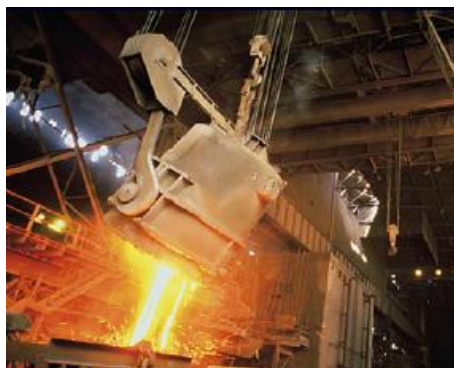
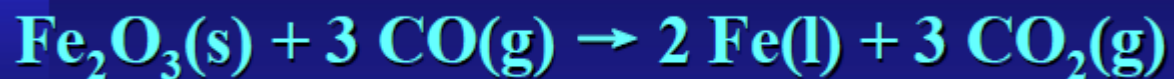


# Chapter 5

## **Thermochemistry**

# ➤ Thermochemistry

- ❑ The study of the energy and heat associated with chemical reactions and/or physical transformations.
- ❑ A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. Thermochemistry focuses on these **energy** changes, particularly on the **system's energy** exchange with its **surroundings**.



## 化学热力学:

用热力学原理研究物质体系中的化学现象和规律, 根据物质体系的宏观可测性质和热力学函数关系来判断体系的稳定性、变化方向和变化的程度。它是物理化学中较早发展起来的一个学科。

## 化学热力学的作用:

- 1) 预测反应发生的可能性
- 2) 判断反应进行的方向 (判据)
- 3) 判断反应进行的限度 (平衡问题)

# 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**.

# 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

# Units of Energy

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

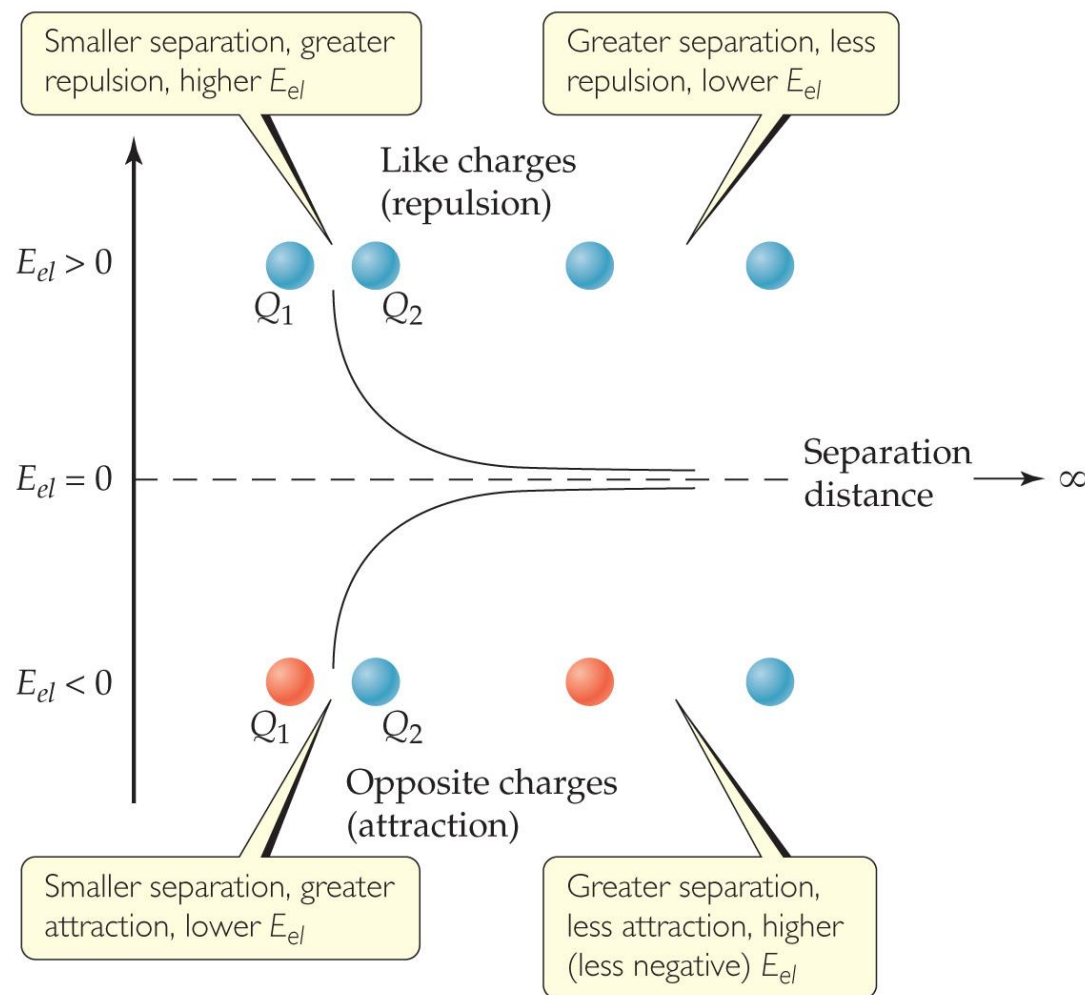
$$1 \text{ J} = 1 \frac{\text{kg m}^2}{\text{s}^2}$$

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

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

$$1 \text{ Cal} = 1000 \text{ cal} = 1 \text{ kcal}$$

# Potential Energy



- **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,  $E_{el}$ :

$$E_{el} = \frac{kQ_1Q_2}{d}$$

$$K = 8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$$

# 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.





# Heat

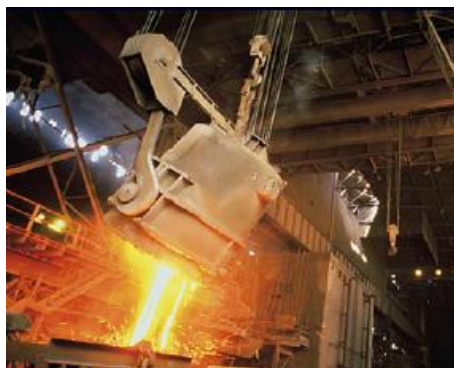
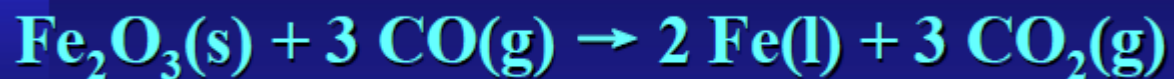
Heat added by burner to water makes water temperature rise



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

# ➤ Thermochemistry

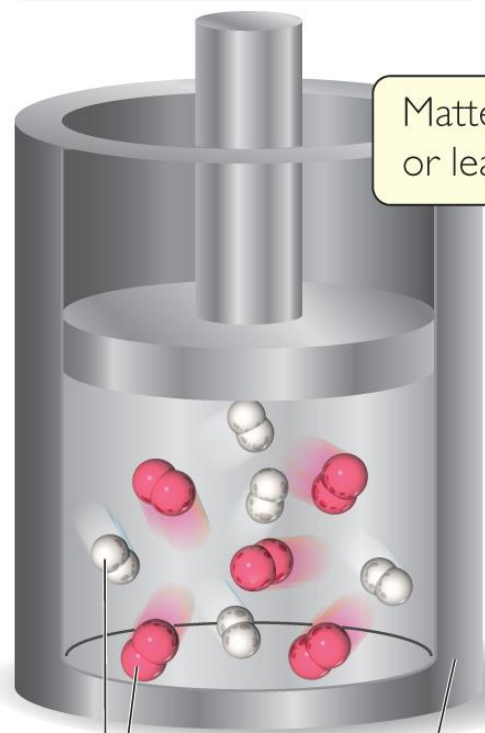
- ❑ The study of the energy and heat associated with chemical reactions and/or physical transformations.
- ❑ A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. Thermochemistry focuses on these **energy** changes, particularly on the **system's energy** exchange with its **surroundings**.



# Definitions: System and Surroundings

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

Matter can not enter or leave system



Surroundings = cylinder, piston, and everything beyond

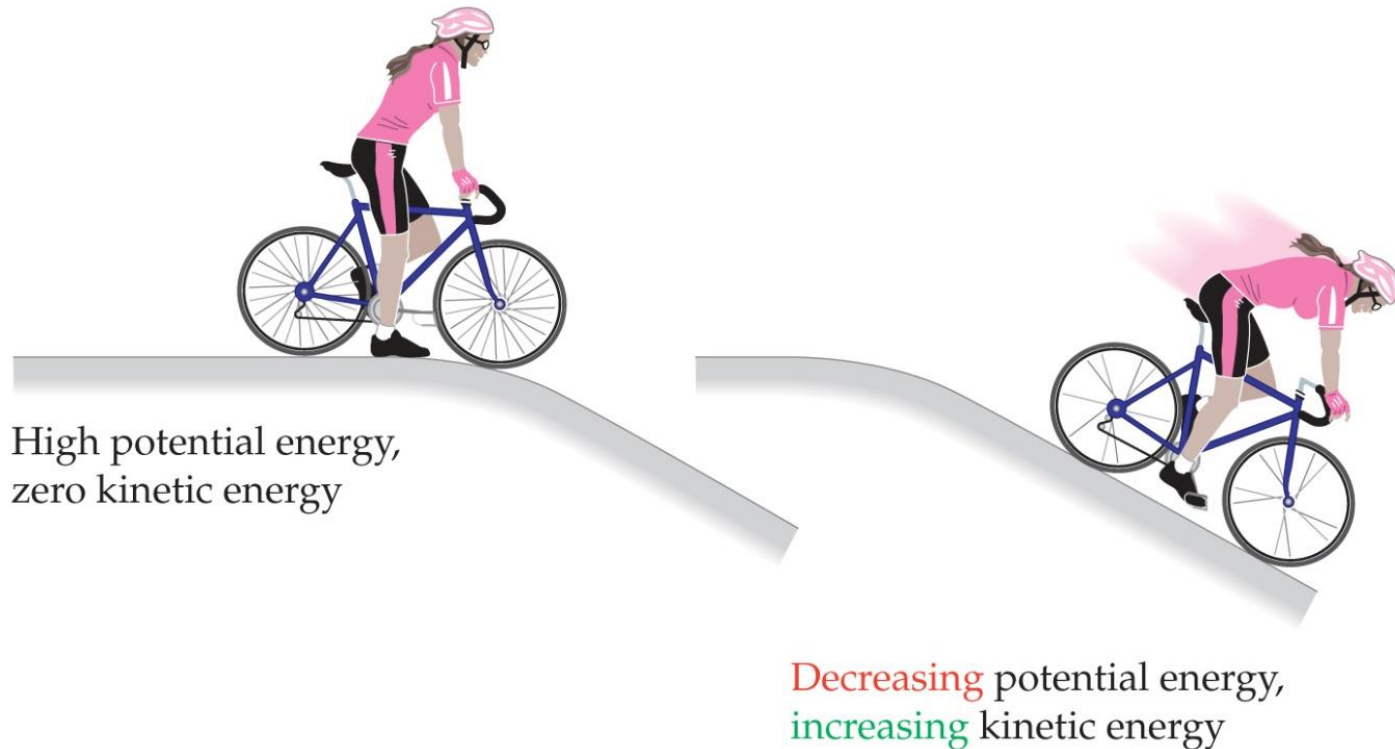
System =  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$

- 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).

# System

- **Open system:** energy and matter can be exchanged with the surroundings.
- **Closed system:** energy but not matter can be exchanged with the surroundings.
- **Isolated system:** neither energy nor matter can be exchanged with the surroundings.

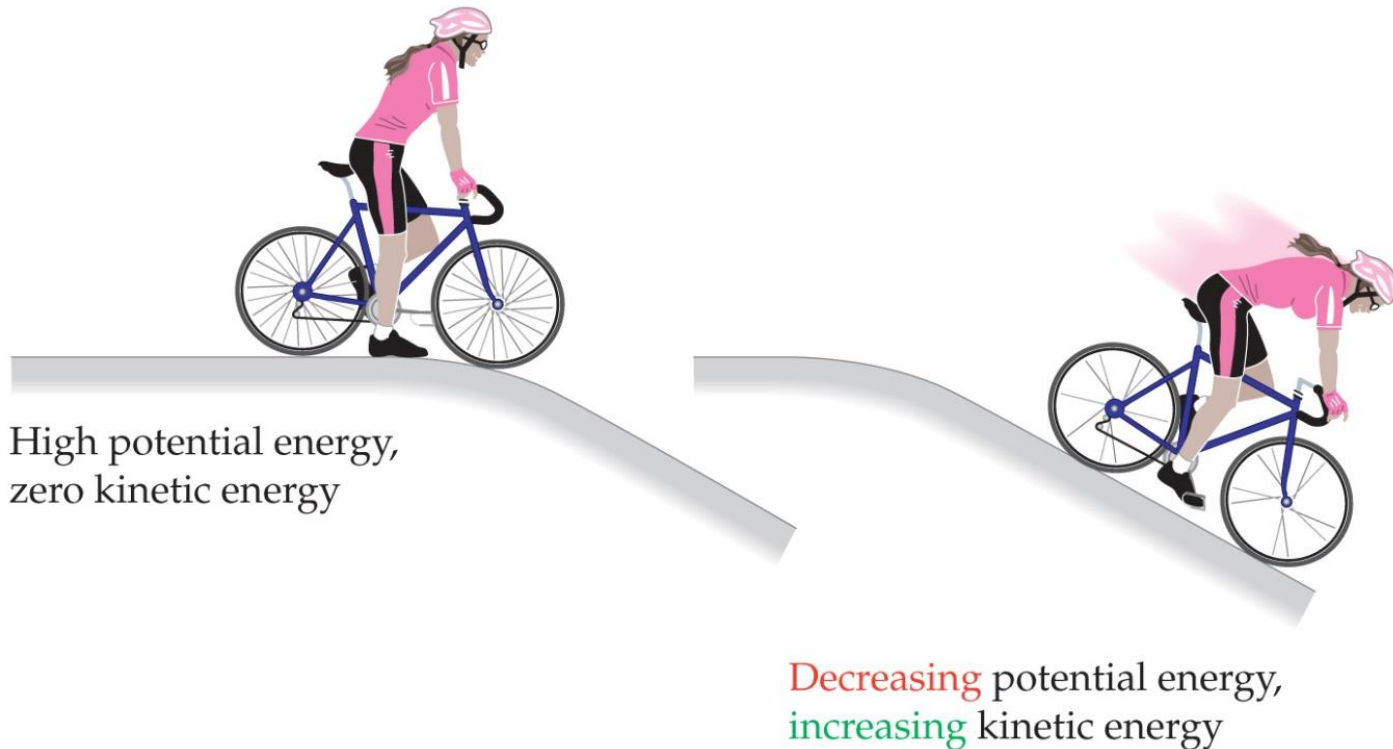
# Conversion of Energy



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- Energy can be converted from one type to another.
- For example, the cyclist in Figure 5.2 has potential energy as she sits on top of the hill.

# Conversion of Energy

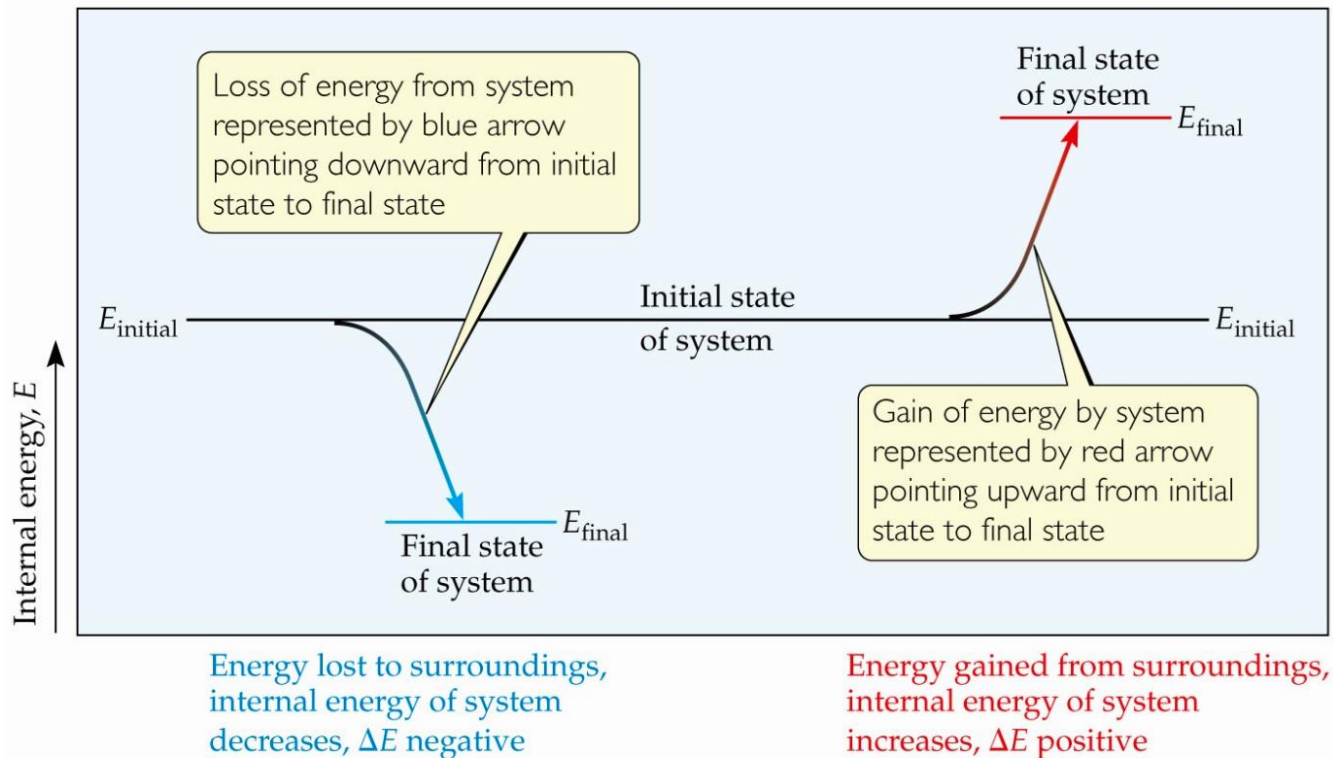


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- As she coasts down the hill, her potential energy is converted to kinetic energy.
- At the bottom, all the potential energy she had at the top of the hill is now kinetic energy.

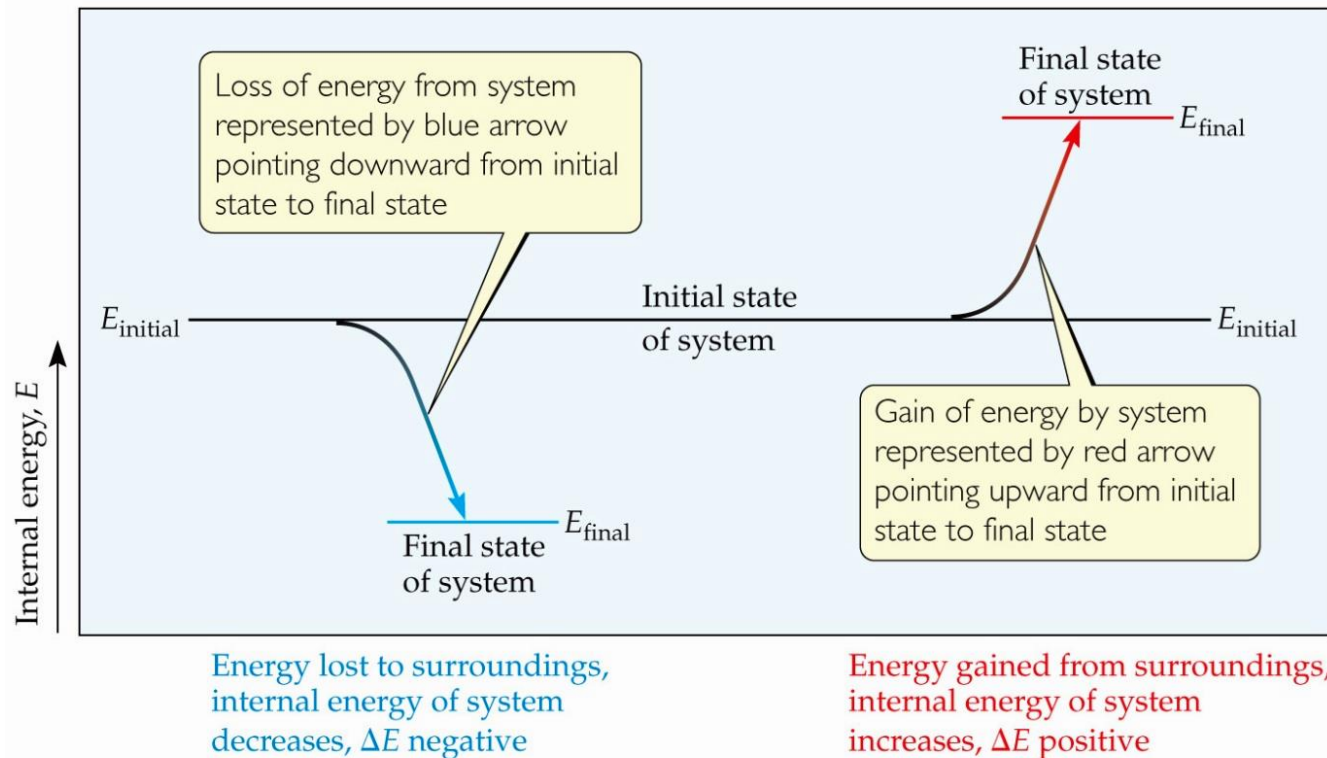
# First Law of Thermodynamics

- 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  $E$ .

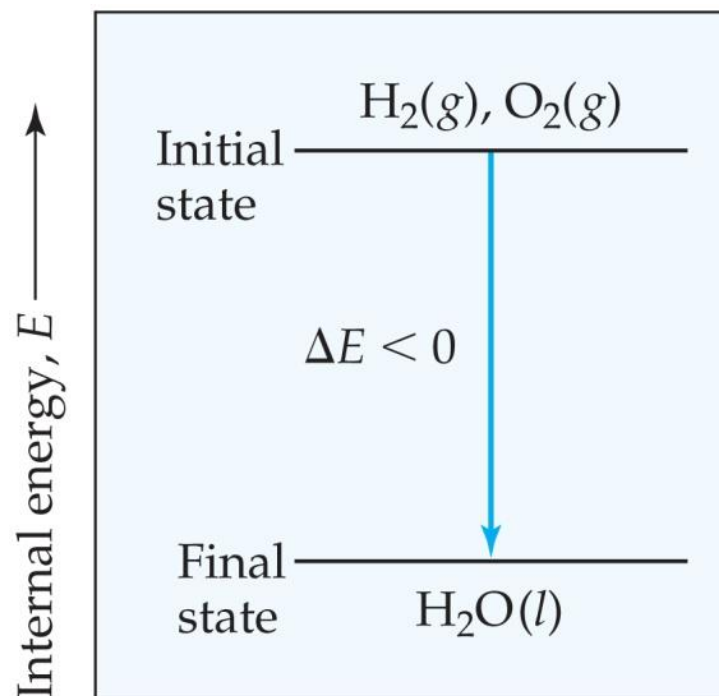




# Changes in Internal Energy

By definition, the change in internal energy,  $\Delta E$ , is the final energy of the system minus the initial energy of the system:

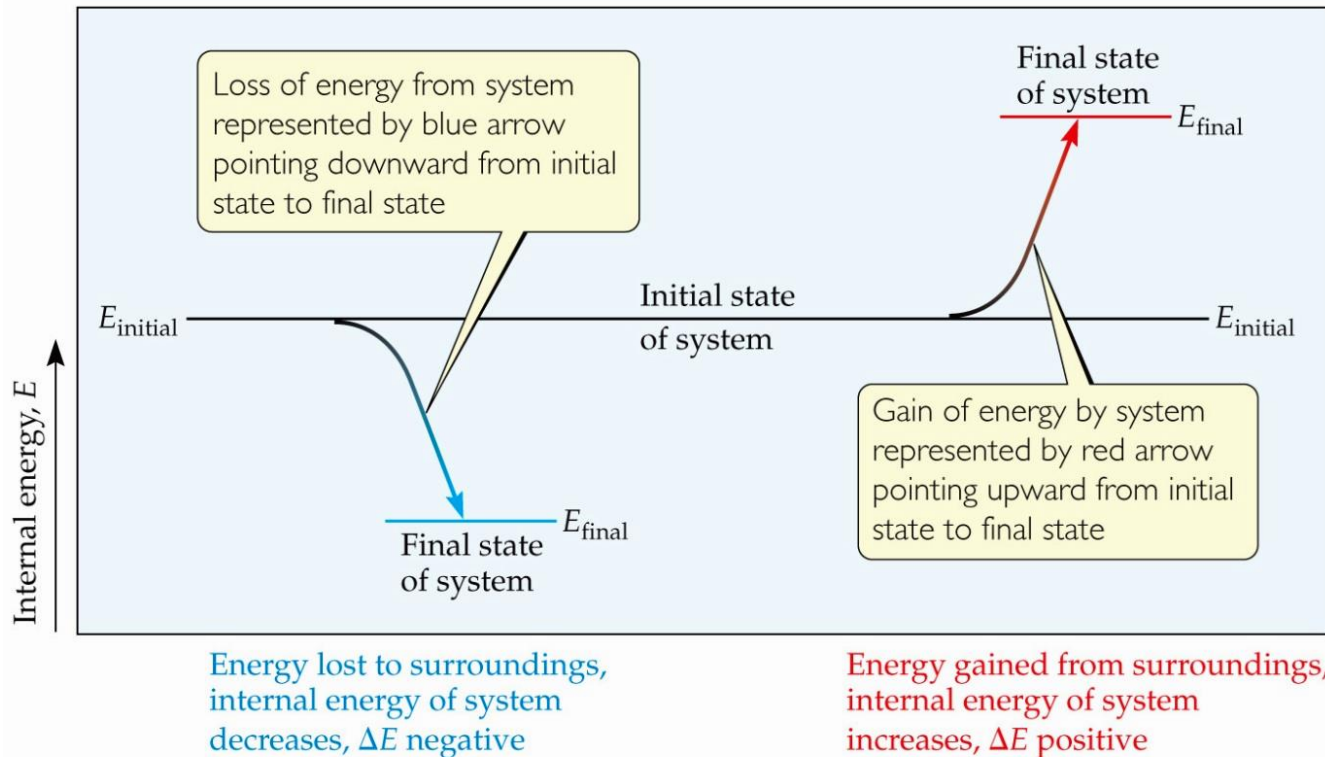
$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$



$E_{\text{initial}}$  greater than  $E_{\text{final}}$ , energy released from system to surroundings during reaction,  $\Delta E < 0$

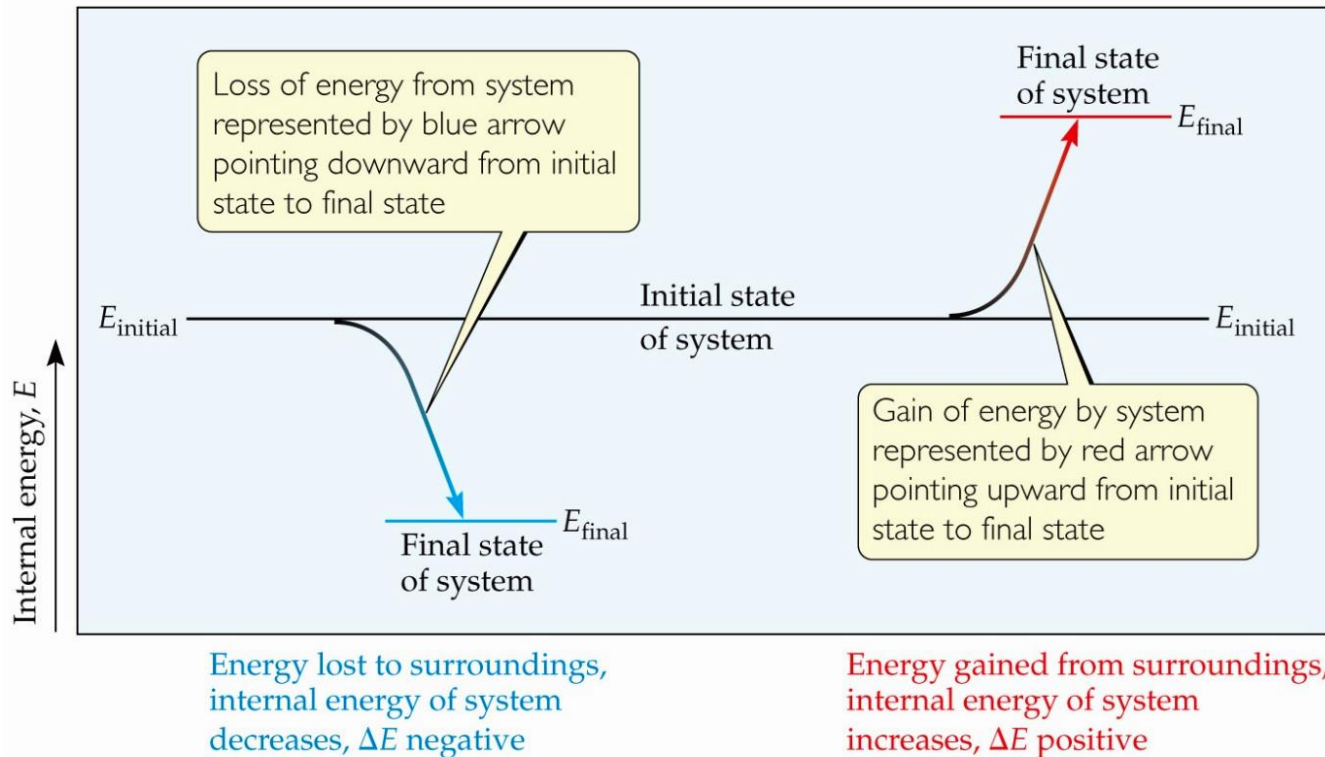
# Changes in Internal Energy

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



# Changes in Internal Energy

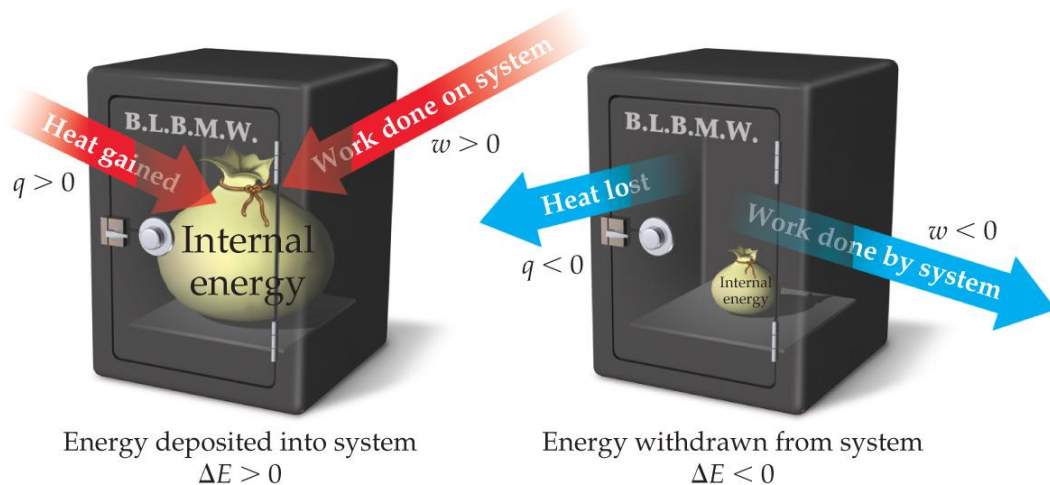
- If  $\Delta E > 0$ ,  $E_{\text{final}} > E_{\text{initial}}$ 
  - Therefore, the system *absorbed* energy from the surroundings.
  - This energy change is called **endergonic**.



# Changes in Internal Energy



System is interior of vault



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- When energy is exchanged between the system and the surroundings, it is exchanged as either heat ( $q$ ) or work ( $w$ ).
- That is,  $\Delta E = q + w$ .

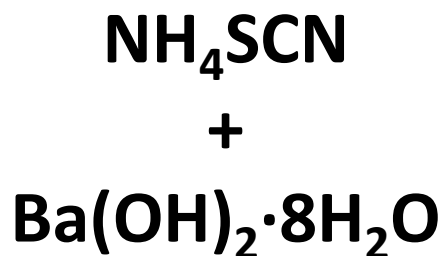
# $\Delta E$ , $q$ , $w$ , and Their Signs

**TABLE 5.1 • Sign Conventions for  $q$ ,  $w$ , and  $\Delta E$**

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 $\Delta E$	+ means <i>net gain</i> of energy by system	– means <i>net loss</i> of energy by system

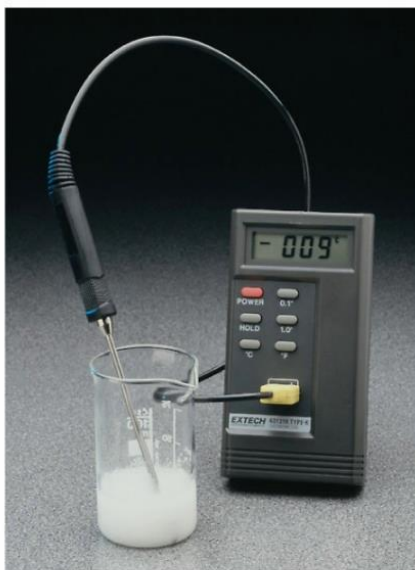
# Exchange of Heat between System and Surroundings

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



**System:** reactants + products

**Surroundings:** solvent,  
initially at room temperature

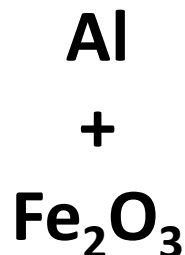


Heat flows from surroundings into system (**endothermic reaction**), temperature of surroundings drops, thermometer reads temperature well below room temperature

dward

# Exchange of Heat between System and Surroundings

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



System: reactants

Surroundings:  
air around reactants

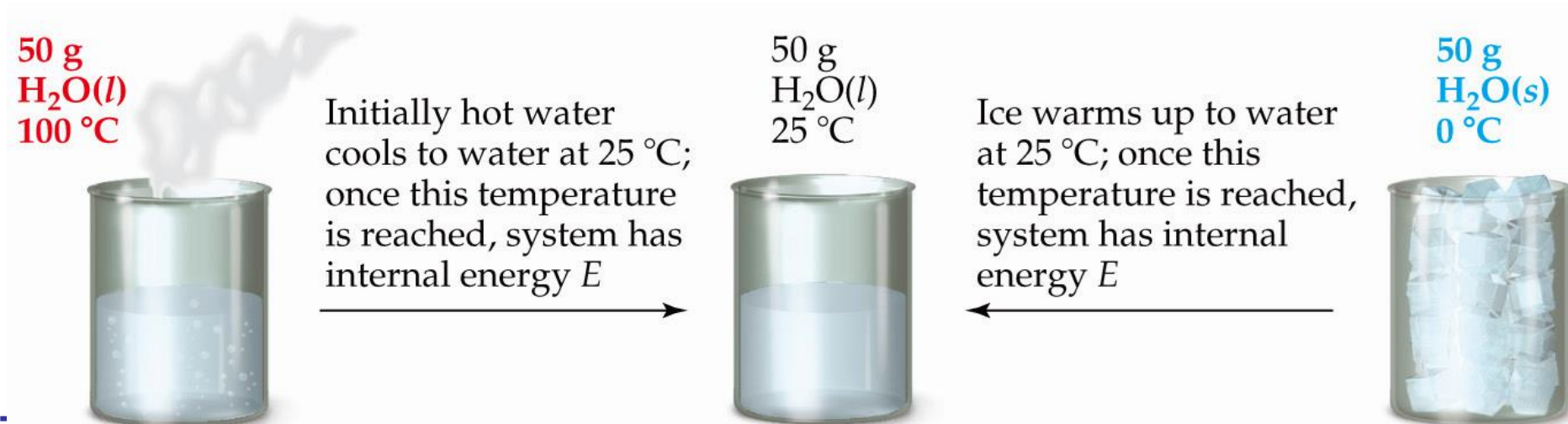


Heat flows (violently) from system into surroundings (**exothermic reaction**), temperature of surroundings increases

odward

# State Functions

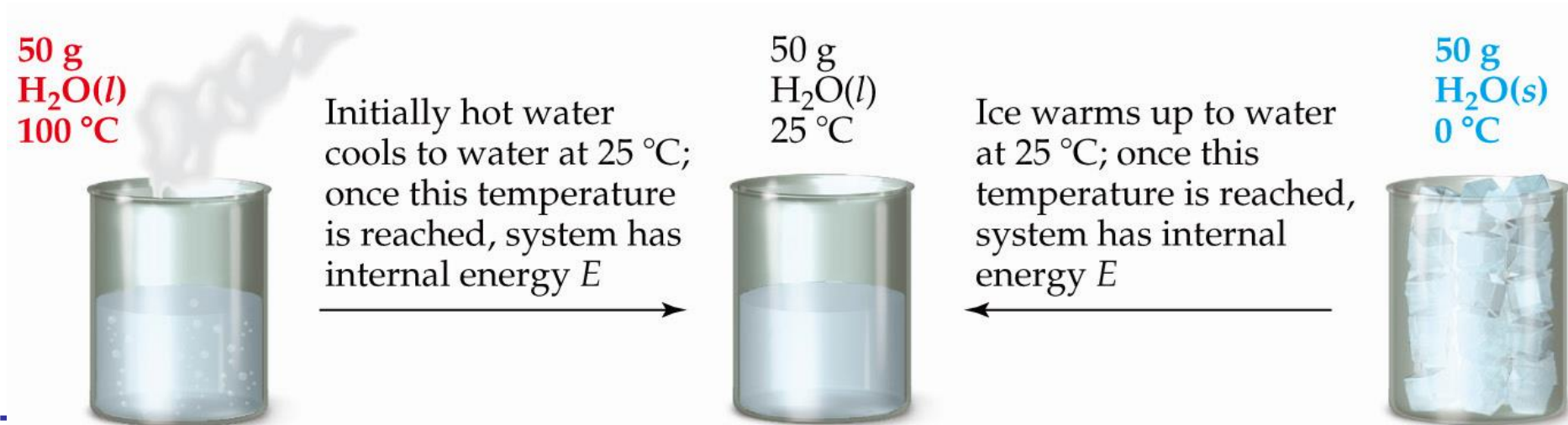
Usually we have no way of knowing the internal energy of a system; finding that value is simply too complex a problem.





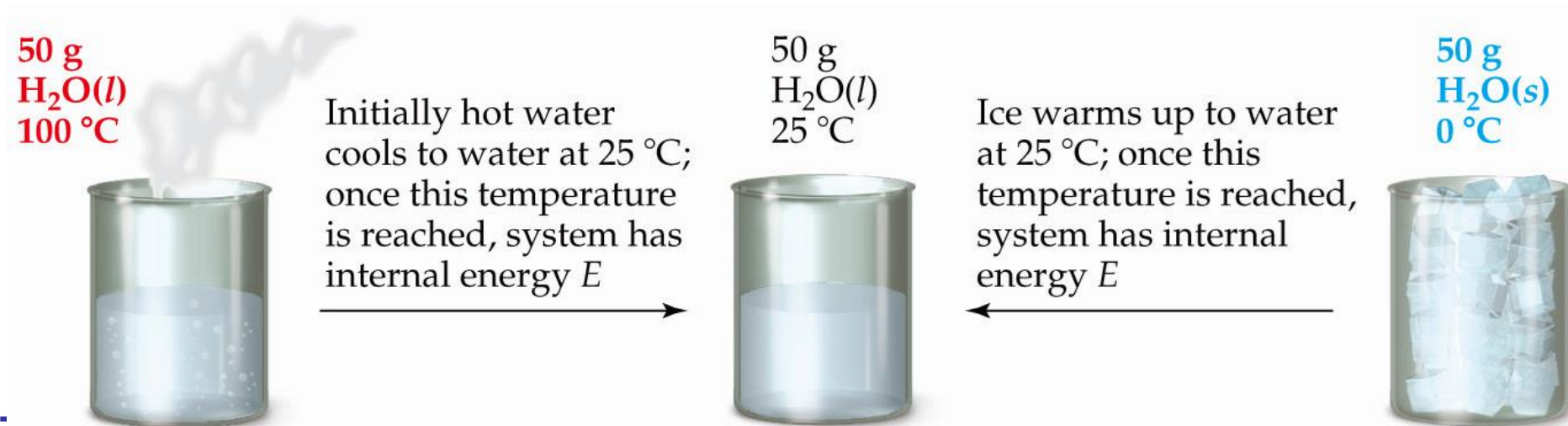
# State Functions

- 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 depicted in Figure 5.9, the water could have reached room temperature from either direction.

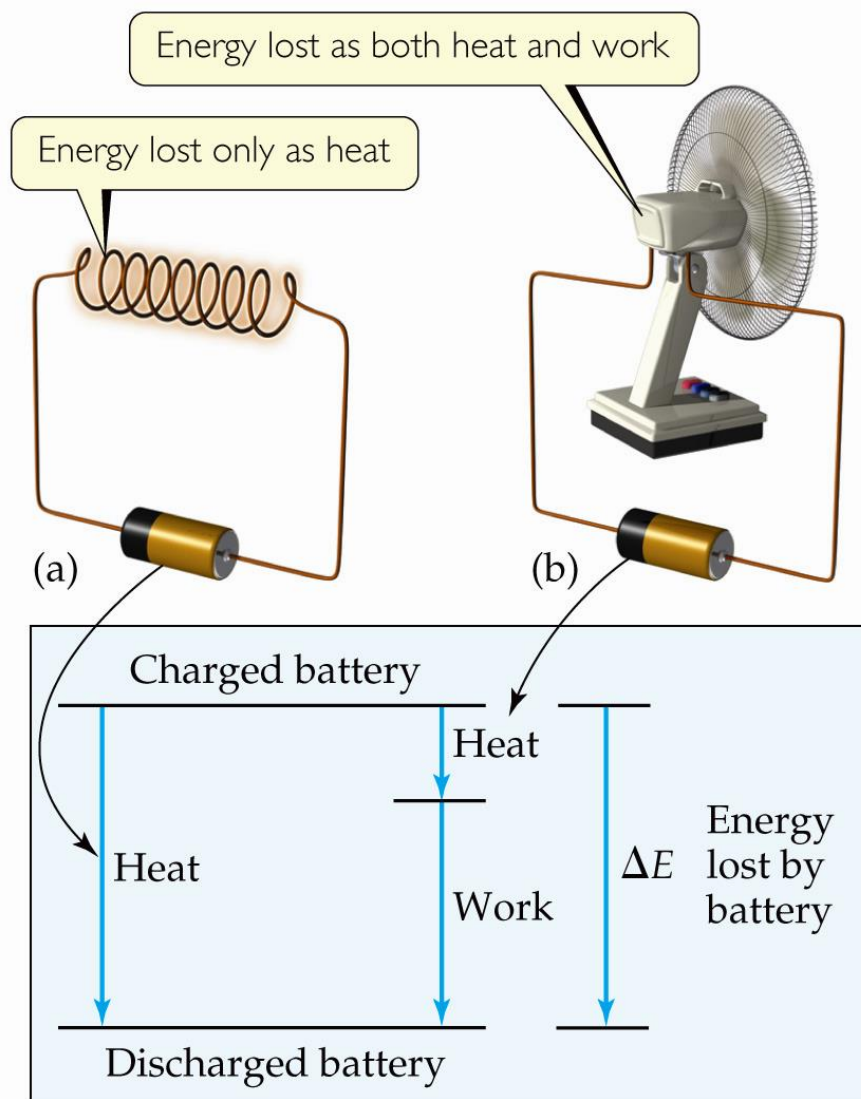


# State Functions

- 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,  $\Delta E$  depends only on  $E_{\text{initial}}$  and  $E_{\text{final}}$ .

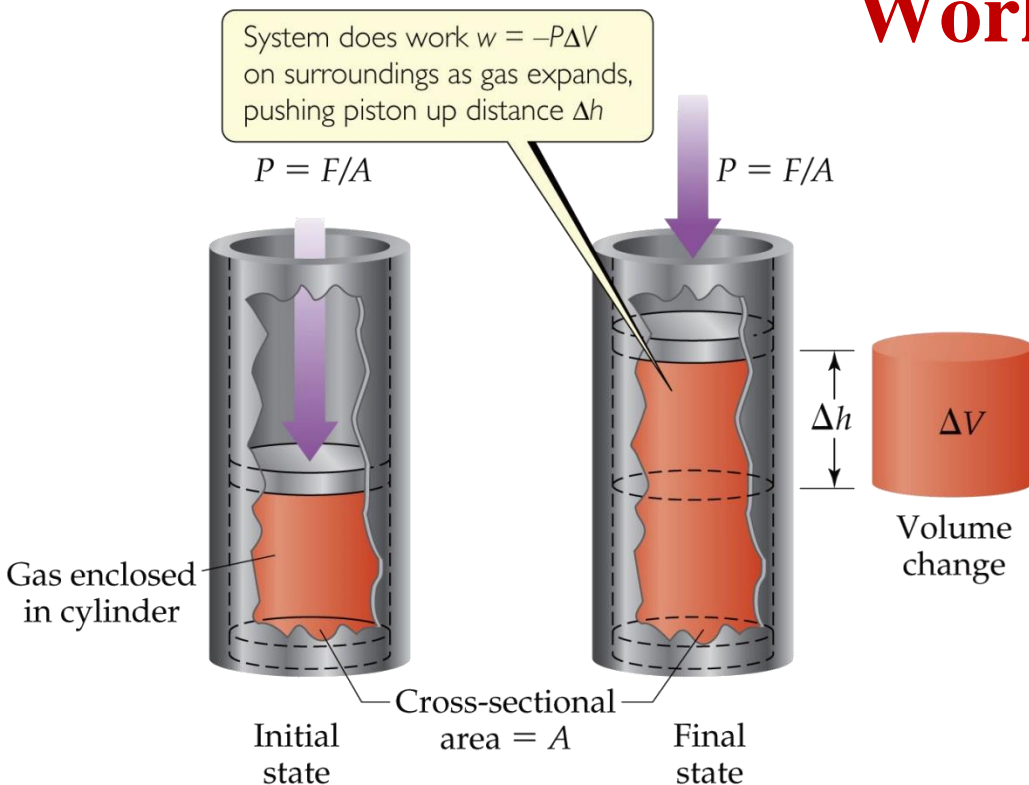


# State Functions



- However,  $q$  and  $w$  are *not* state functions.
- Whether the battery is shorted out or is discharged by running the fan, its  $\Delta E$  is the same.
  - But  $q$  and  $w$  are different in the two cases.

# Work



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).

$$P \text{ (Pressure)} = F \text{ (Force)} / A \text{ (Area)}; F = P \times A$$

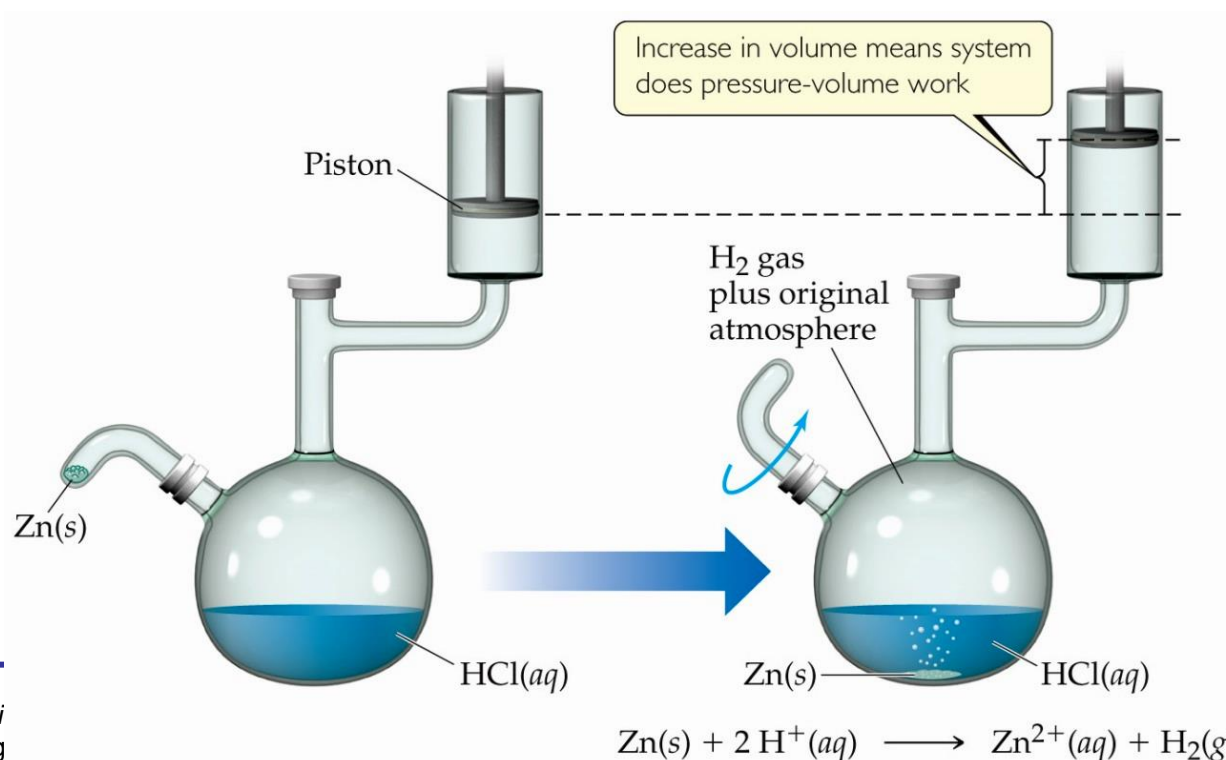
$$\Delta V \text{ (volume)} = A \times \Delta h \text{ (distance)}$$

$$w = -F \times \Delta h = -P \times A \times \Delta h = -P \times \Delta V$$

# 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:

$$w = -P\Delta V$$



[**en**-thal-pee, en-**thal**-]    /'ɛnθælpɪ, ɛn'θæɪ-/

## 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,  $\Delta H$ , 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:

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

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

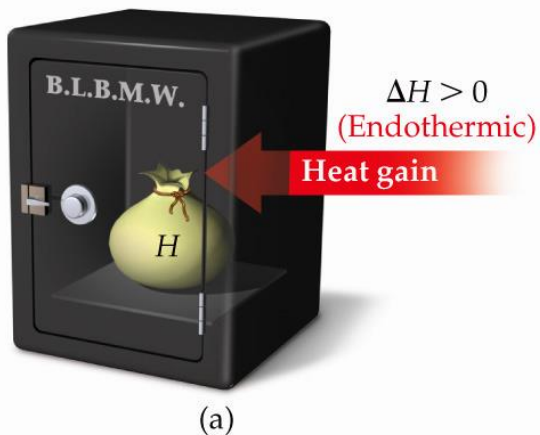
$$\Delta H = q$$

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

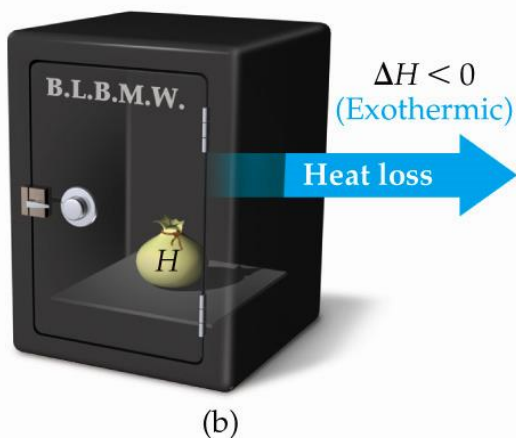


# Endothermicity and Exothermicity

Constant pressure  
maintained in system



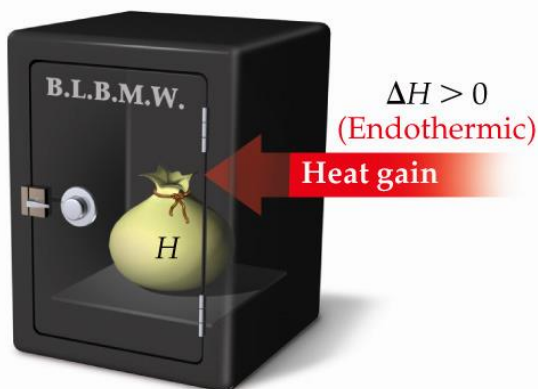
- A process is endothermic when  $\Delta H$  is positive.



$\Delta H$  is amount of heat that  
flows into or out of system  
under constant pressure

# Endothermicity and Exothermicity

Constant pressure  
maintained in system



(a)



(b)

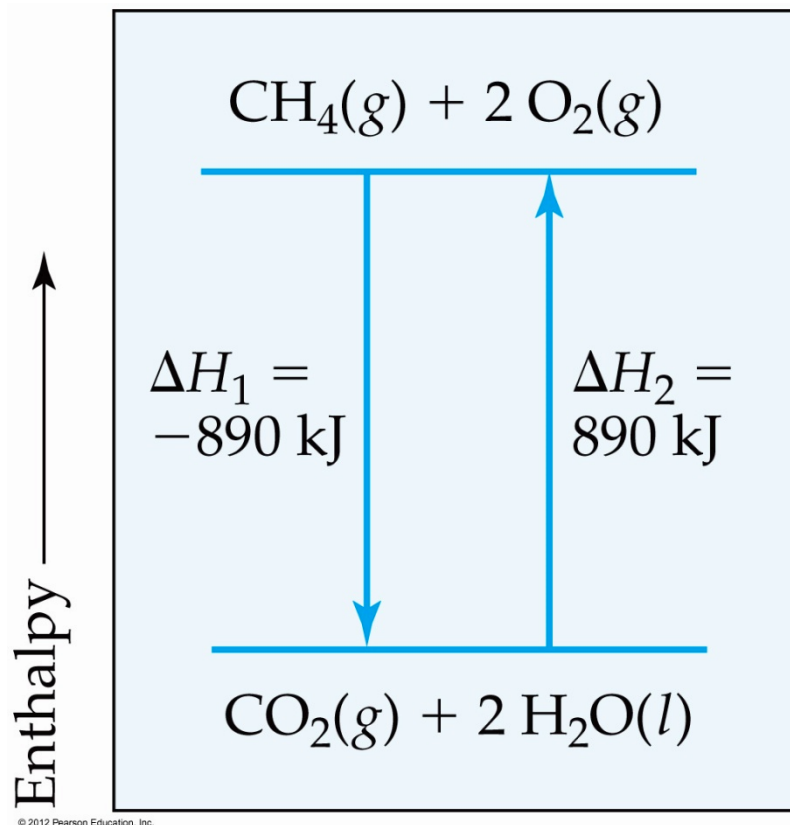
$\Delta H$  is amount of heat that  
flows into or out of system  
under constant pressure

- A process is endothermic when  $\Delta H$  is positive.
- A process is exothermic when  $\Delta H$  is negative.

# Enthalpy of Reaction

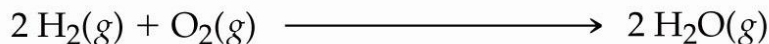
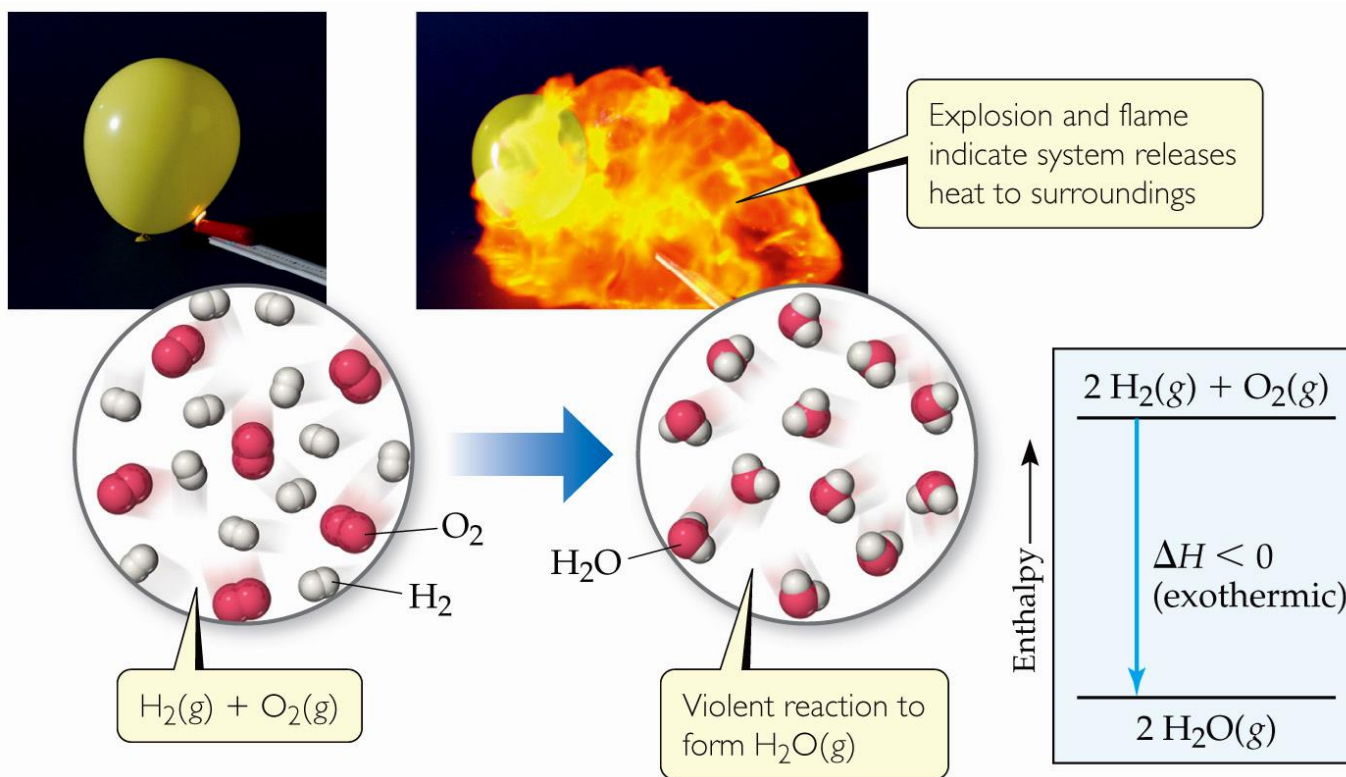
The *change* in enthalpy of reaction,  $\Delta H$ , is the enthalpy of the products minus the enthalpy of the reactants:

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



# Enthalpy of Reaction

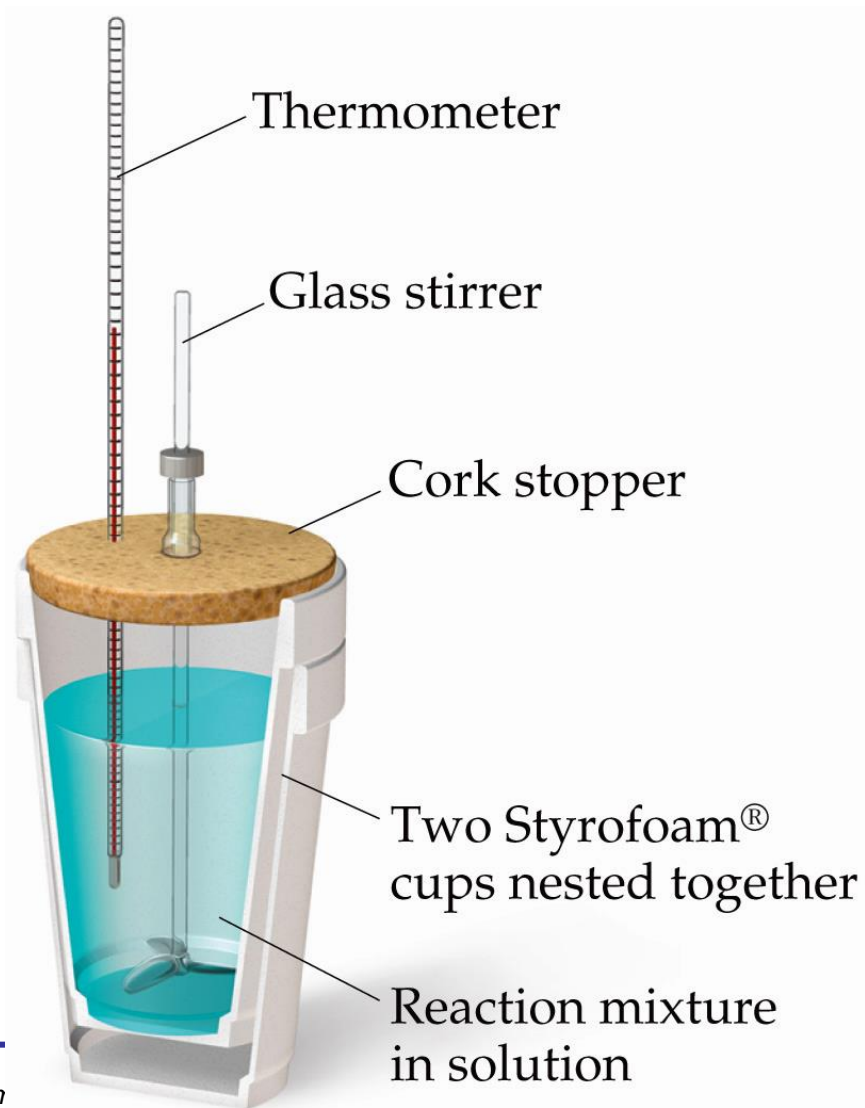
This quantity,  $\Delta H$ , or  $\Delta H_{\text{rxn}}$ , is called the **enthalpy of reaction**, or the **heat of reaction**.



# The Truth about Enthalpy

1. Enthalpy is an extensive property.
2.  $\Delta H$  for a reaction in the forward direction is equal in size, but opposite in sign, to  $\Delta H$  for the reverse reaction.
3.  $\Delta H$  for a reaction depends on the state of the products and the state of the reactants.

# Calorimetry (method) – calorimeter (device)



Since we cannot know the exact enthalpy of the reactants and products, we measure  $\Delta H$  through calorimetry, the measurement of heat flow.

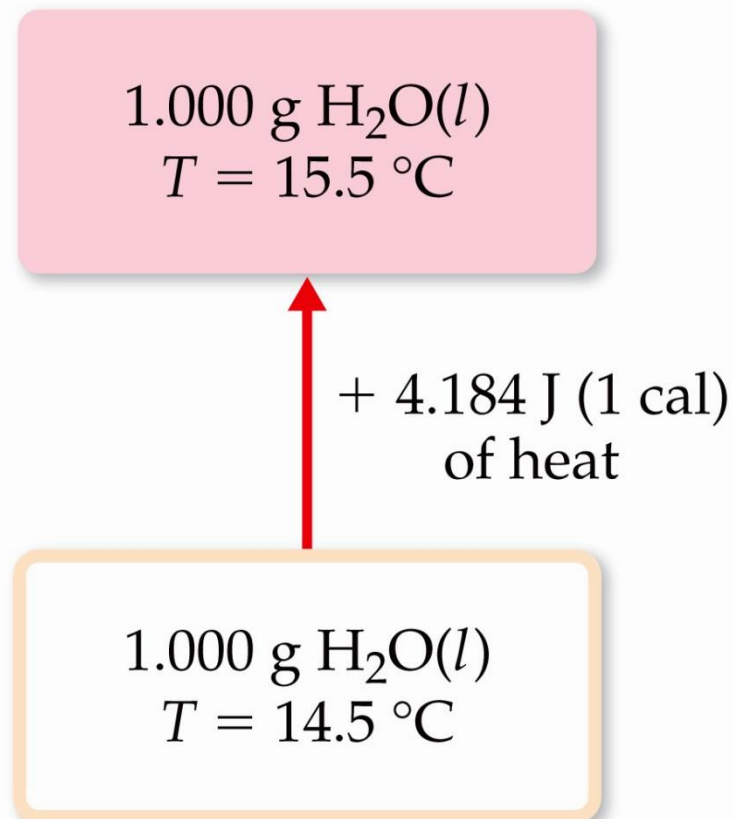
# Heat Capacity and Specific Heat

The amount of energy required to raise the temperature of a substance by 1 K ( $1^{\circ}\text{C}$ ) is its **heat capacity**.

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  $1^{\circ}\text{C}$ ).

# 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).



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# Heat Capacity and Specific Heat

**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)
$\text{N}_2(g)$	1.04	$\text{H}_2\text{O}(l)$	4.18
$\text{Al}(s)$	0.90	$\text{CH}_4(g)$	2.20
$\text{Fe}(s)$	0.45	$\text{CO}_2(g)$	0.84
$\text{Hg}(l)$	0.14	$\text{CaCO}_3(s)$	0.82

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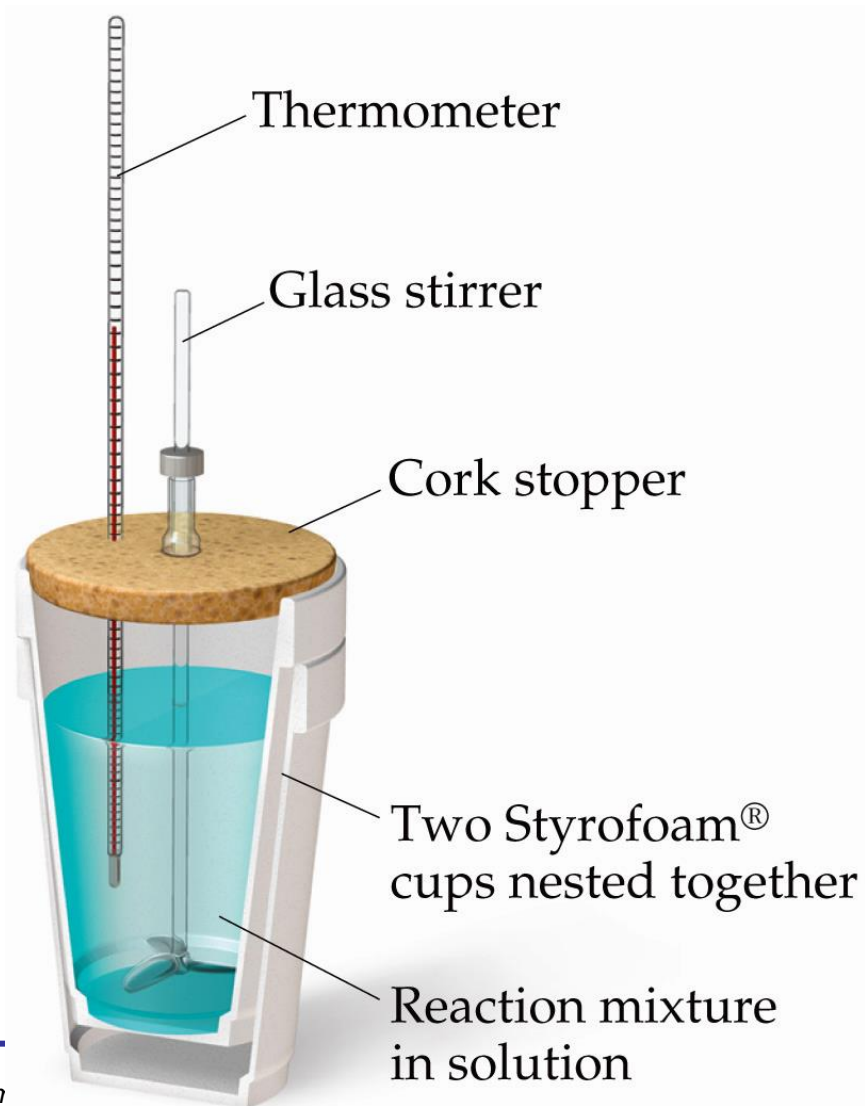
# Heat Capacity and Specific Heat

Specific heat, then, is

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

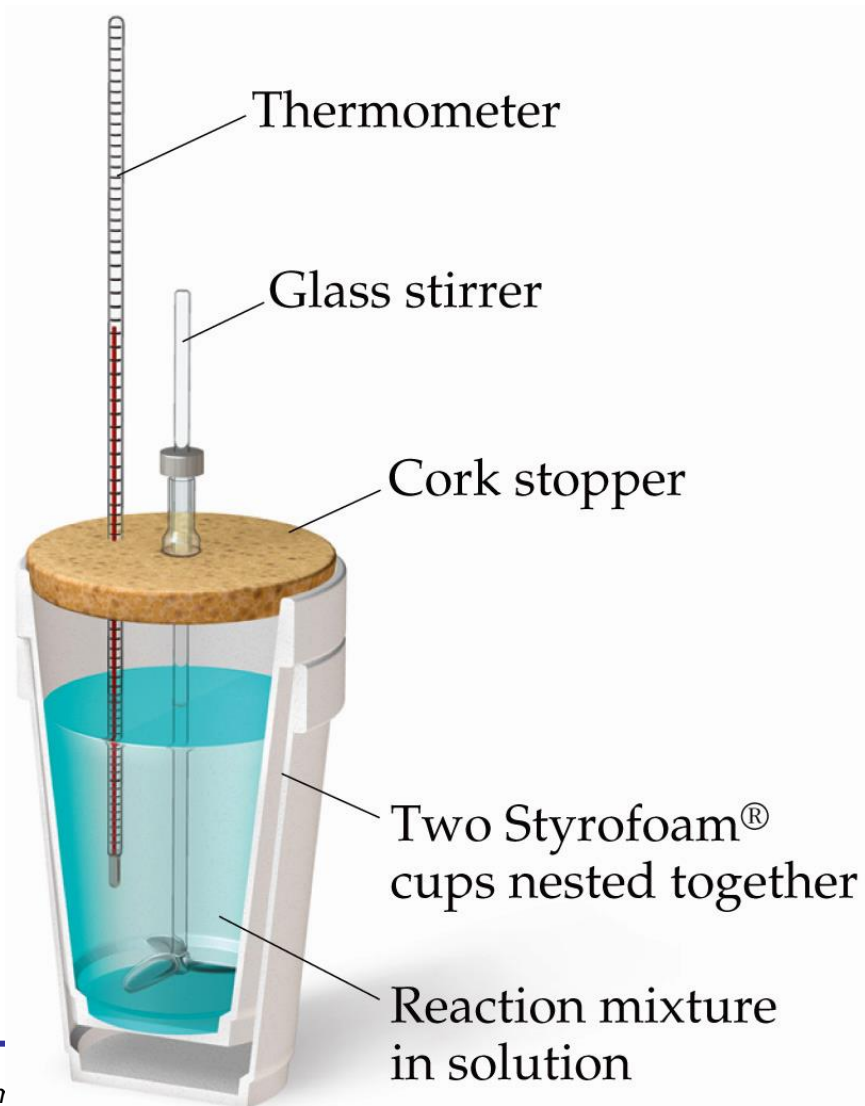
$$C_s = \frac{q}{m \times \Delta T}$$

# Constant Pressure (heat versus $\Delta H$ ) Calorimetry



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

# Constant Pressure Calorimetry



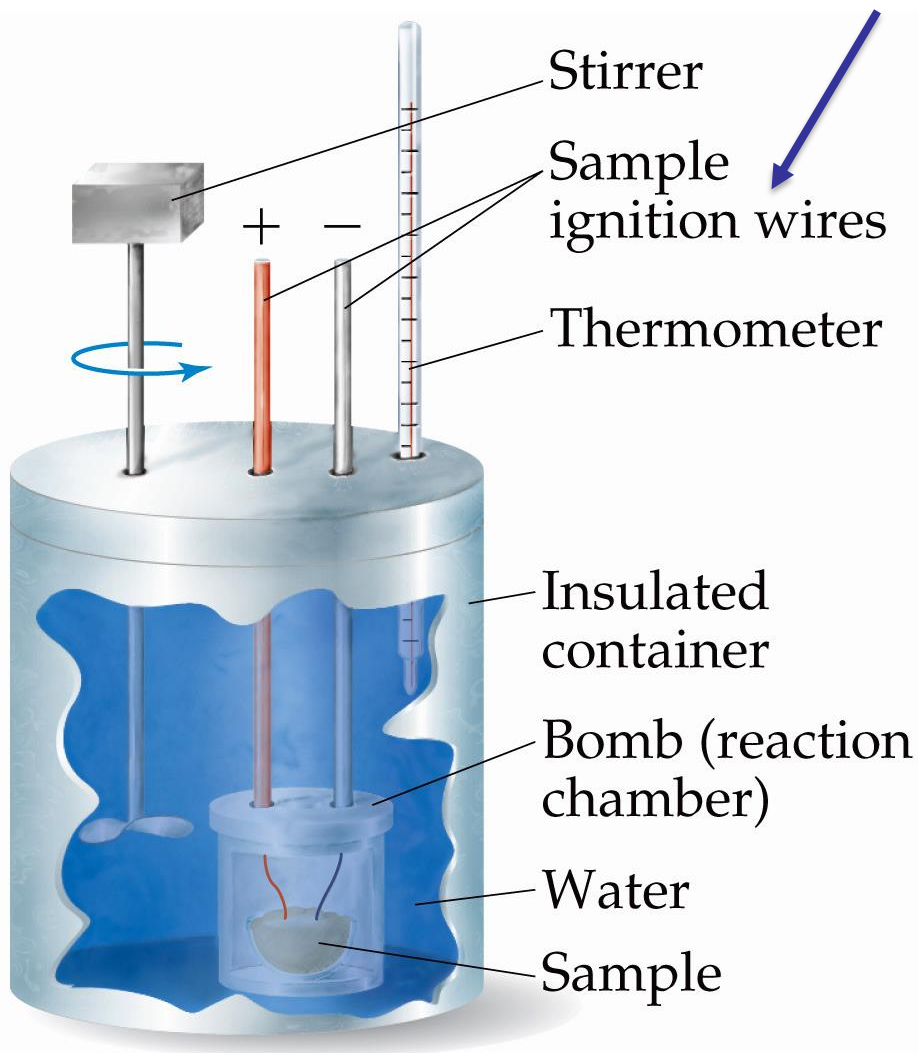
Because the specific heat for water is well known (4.184 J/g-K), we can measure  $\Delta H$  for the reaction with this equation:

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

Specific heat

# Bomb Calorimetry (fixed volume but not pressure)

- 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.

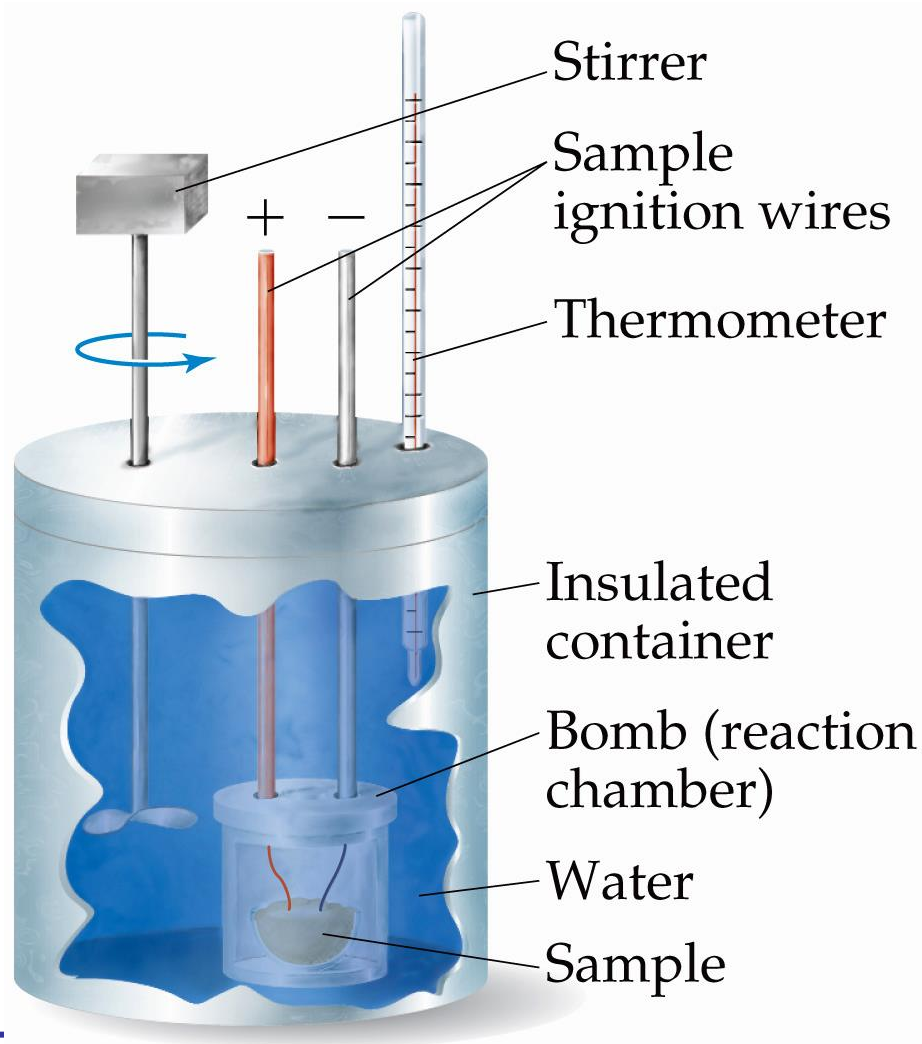


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# Bomb Calorimetry

- Because the volume in the bomb calorimeter is constant, what is measured is really the change in internal energy,  $\Delta E$ , not  $\Delta H$ .
- For most reactions, the difference is very small.



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# Bomb Calorimetry

$$\Delta E = q + w$$

If P-V work is the only work that can be done,

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

When the reaction is carried out in a **constant-volume** container ( $\Delta V = 0$ ),

$$\Delta E = q_v$$

Most reactions are run under **constant pressure**,

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

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

$$\Delta(E + PV) = q_p \quad H = E + PV \text{ (a new state function)}$$

$$\Delta H = q_p$$

# Enthalpies of Formation

An enthalpy of formation,  $\Delta H_f$ , 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,  $\Delta H_f^\circ$ , are measured under standard conditions (25 °C and 1.00 atm pressure).

**TABLE 5.3 • Standard Enthalpies of Formation,  $\Delta H_f^\circ$ , at 298 K**

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)	Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Acetylene	$\text{C}_2\text{H}_2(\text{g})$	226.7	Hydrogen chloride	$\text{HCl}(\text{g})$	−92.30
Ammonia	$\text{NH}_3(\text{g})$	−46.19	Hydrogen fluoride	$\text{HF}(\text{g})$	−268.60
Benzene	$\text{C}_6\text{H}_6(\text{l})$	49.0	Hydrogen iodide	$\text{HI}(\text{g})$	25.9
Calcium carbonate	$\text{CaCO}_3(\text{s})$	−1207.1	Methane	$\text{CH}_4(\text{g})$	−74.80
Calcium oxide	$\text{CaO}(\text{s})$	−635.5	Methanol	$\text{CH}_3\text{OH}(\text{l})$	−238.6
Carbon dioxide	$\text{CO}_2(\text{g})$	−393.5	Propane	$\text{C}_3\text{H}_8(\text{g})$	−103.85
Carbon monoxide	$\text{CO}(\text{g})$	−110.5	Silver chloride	$\text{AgCl}(\text{s})$	−127.0
Diamond	$\text{C}(\text{s})$	1.88	Sodium bicarbonate	$\text{NaHCO}_3(\text{s})$	−947.7
Ethane	$\text{C}_2\text{H}_6(\text{g})$	−84.68	Sodium carbonate	$\text{Na}_2\text{CO}_3(\text{s})$	−1130.9
Ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	−277.7	Sodium chloride	$\text{NaCl}(\text{s})$	−410.9
Ethylene	$\text{C}_2\text{H}_4(\text{g})$	52.30	Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$	−2221
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	−1273	Water	$\text{H}_2\text{O}(\text{l})$	−285.8
Hydrogen bromide	$\text{HBr}(\text{g})$	−36.23	Water vapor	$\text{H}_2\text{O}(\text{g})$	−241.8

# Standard Enthalpies of Formation

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  $\Delta H_f^\circ$  for C(graphite),  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ , and the standard states of other elements are **zero** by definition.

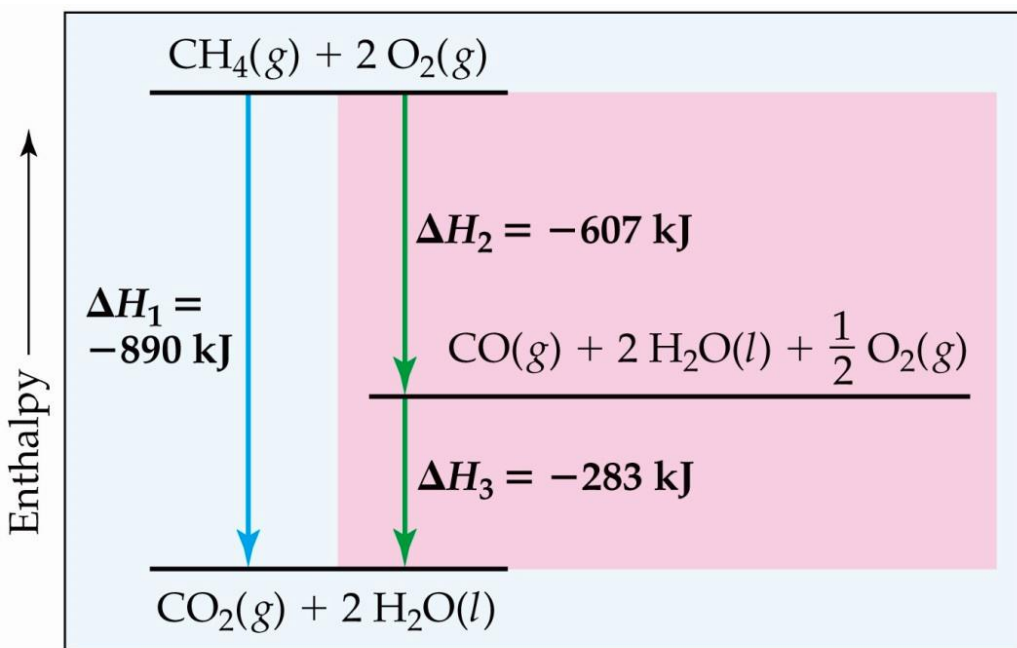
See **Table 5.3** and **Appendix C** for listed  $\Delta H_f^\circ$  data.

## Hess's Law

- $\Delta H$  is well known for many reactions, and it is inconvenient to measure  $\Delta H$  for every reaction in which we are interested.
- However, we can estimate  $\Delta H$  using published  $\Delta H$  values and the properties of enthalpy.

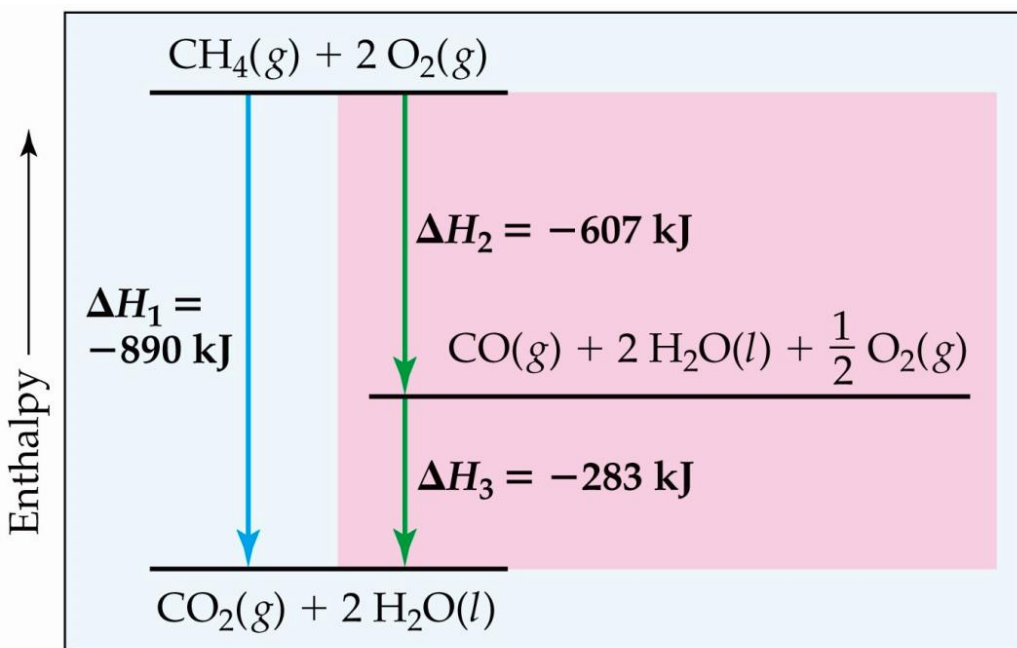
from known reactions to **unknown** reactions

# Hess's Law



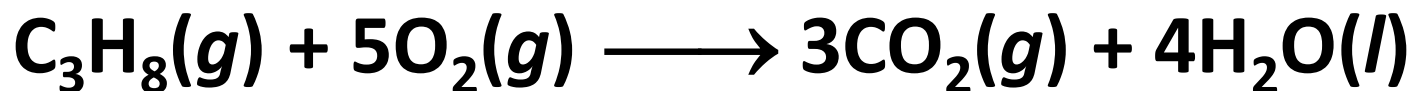
Hess's law states that “if a reaction is carried out in a series of steps,  $\Delta H$  for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps.”

# Hess's Law

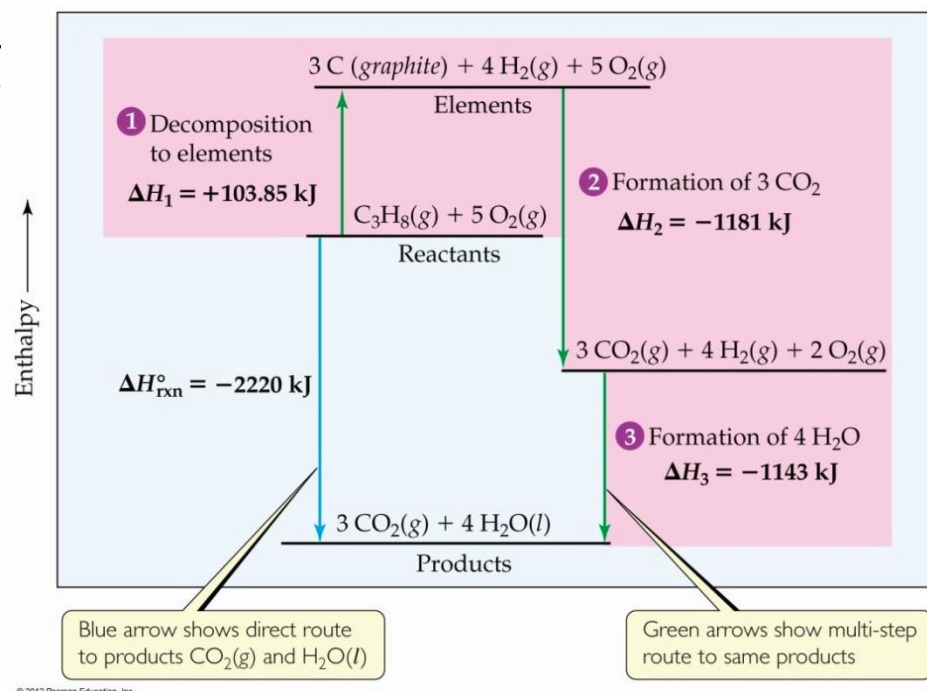
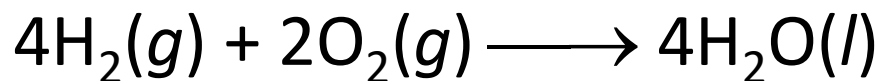
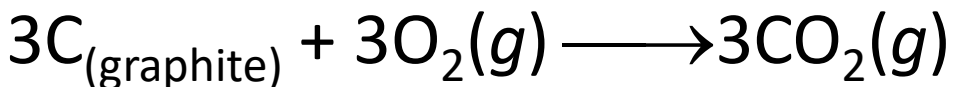
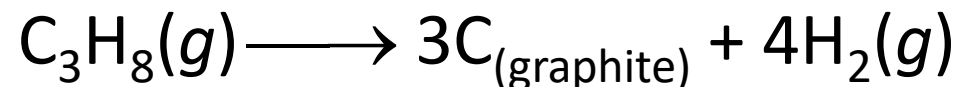


Because  $\Delta H$  is a **state function**, the total enthalpy change depends only on the initial state of the reactants and the final state of the products.

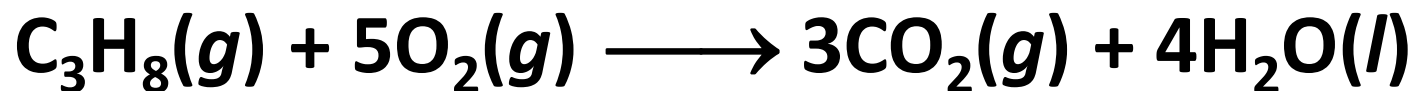
# Calculation of $\Delta H$



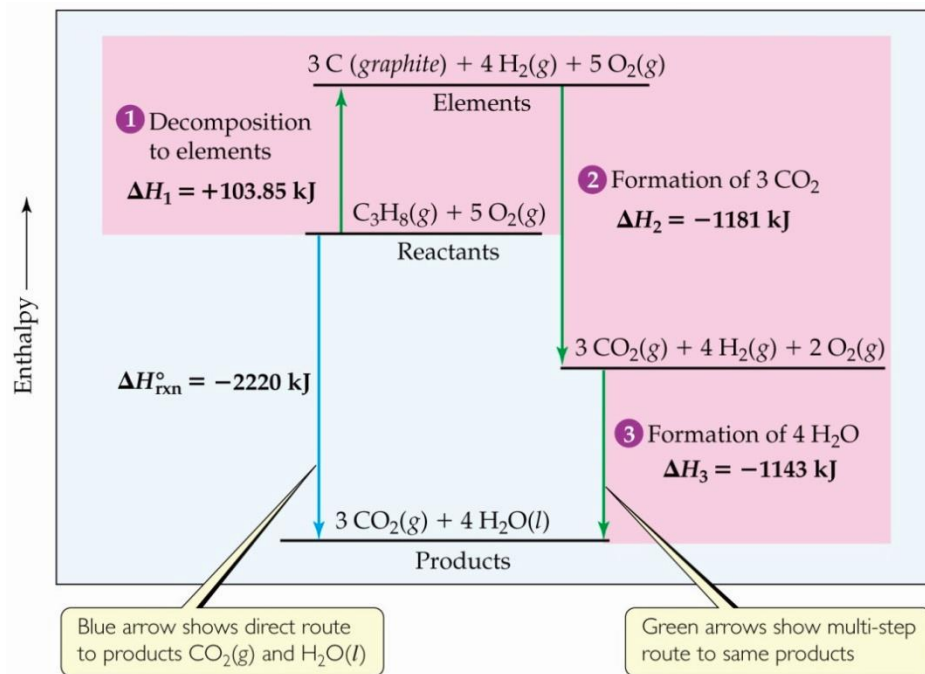
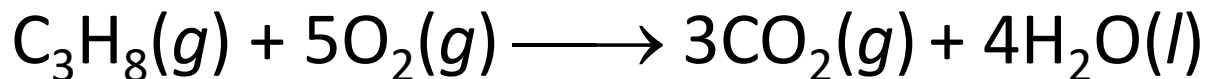
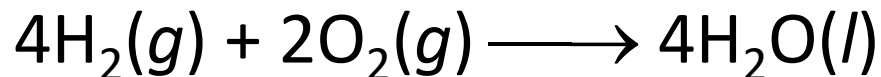
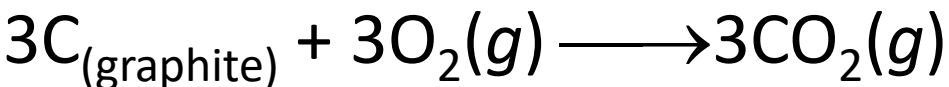
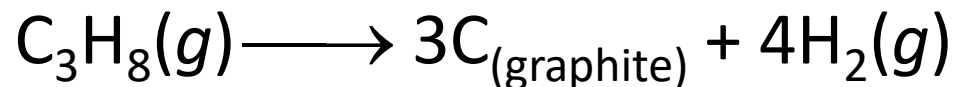
- Imagine this as occurring in three steps:



## Calculation of $\Delta H$



- The sum of these equations is



## Calculation of $\Delta H$

We can use Hess's law in this way:

$$\Delta H = \sum n \Delta H_f^\circ, \text{products} - \sum m \Delta H_f^\circ, \text{reactants}$$

where  $n$  and  $m$  are the stoichiometric coefficients. 化学计量系数



# Standard Enthalpies of Formation

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

**TABLE 5.3 • Standard Enthalpies of Formation,  $\Delta H_f^\circ$ , at 298 K**

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)	Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Acetylene	$\text{C}_2\text{H}_2(\text{g})$	226.7	Hydrogen chloride	$\text{HCl}(\text{g})$	−92.30
Ammonia	$\text{NH}_3(\text{g})$	−46.19	Hydrogen fluoride	$\text{HF}(\text{g})$	−268.60
Benzene	$\text{C}_6\text{H}_6(\text{l})$	49.0	Hydrogen iodide	$\text{HI}(\text{g})$	25.9
Calcium carbonate	$\text{CaCO}_3(\text{s})$	−1207.1	Methane	$\text{CH}_4(\text{g})$	−74.80
Calcium oxide	$\text{CaO}(\text{s})$	−635.5	Methanol	$\text{CH}_3\text{OH}(\text{l})$	−238.6
Carbon dioxide	$\text{CO}_2(\text{g})$	−393.5	Propane	$\text{C}_3\text{H}_8(\text{g})$	−103.85
Carbon monoxide	$\text{CO}(\text{g})$	−110.5	Silver chloride	$\text{AgCl}(\text{s})$	−127.0
Diamond	$\text{C}(\text{s})$	1.88	Sodium bicarbonate	$\text{NaHCO}_3(\text{s})$	−947.7
Ethane	$\text{C}_2\text{H}_6(\text{g})$	−84.68	Sodium carbonate	$\text{Na}_2\text{CO}_3(\text{s})$	−1130.9
Ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	−277.7	Sodium chloride	$\text{NaCl}(\text{s})$	−410.9
Ethylene	$\text{C}_2\text{H}_4(\text{g})$	52.30	Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$	−2221
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	−1273	Water	$\text{H}_2\text{O}(\text{l})$	−285.8
Hydrogen bromide	$\text{HBr}(\text{g})$	−36.23	Water vapor	$\text{H}_2\text{O}(\text{g})$	−241.8

# Energy in Foods

Most of the fuel in the food we eat comes from carbohydrates and fats.

**TABLE 5.4 • Compositions and Fuel Values of Some Common Foods**

	Approximate Composition (% by mass)			Fuel Value	
	Carbohydrate	Fat	Protein	kJ/g	kcal/g (Cal/g)
Carbohydrate	100	—	—	17	4
Fat	—	100	—	38	9
Protein	—	—	100	17	4
Apples	13	0.5	0.4	2.5	0.59
Beer <sup>†</sup>	1.2	—	0.3	1.8	0.42
Bread	52	3	9	12	2.8
Cheese	4	37	28	20	4.7
Eggs	0.7	10	13	6.0	1.4
Fudge	81	11	2	18	4.4
Green beans	7.0	—	1.9	1.5	0.38
Hamburger	—	30	22	15	3.6
Milk (whole)	5.0	4.0	3.3	3.0	0.74
Peanuts	22	39	26	23	5.5

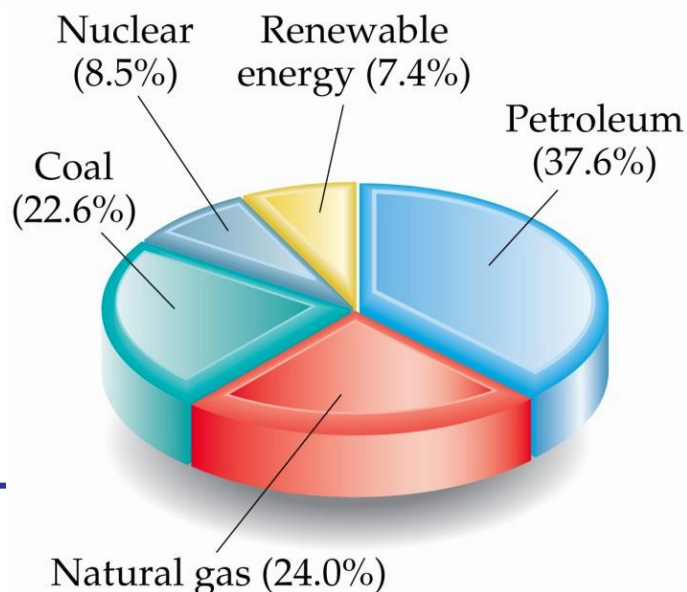
<sup>†</sup>Beer typically contains 3.5% ethanol, which has fuel value.

# Energy in Fuels

TABLE 5.5 • Fuel Values and Compositions of Some Common Fuels

	Approximate Elemental Composition (mass %)			Fuel Value (kJ/g)
	C	H	O	
Wood (pine)	50	6	44	18
Anthracite coal (Pennsylvania)	82	1	2	31
Bituminous coal (Pennsylvania)	77	5	7	32
Charcoal	100	0	0	34
Crude oil (Texas)	85	12	0	45
Gasoline	85	15	0	48
Natural gas	70	23	0	49
Hydrogen	0	100	0	142

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The vast majority of the energy consumed in the USA comes from fossil fuels.