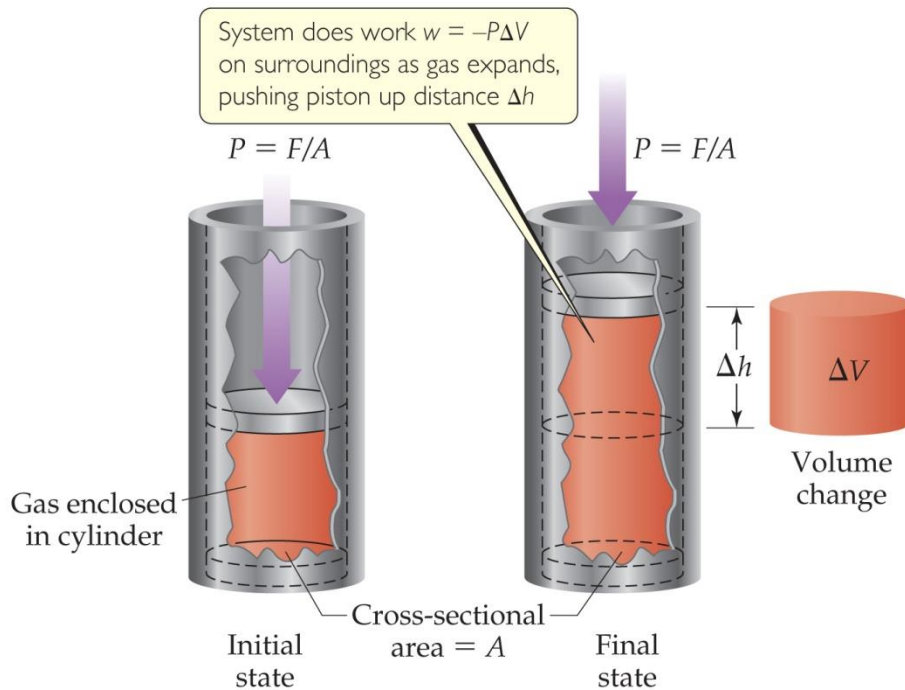- And so, ΔE depends only on $E_{initial}$ and E_{final}.

50 g
$H_2O(l)$
100 °C

Initially hot water cools to water at 25 °C; once this temperature is reached, system has internal energy E

50 g
$H_2O(l)$
25 °C

Ice warms up to water at 25 °C; once this temperature is reached, system has internal energy E

50 g
$H_2O(s)$
0 °C

State Functions

Energy lost as both heat and work

Energy lost only as heat

(a)   (b)

Charged battery

Heat

Heat   Work ΔE Energy lost by battery

Discharged battery

- 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.

Work

System does work $w = -P\Delta V$ on surroundings as gas expands, pushing piston up distance Δh

$P = F/A$

$P = F/A$

Δh

ΔV

Volume change

Gas enclosed in cylinder

Cross-sectional area = A

Initial state

Final state

Usually in an open container the only work done is by a gas pushing on the surroundings (or by the surroundings pushing on the gas).

Work

We can measure the work done by the gas if the reaction is done in a vessel that has been fitted with a piston:

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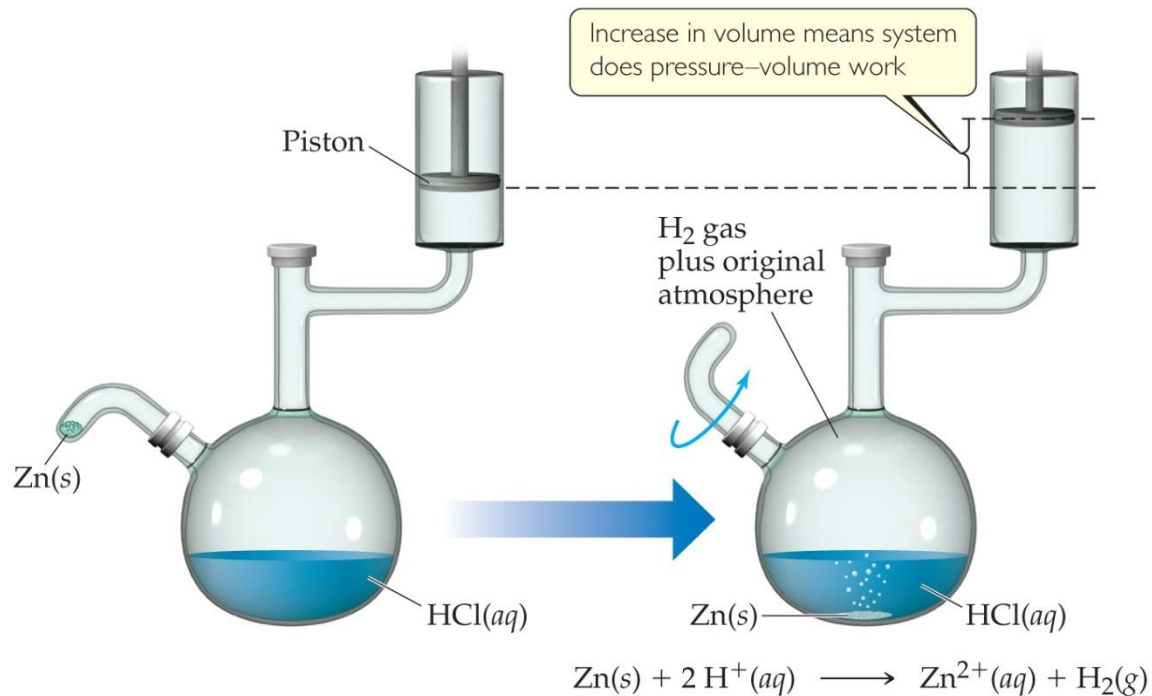
Enthalpy

- If a process takes place at constant pressure (as the majority of processes we study do) 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** is the internal energy plus the product of pressure and volume:

$$H = E + PV$$

Enthalpy

- When the system changes at constant pressure, the change in enthalpy, ΔH, is

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

- This can be written

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

Enthalpy

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

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

$$\Delta H = (q + w) - w$$

$$\Delta H = q$$

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

Endothermic and Exothermic

Constant pressure maintained in system

$\Delta H > 0$

Heat gain

H

(a) An endothermic reaction

$\Delta H < 0$

Heat loss

H
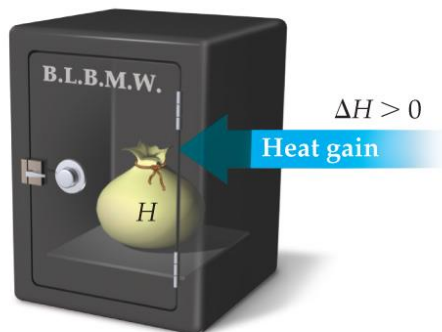
(b) An exothermic reaction

ΔH is amount of heat that flows into or out of system under constant pressure

- A process is endothermic when ΔH is positive.

- A process is exothermic when ΔH is negative.
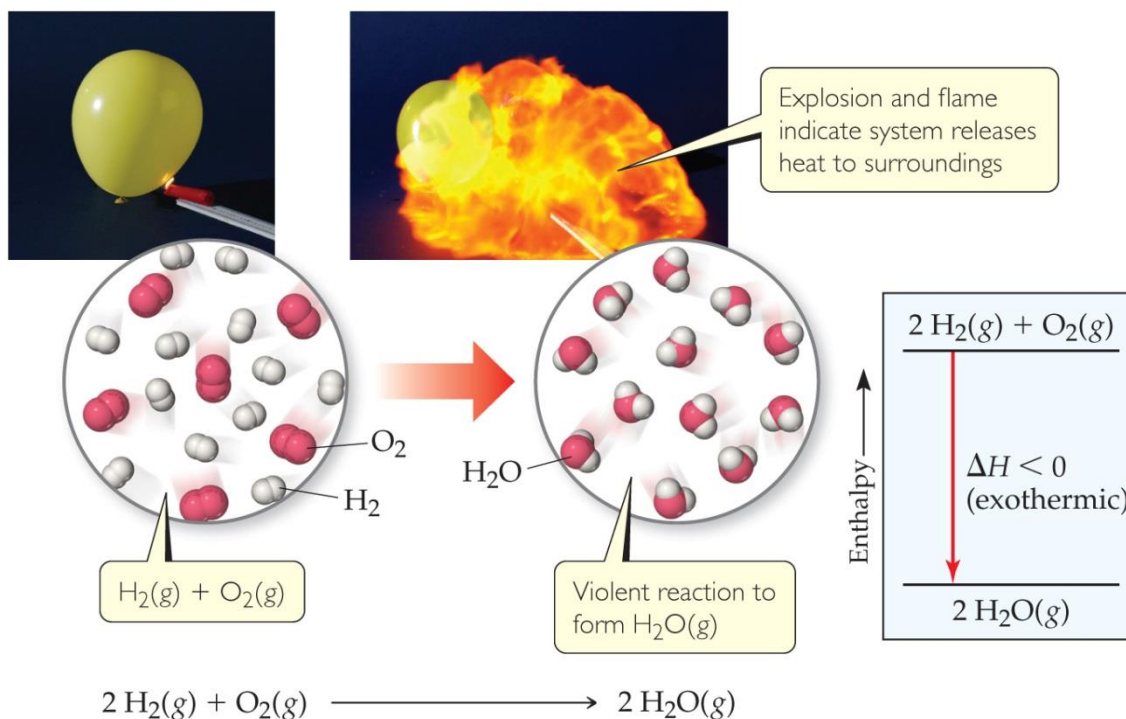
Enthalpy of Reaction

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

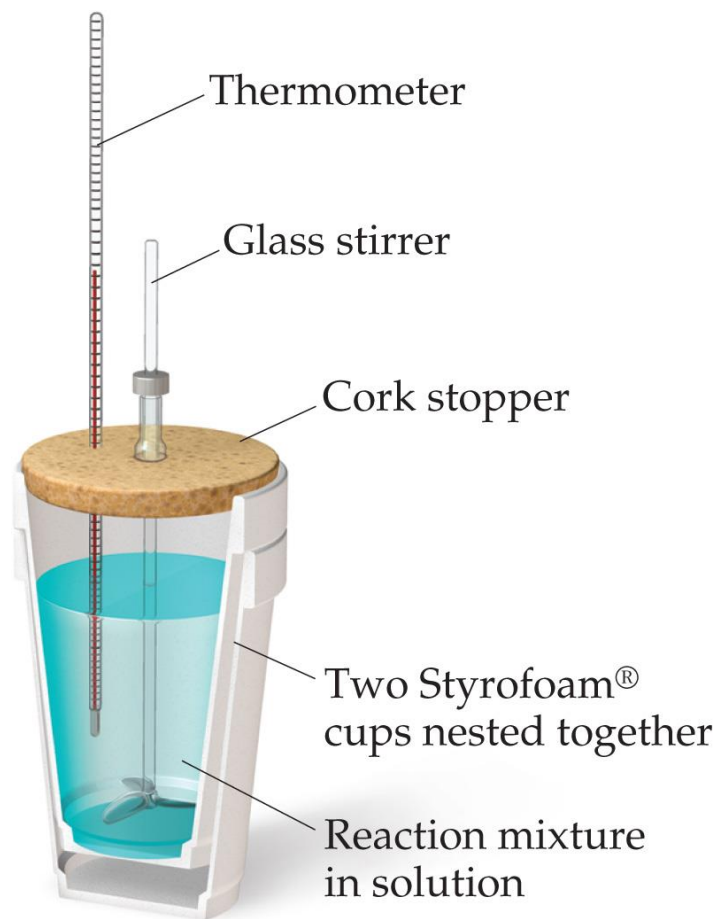$$\Delta H = H_{products} - H_{reactants}$$
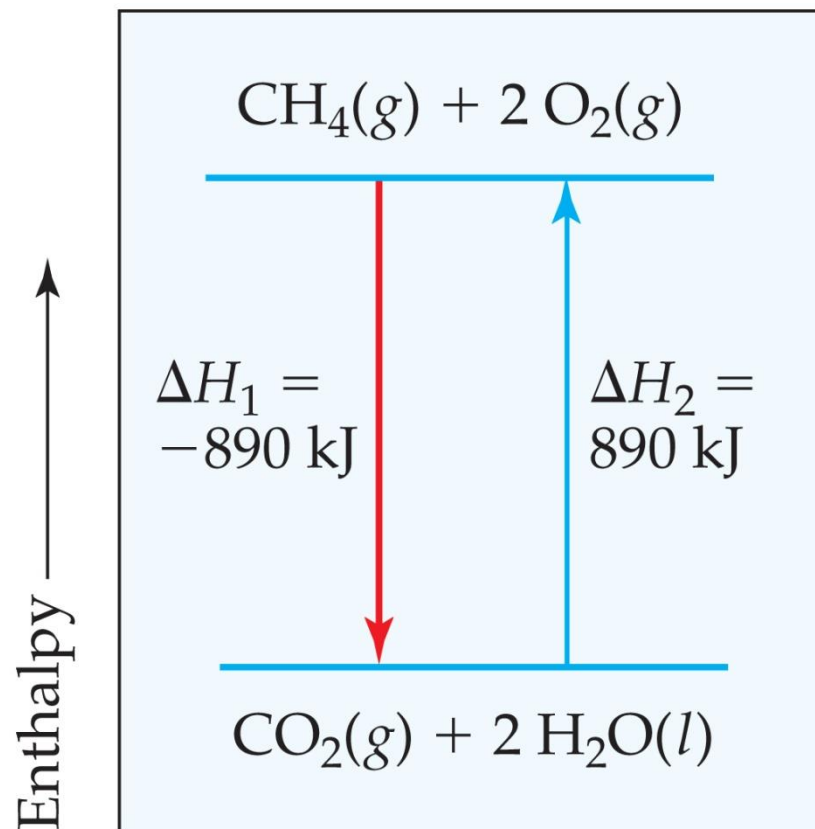
Enthalpy of Reaction

This quantity, ΔH, is called the **enthalpy of reaction**, or the **heat of reaction**.

The Truth about Enthalpy

1. Enthalpy is an extensive property.

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.

Calorimetry

Thermometer

Glass stirrer

Cork stopper

Two Styrofoam® cups nested together

Reaction mixture in solution

- Since we cannot know the exact enthalpy of the reactants and products, we measure ΔH through **calorimetry**, the measurement of heat flow.

- The instrument used to measure heat flow is called a **calorimeter**.

Heat Capacity and Specific Heat

The amount of energy required to raise the temperature of a substance by 1 K (1 °C) is its **heat capacity**, usually given for one mole of the substance.

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

Heat Capacity and Specific Heat

We define **specific heat capacity** (or simply **specific heat**) as the amount of energy required to raise the temperature of 1 g of a substance by 1 K (or 1 °C).

1.000 g $H_2O(l)$
$T = 15.5\,°C$

$+ 4.184$ J (1 cal) of heat

1.000 g $H_2O(l)$
$T = 14.5\,°C$
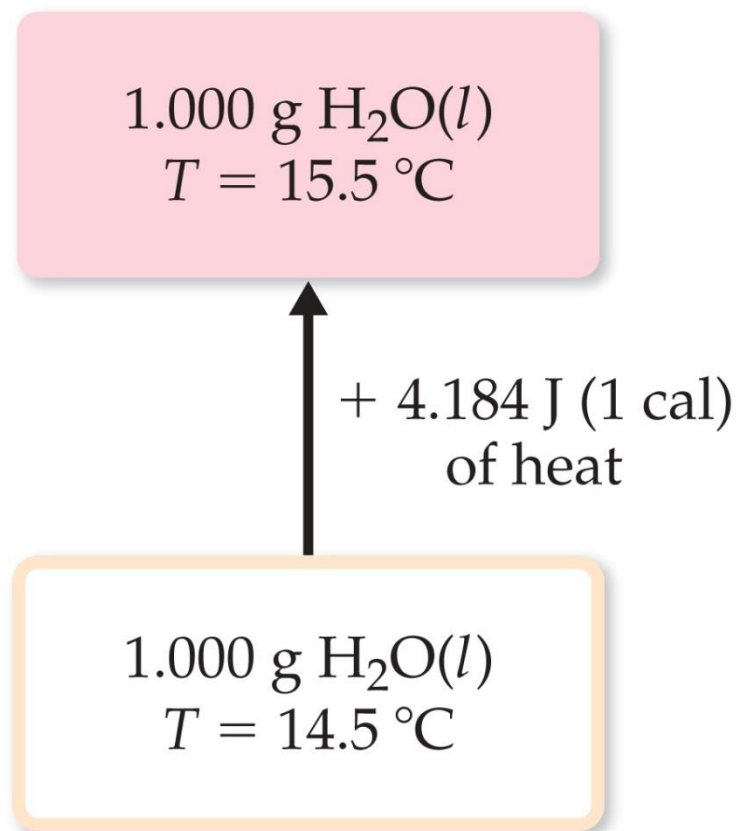
Heat Capacity and Specific Heat
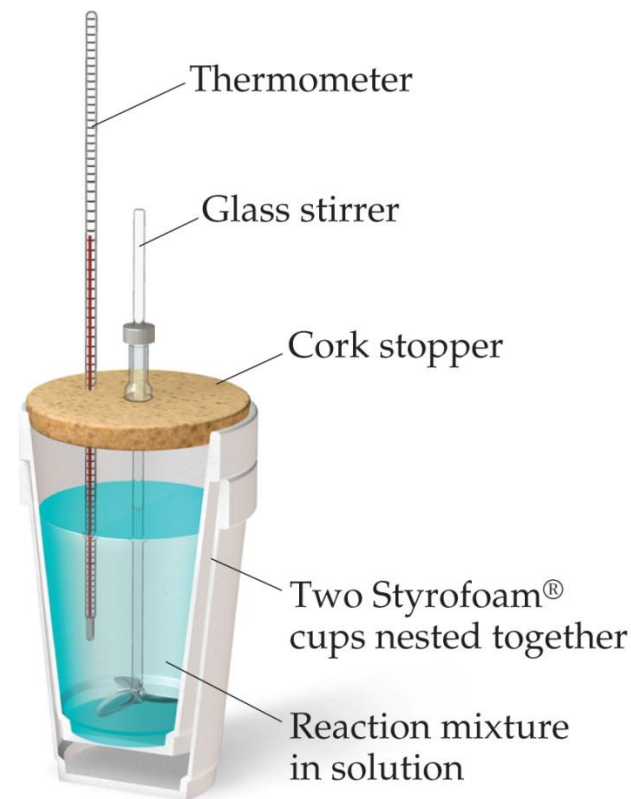
Specific heat, then, is

$$\text{Specific heat} = \frac{\text{heat transferred}}{\text{mass} \times \text{temperature change}}$$

$$C_s = \frac{q}{m \times \Delta T}$$
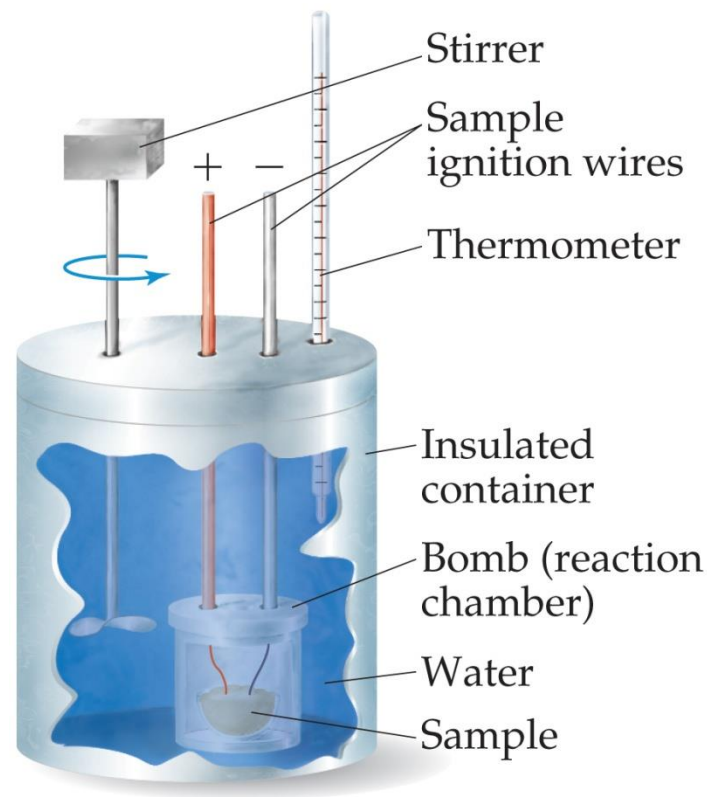
Constant Pressure Calorimetry

- By carrying out a reaction in aqueous solution in a simple calorimeter, the heat change for the system can be found by measuring the heat change for the water in the calorimeter.

- The specific heat for water is well known (4.184 J/g·K).

- We can calculate ΔH for the reaction with this equation:
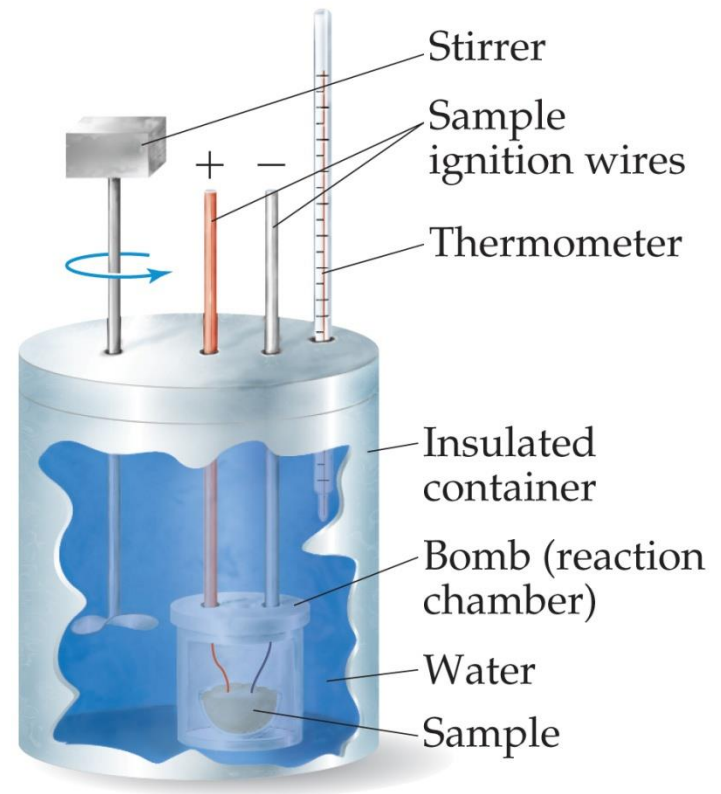
$q = m \times C_s \times \Delta T$

Thermometer

Glass stirrer

Cork stopper

Two Styrofoam® cups nested together

Reaction mixture in solution

Bomb Calorimetry

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

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

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

Stirrer

Sample ignition wires

Thermometer

Insulated container

Bomb (reaction chamber)

Water

Sample

Bomb Calorimetry

- 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.

Stirrer

Sample ignition wires

Thermometer

Insulated container

Bomb (reaction chamber)

Water

Sample

Hess's Law

- ΔH is well known for many reactions, and it is inconvenient to measure ΔH for every reaction in which we are interested.

- However, we can estimate ΔH using published ΔH values and the properties of enthalpy.

Hess's Law
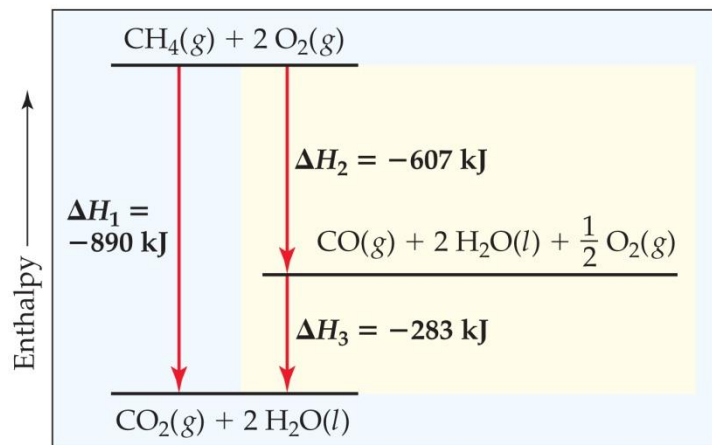
- Hess's law: If a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps.
- Because ΔH is a state function, the total enthalpy change depends only on the initial state (reactants) and the final state (products) of the reaction.

The diagram shows an enthalpy level diagram:

$CH_4(g) + 2 O_2(g)$

$\Delta H_2 = -607 \text{ kJ}$

$\Delta H_1 = -890 \text{ kJ}$

$CO(g) + 2 H_2O(l) + \frac{1}{2} O_2(g)$

$\Delta H_3 = -283 \text{ kJ}$

$CO_2(g) + 2 H_2O(l)$

Enthalpy

Enthalpies of Formation

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

Standard Enthalpies of Formation

Standard enthalpies of formation, $\Delta H_f°$, are measured under standard conditions (25 ⁰C and 1.00 atm pressure).

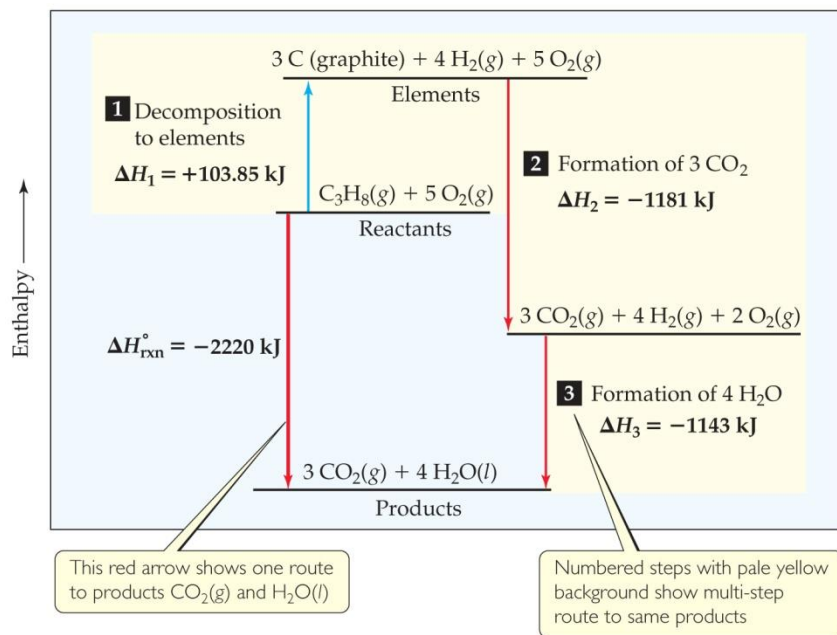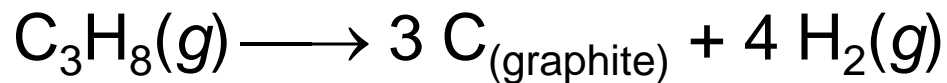**Table 5.3 Standard Enthalpies of Formation, ΔH_f^o, at 298 K**

Substance	Formula	$\Delta H_f°$ (kJ/mol)	Substance	Formula	$\Delta H_f°$ (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

Calculation of ΔH
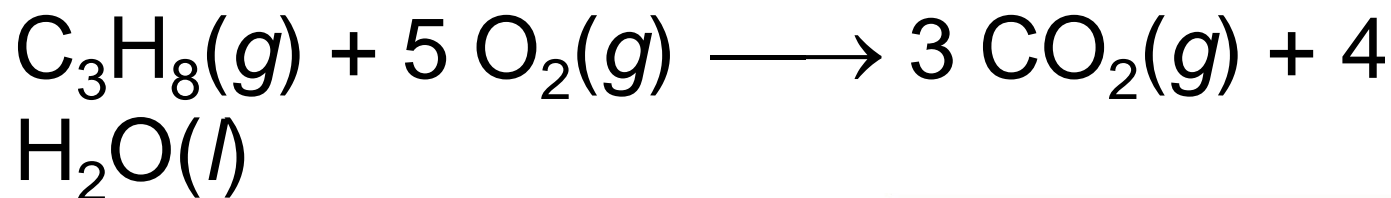
$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$$
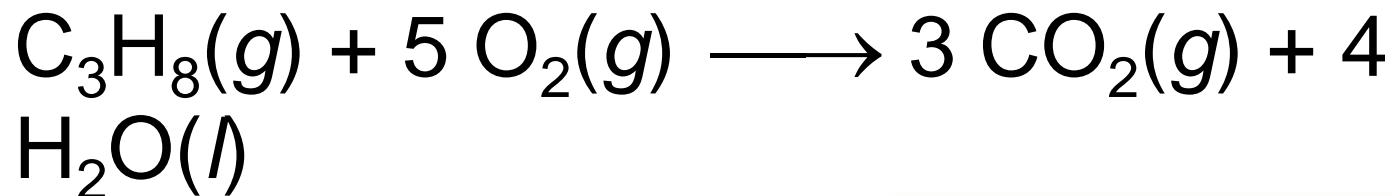
- Imagine this as occurring in three steps:

1) Decomposition of propane to the elements:

$$C_3H_8(g) \longrightarrow 3\ C_{(graphite)} + 4\ H_2(g)$$

Calculation of ΔH

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

- Imagine this as occurring in three steps:

2) Formation of CO_2:

$$3\ C_{(graphite)} + 3\ O_2(g) \longrightarrow 3\ CO_2(g)$$

Calculation of ΔH

$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$$
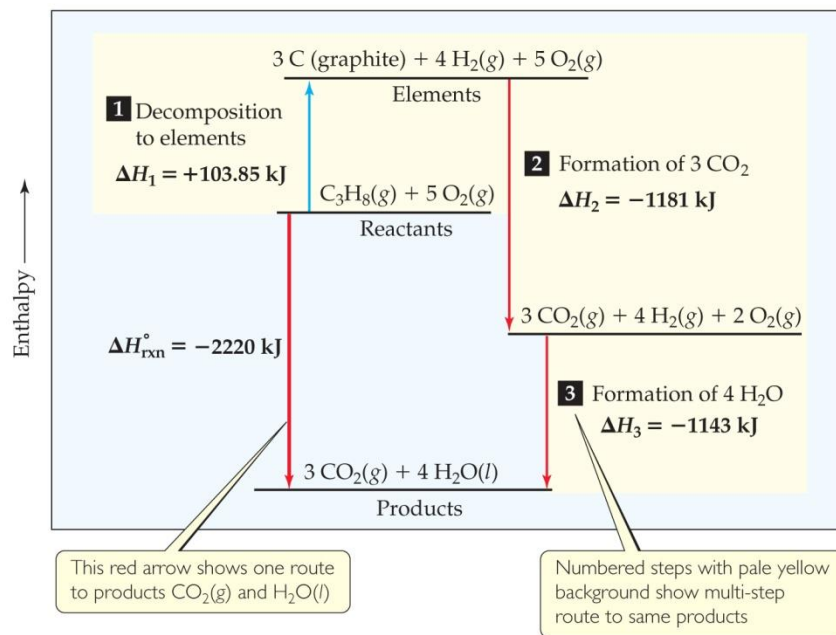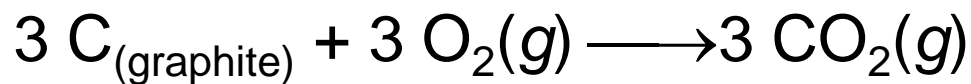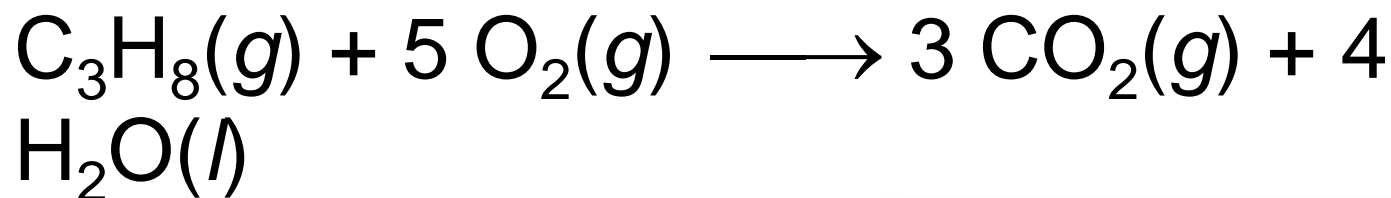
- Imagine this as occurring in three steps:

3) Formation of H_2O:

$$4\ H_2(g) + 2\ O_2(g) \longrightarrow 4\ H_2O(l)$$

Enthalpy

3 C (graphite) + 4 $H_2(g)$ + 5 $O_2(g)$
Elements

1 Decomposition to elements
$\Delta H_1 = +103.85$ kJ

$C_3H_8(g) + 5\ O_2(g)$
Reactants

2 Formation of 3 CO_2
$\Delta H_2 = -1181$ kJ

3 $CO_2(g)$ + 4 $H_2(g)$ + 2 $O_2(g)$

$\Delta H^{\circ}_{rxn} = -2220$ kJ

3 Formation of 4 H_2O
$\Delta H_3 = -1143$ kJ

3 $CO_2(g)$ + 4 $H_2O(l)$
Products

This red arrow shows one route to products $CO_2(g)$ and $H_2O(l)$

Numbered steps with pale yellow background show multi-step route to same products

Calculation of ΔH

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

- So, all steps look like this:

$$C_3H_8(g) \longrightarrow 3\ C_{(graphite)} + 4\ H_2(g)$$
$$3\ C_{(graphite)} + 3\ O_2(g) \longrightarrow 3\ CO_2(g)$$
$$4\ H_2(g) + 2\ O_2(g) \longrightarrow 4\ H_2O(l)$$

$3\ C\ (graphite) + 4\ H_2(g) + 5\ O_2(g)$
Elements

1 Decomposition to elements
$\Delta H_1 = +103.85$ kJ

$C_3H_8(g) + 5\ O_2(g)$
Reactants

2 Formation of $3\ CO_2$
$\Delta H_2 = -1181$ kJ

$\Delta H^{\circ}_{rxn} = -2220$ kJ

$3\ CO_2(g) + 4\ H_2(g) + 2\ O_2(g)$

3 Formation of $4\ H_2O$
$\Delta H_3 = -1143$ kJ

$3\ CO_2(g) + 4\ H_2O(l)$
Products

Enthalpy

This red arrow shows one route to products $CO_2(g)$ and $H_2O(l)$

Numbered steps with pale yellow background show multi-step route to same products

Calculation of ΔH

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

- The sum of these equations is the overall equation!

This red arrow shows one route to products $CO_2(g)$ and $H_2O(l)$

Numbered steps with pale yellow background show multi-step route to same products

$$C_3H_8(g) \longrightarrow 3\ C_{(graphite)} + 4\ H_2(g)$$

$$3\ C_{(graphite)} + 3\ O_2(g) \longrightarrow 3\ CO_2(g)$$

$$4\ H_2(g) + 2\ O_2(g) \longrightarrow 4\ H_2O(l)$$

—————————————————————

$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$$
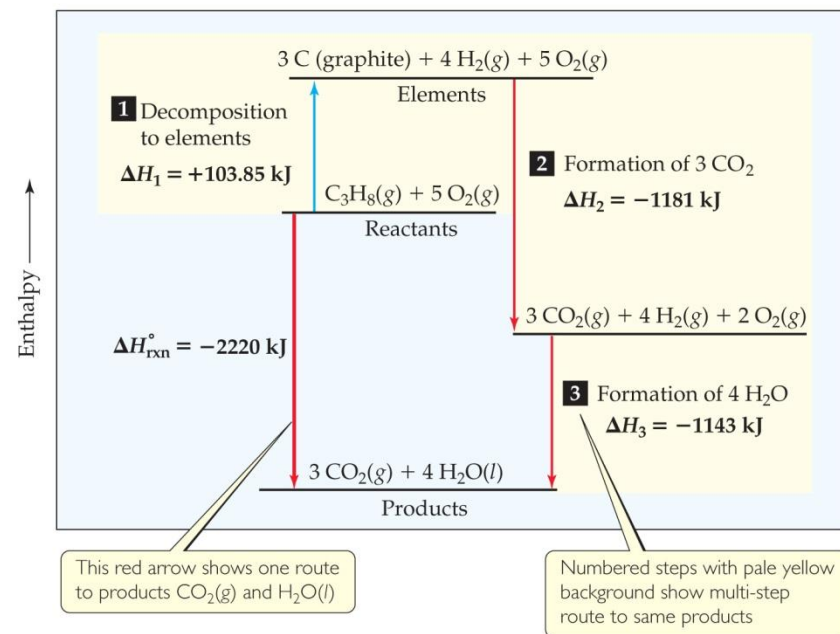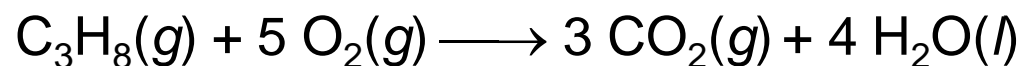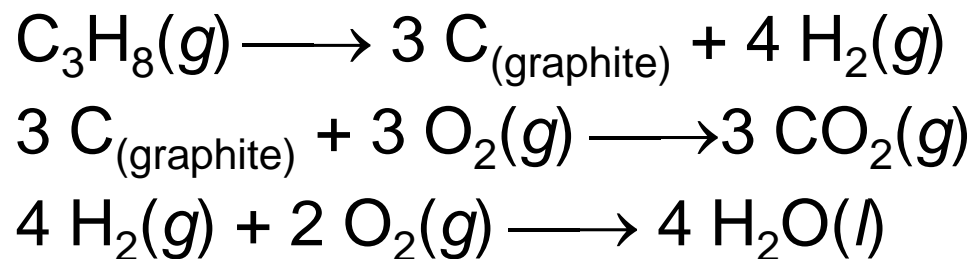
Calculation of ΔH

We can use Hess's law in this way:

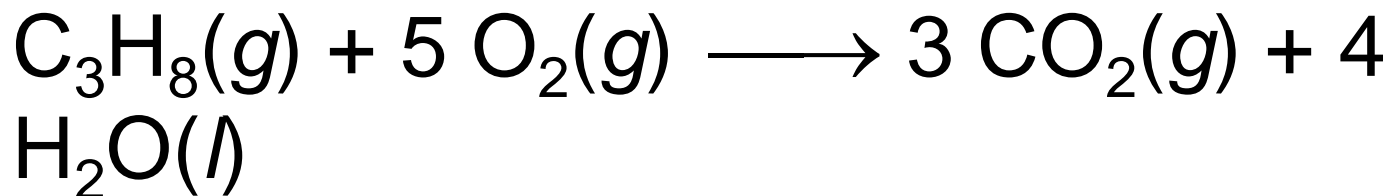$$\Delta H = \Sigma n \Delta H_{f,\text{products}} - \Sigma m \Delta H_f^{\circ}{}_{,\text{reactants}}$$

where *n* and *m* are the stoichiometric coefficients.

Calculation of ΔH using Values from the Standard Enthalpy Table

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

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

$\quad = [(-1180.5\text{ kJ}) + (-1143.2\text{ kJ})] - [(-103.85\text{ kJ}) + (0\text{ kJ})]$

$\quad = (-2323.7\text{ kJ}) - (-103.85\text{ kJ}) \quad = \quad -2219.9\text{ kJ}$

3 C (graphite) + 4 H₂(g) + 5 O₂(g)
Elements

1 Decomposition to elements
$\Delta H_1 = +103.85$ kJ

2 Formation of 3 CO₂
$\Delta H_2 = -1181$ kJ

$C_3H_8(g) + 5\,O_2(g)$
Reactants

Enthalpy

$\Delta H^\circ_{rxn} = -2220$ kJ

3 CO₂(g) + 4 H₂(g) + 2 O₂(g)

3 Formation of 4 H₂O
$\Delta H_3 = -1143$ kJ

3 CO₂(g) + 4 H₂O(l)
Products

This red arrow shows one route to products CO₂(g) and H₂O(l)

Numbered steps with pale yellow background show multi-step route to same products