

# Chapter 5 Thermochemistry



Learning Outcomes:

- **Interconvert energy units**
- **Distinguish between the system and the surroundings in thermodynamics**
- **Calculate internal energy from heat and work and state sign conventions of these quantities**
- **Explain the concept of a state function and give examples**
- **Calculate  $H$  from  $E$  and  $P \Delta V$**
- **Relate  $q_p$  to  $H$  and indicate how the signs of  $q$  and  $H$  relate to whether a process is exothermic or endothermic**
- **Use thermochemical equations to relate the amount of heat energy transferred in reactions in reactions at constant pressure ( $H$ ) to the amount of substance involved in the reaction**

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- **Energy is the ability to do work or transfer heat**
- **Thermodynamics is the study of energy and its transformations**
- **Thermochemistry is the study of chemical reactions and the energy changes that involve heat**

## Heat

Energy used to cause the temperature of an object to increase.

Chemical reactions that release heat



(a)

## Work

Energy used to cause an object that has mass to move.  $w = F \times d$

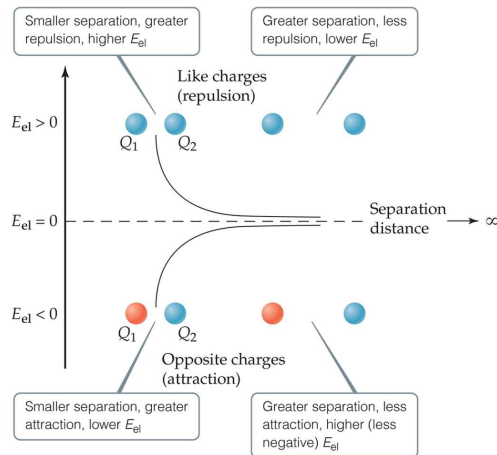
Chemical reactions that do work



(b)

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## Electrostatic potential energy



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

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

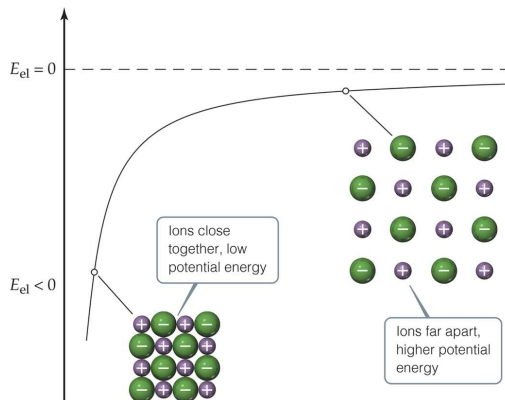
where  $\kappa = 8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$

- Electron charge:  
 $1.602 \times 10^{-19} \text{ C}$
- The unit of energy commonly used is the Joule:

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

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## Attraction between ions



- Electrostatic attraction occurs between oppositely charged ions.
- Energy is released when chemical bonds are formed; energy is consumed when chemical bonds are broken.

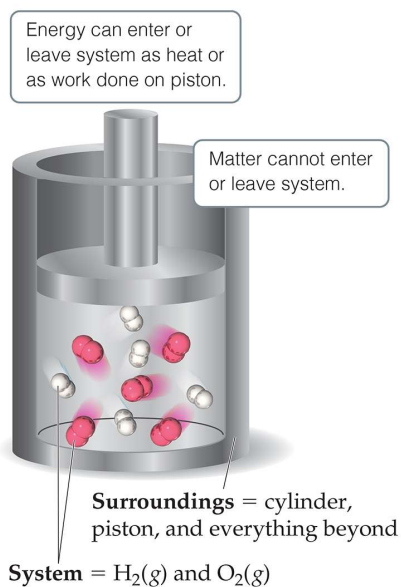
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## First Law of Thermodynamics

- Energy can be converted from one form to another, but it is neither created nor destroyed.
- Energy can be transferred between the system and surroundings.
- Chemical energy is converted to heat in grills.
- Sunlight is converted to chemical energy in green plants.
- There are many examples of conversion of energy from one form to another.

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## System and Surroundings



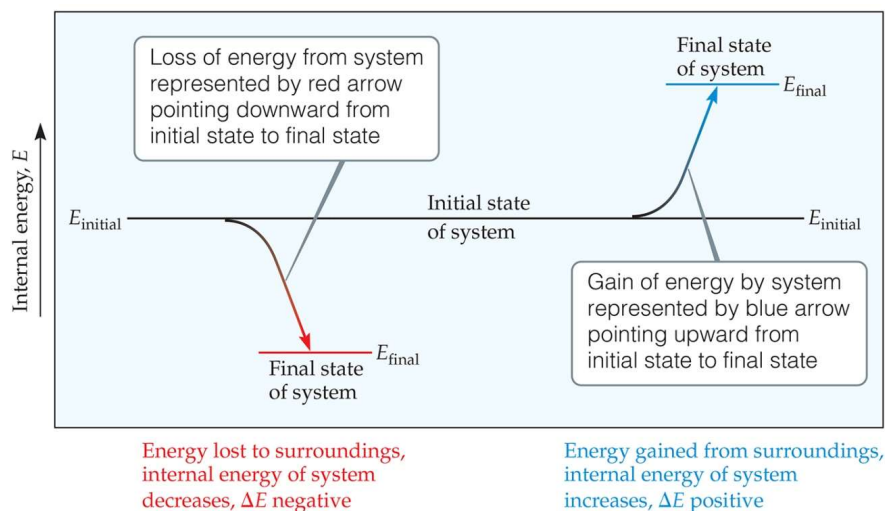
- The **system** includes the molecules of interest.
- The **surroundings** are everything else.
- In thermochemistry we study the **exchange** of energy between the system and surroundings.
- **open system** - matter and energy can be exchanged with the surroundings
- **closed system** - exchange energy--but not matter--with the surroundings.
- **isolated system** - neither matter nor energy may be exchanged with surroundings.

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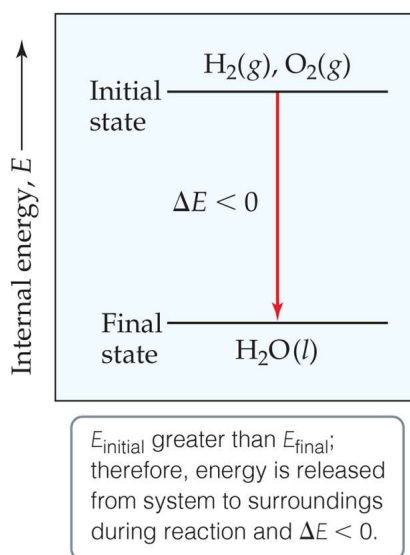
# Internal Energy

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

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



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

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

$\Delta E < 0$ ,  $E_{\text{final}} < E_{\text{initial}}$   
the system **released** energy to the surroundings.

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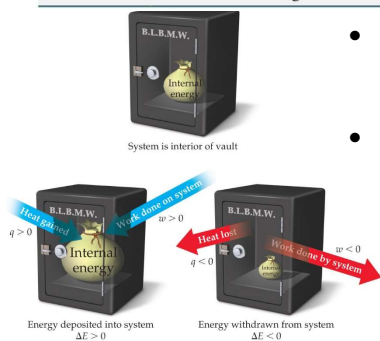
## Thermodynamic Quantities: Three Parts

1) A number, 2) a unit, 3) a sign

- A positive  $\Delta E$  results when the system gains energy from the surroundings.
- A negative  $\Delta E$  results when the system loses energy to the surroundings.

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



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

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## Exchange of Heat between System and Surroundings

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

System =  $\text{NH}_4\text{SCN} + \text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$

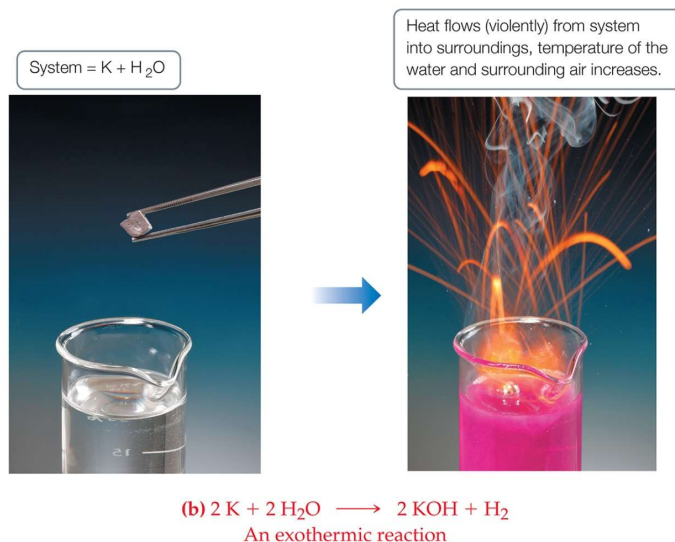
Heat flows from surroundings into system, temperature of beaker and surrounding air drops.



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## Exchange of Heat between System and Surroundings

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

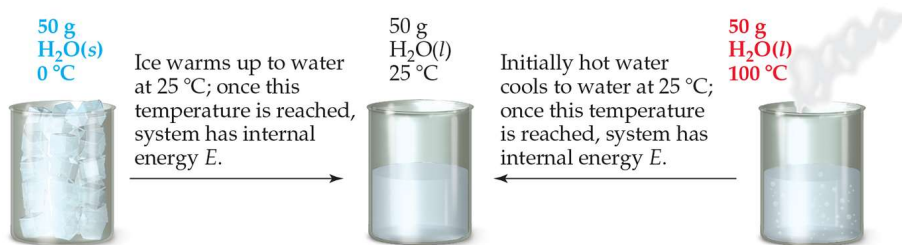


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## State Functions

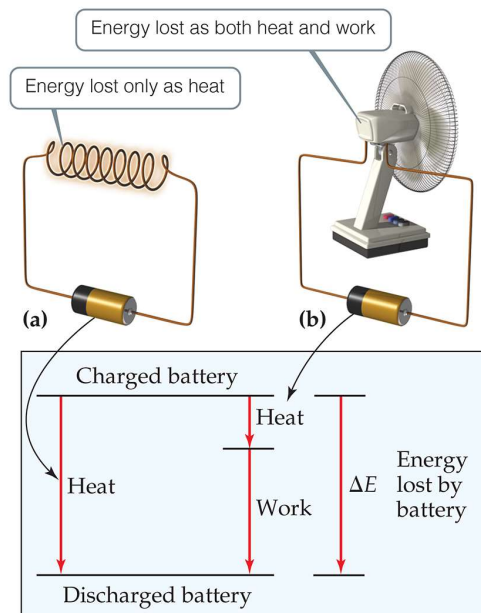
The internal energy of a system is independent of the path by which the system achieved that state.

Internal energy, **E**, is a state function.



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# State Functions



$q$  and  $w$  are **not** state functions.

$\Delta E$  is the same whether the battery is shorted out or is discharged by running the fan.

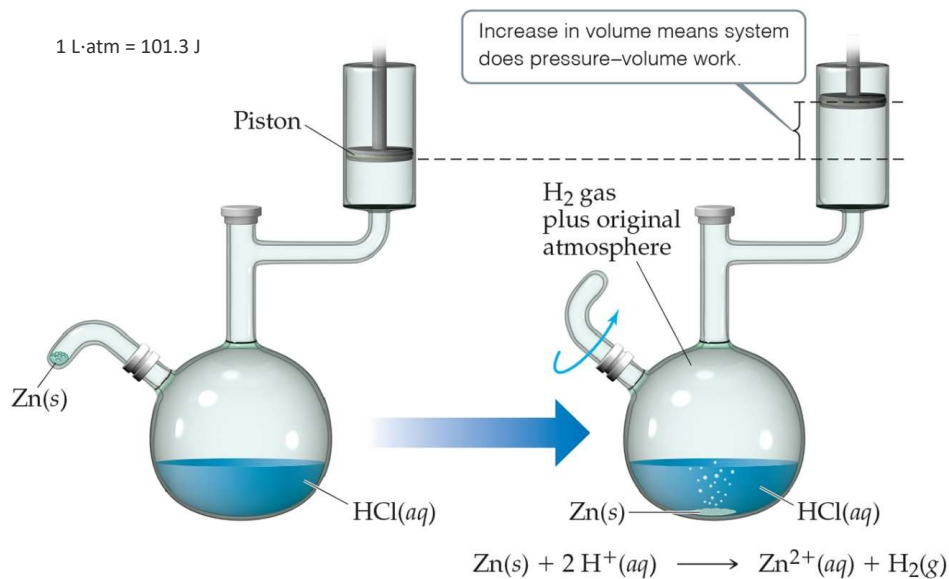
–  $q$  and  $w$  are different in the two cases.

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## Work

$$w = -P\Delta V$$

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



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## Example

Calculate the work (in J) associated with the expansion of a gas from 44 mL to 63 mL at a constant pressure of 14 atm.

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## Enthalpy

- Enthalpy is a thermodynamic function equal to the internal energy plus pressure×volume:  $H = E + PV$

When the system changes at constant pressure, the change in enthalpy,  $\Delta H$ , is

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

This can be written

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

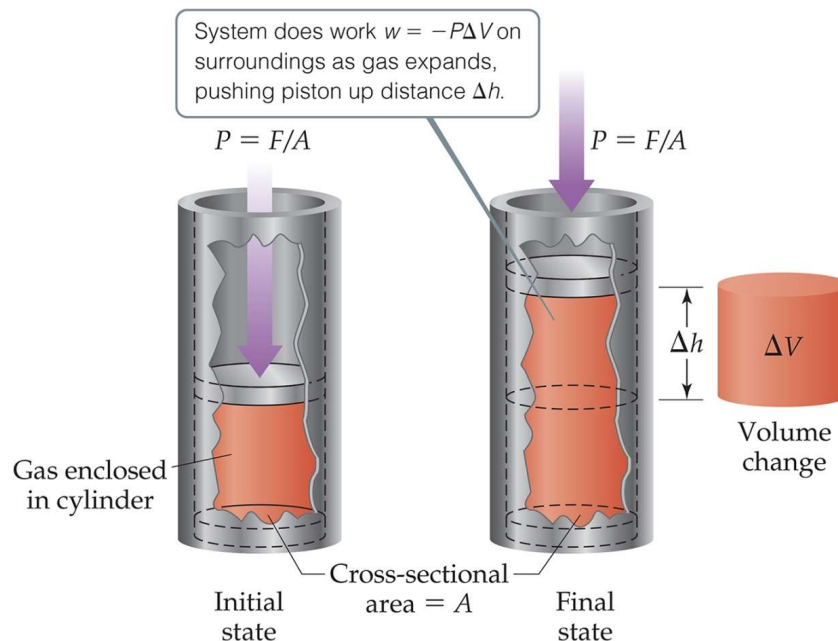
Since  $\Delta E = q + w$  and  $w = -P\Delta V$ , we can substitute these into the enthalpy expression:

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

The **enthalpy change**,  $\Delta H$ , is defined as the heat gained or lost by the system under *constant pressure*.

$$\Delta H = q_p$$

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## Properties of Enthalpy

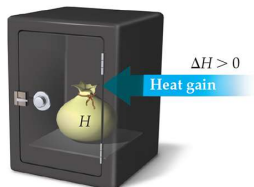
1. Enthalpy is a **state function**.
2. Enthalpy is an **extensive property**.
3. Enthalpy is **reversible**. The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to  $\Delta H$  for the reverse reaction.
4.  $\Delta H$  for a reaction depends on the **state** of the products and the **state** of the reactants.

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## Endothermic and Exothermic

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

Constant pressure  
maintained in system



(a) An endothermic reaction

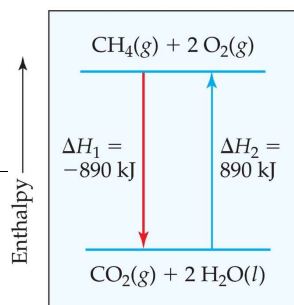


(b) An exothermic reaction

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

- A process is **endothermic** when  $\Delta H$  is positive ( $>0$ ).

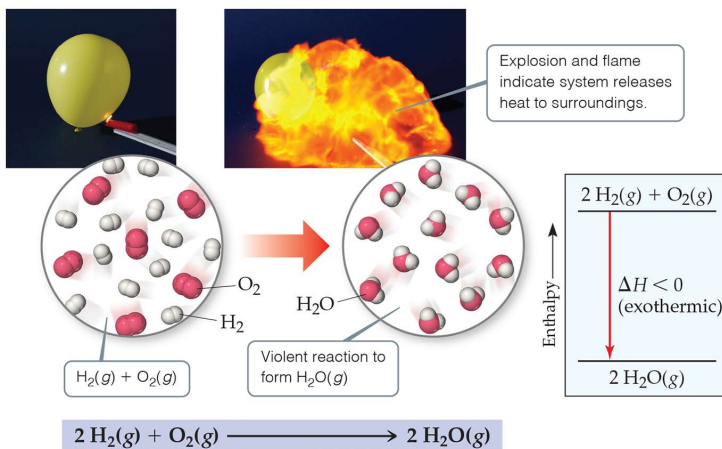
- A process is **exothermic** when  $\Delta H$  is negative ( $<0$ ).



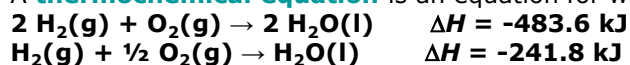
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## Enthalpies of Reaction

This quantity,  $\Delta H$ , is called the **enthalpy of reaction**, or the **heat of reaction**.



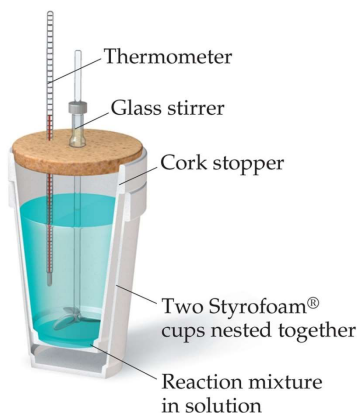
A **thermochemical equation** is an equation for which  $\Delta H$  is given:



The enthalpy changes assume the coefficients are moles of the substances

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# Calorimetry



- **Calorimetry**, the measurement of heat released or absorbed by a chemical reaction.
- A **calorimeter** is the device used to measure heat
- The quantity of heat *transferred* by the reaction causes a *change in temperature* of the *solution*.

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## 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** ( $C$  in units of J/K).

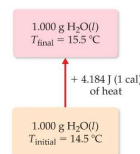
$$C = \frac{q}{\Delta T}$$

- We define **specific heat capacity** (or simply **specific heat**;  $C_s$  or  $s$  in units of J/g·K) as the amount of energy required to raise the temperature of 1 g of a substance by 1 K.
- If the amount is one mole, it is the **molar heat capacity**.

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

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 <sub>2</sub> (g)	1.04	H <sub>2</sub> O(l)	4.18
Al(s)	0.90	CH <sub>4</sub> (g)	2.20
Fe(s)	0.45	CO <sub>2</sub> (g)	0.84
Hg(l)	0.14	CaCO <sub>3</sub> (s)	0.82



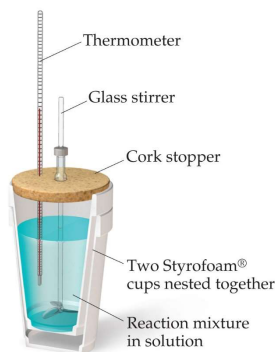
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## Constant Pressure Calorimetry

**Indirectly** measure the **heat change** for the system

Because the specific heat for water is well known ( $4.184 \text{ J/g}\cdot\text{K}$ ), we can measure  $q$  for the reaction with this equation:

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



The calorimeter and its contents are the *surroundings*, so  $q_{\text{soln}}$  is found from the mass, heat capacity, and temperature change.

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### Example

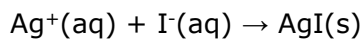
A metal pellet with mass  $100.0 \text{ g}$ , originally at  $88.4^\circ\text{C}$ , is dropped into  $125 \text{ g}$  of water originally at  $25.1^\circ\text{C}$ . The final temperature of both the pellet and the water is  $31.3^\circ\text{C}$ .

Calculate the heat capacity  $C$  (in  $\text{J}/^\circ\text{C}$ ) and specific heat capacity  $C_s$  (in  $\text{J/g}\cdot^\circ\text{C}$ ) of the pellet. The specific heat of water is  $4.184 \text{ J/g}\cdot^\circ\text{C}$ .

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## Example

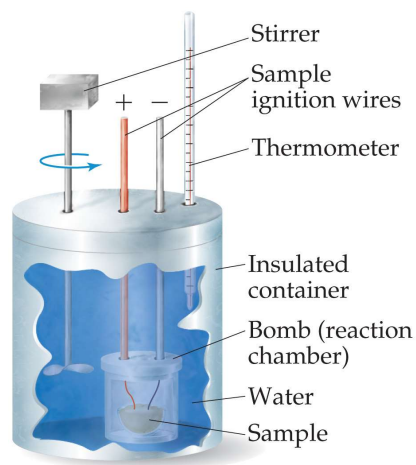
When 200. g of a  $\text{AgNO}_3$  solution mixes with 150. g of  $\text{NaI}$  solution, 2.93 g of  $\text{AgI}$  precipitates, and the temperature of the solution rises by  $1.34^\circ\text{C}$ . Assume 350. g of solution and a specific heat capacity of  $4.184 \text{ J/g}\cdot^\circ\text{C}$ . Calculate  $\Delta H$  for the following:



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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 small.
- The heat absorbed (or released) by the water is a very good approximation of the enthalpy change for the reaction.
- $q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T$



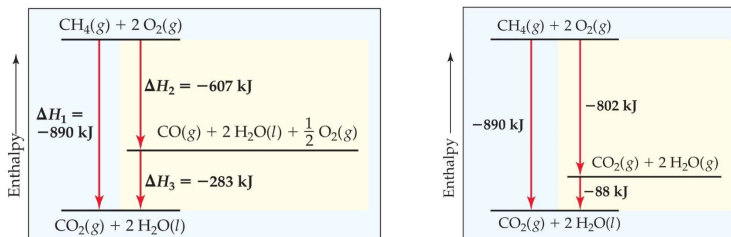
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## Example

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## Hess's Law

- $\Delta H$  is known for many reactions, but it is inconvenient to measure  $\Delta H$  for every reaction in which we are interested.
- However, we can calculate  $\Delta H$  using published  $\Delta H$  values and the properties of enthalpy.
- 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**."  $\Delta H$  is a state function



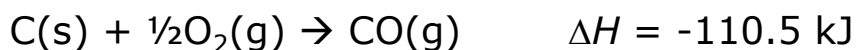
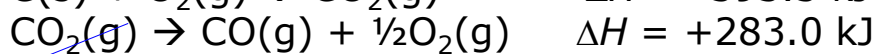
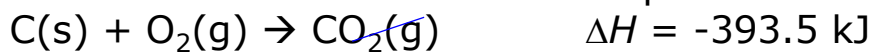
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## Hess's Law

Most  $\Delta H$  values are labeled  $\Delta H^\circ$ , and measured under standard conditions

- $P = 1 \text{ atm}$  (but for gases  $P = 1 \text{ bar}$ )
- $T = \text{usually } 298.15 \text{ K } (25.0^\circ\text{C})$
- Concentration =  $1 \text{ mol/L}$

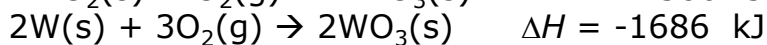
Using **Hess's law** - when two or more thermochemical equations are added, the enthalpy change of the resulting equation is the sum of those for the added equations.



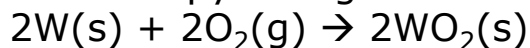
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## Example

Given the thermochemical equations



calculate the enthalpy change for:



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## 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 Enthalpy of Formation

- Only one enthalpy value is needed for each substance, called the *standard enthalpy of formation*.
- The **standard enthalpy of formation** is the enthalpy change when *one mole* of a substance in its standard state is formed from the most stable form of the elements in their *standard states*.

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## Standard State

- Enthalpy changes depend on the temperature and pressure at which they are measured
  - When applying Hess's law, all values must refer to the same conditions of pressure and temperature
- The **standard state** of a substance at a specified temperature is the pure form at 1 atm pressure
  - Tabulated values for enthalpy refer to the standard state, usually at a temperature of 25°C

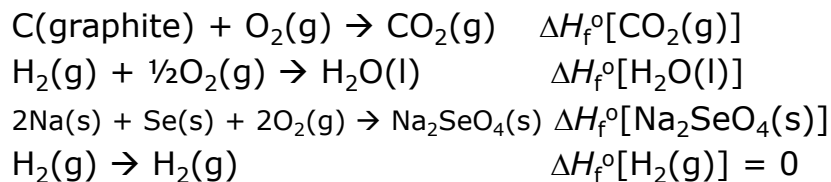
TABLE 5.3 Standard Enthalpies of Formation,  $\Delta H_f^\circ$ , at 298 K

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)	Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Acetylene	$C_2H_2(g)$	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

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## Standard Enthalpy of Formation

- The symbol used for standard enthalpy of formation is  $\Delta H_f^\circ$ , where the  $^\circ$  designates standard state.
- The product is always one mole of a single substance.
- The standard enthalpy of formation of the elements in their most stable form is **zero**.
- Some examples of standard enthalpies of formation:

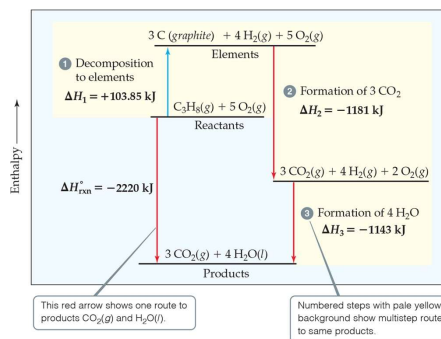


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## Enthalpies of Reaction



- Imagine this as occurring in 3 steps:



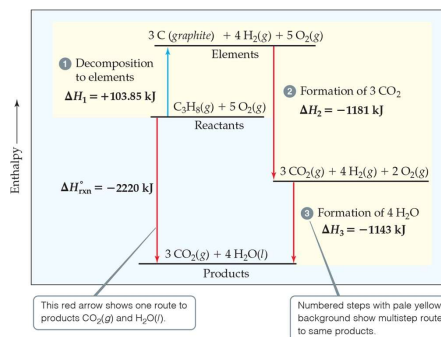
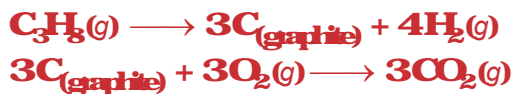
$$\Delta H = \sum n \Delta H_f^\circ(\text{products}) - \sum m \Delta H_f^\circ(\text{reactants})$$

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

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- Imagine this as occurring in 3 steps:



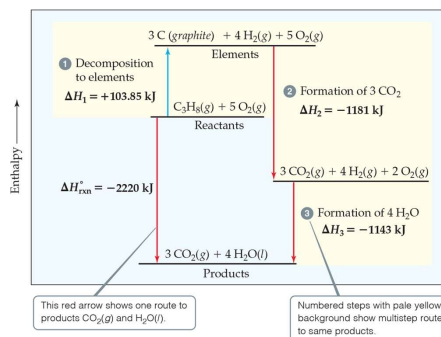
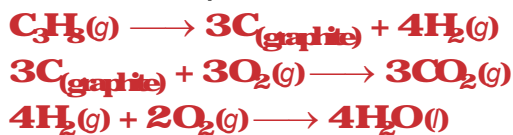
$$\Delta H = \sum n \Delta H_f^\circ (\text{products}) - \sum m \Delta H_f^\circ (\text{reactants})$$

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

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- Imagine this as occurring in 3 steps:



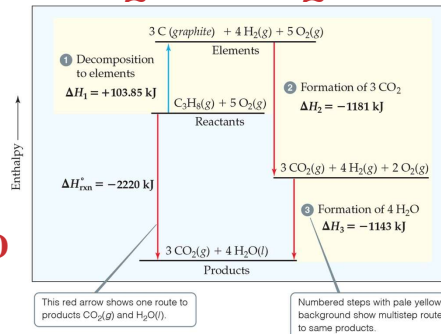
$$\Delta H = \sum n \Delta H_f^\circ (\text{products}) - \sum m \Delta H_f^\circ (\text{reactants})$$

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

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- The sum of these equations is:



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

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

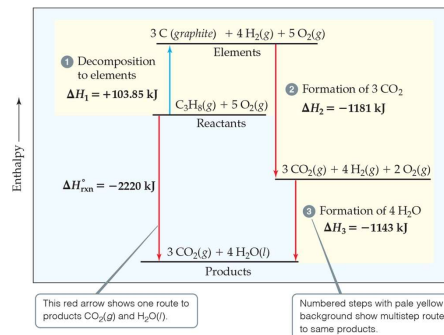
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$$\Delta H = \sum n \Delta H_f^\circ (\text{products}) - \sum m \Delta H_f^\circ (\text{reactants})$$

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

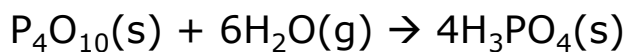
$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= [(3 \text{ mol})(-393.5 \text{ kJ/mol}) + (4 \text{ mol})(-285.8 \text{ kJ/mol})] - [(1 \text{ mol})(-103.85 \text{ kJ/mol}) + (5 \text{ mol})(0 \text{ kJ})] \\ &= [(-1180.5 \text{ kJ}) + (-1143.2 \text{ kJ})] - [(-103.85 \text{ kJ}) + (0 \text{ kJ})] \\ &= (-2323.7 \text{ kJ}) - (-103.85 \text{ kJ}) \\ &= -2219.9 \text{ kJ} \end{aligned}$$



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## Example

Use standard enthalpies of formation to calculate the enthalpy change for the reaction:



Substance	$\Delta H_f^\circ$ (kJ/mol)
$\text{P}_4\text{O}_{10}(\text{s})$	-2940
$\text{H}_2\text{O}(\text{g})$	- 242
$\text{H}_3\text{PO}_4(\text{s})$	-1279

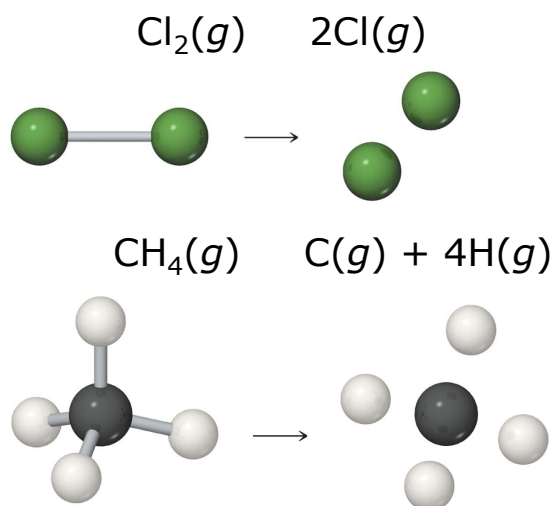
$$\Delta H = \Sigma n \Delta H_f^\circ (\text{products}) - \Sigma m \Delta H_f^\circ (\text{reactants})$$

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

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## Bond Enthalpy

The enthalpy associated with breaking one mole of a particular bond in a gaseous substance.



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- Bond enthalpy is always positive because energy is required to break chemical bonds.
- Energy is released when a bond forms between gaseous fragments.
- The greater the bond enthalpy, the stronger the bond.

**TABLE 5.4 Average Bond Enthalpies (kJ/mol)**

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C=C	614	N—O	201	O=O	495	Cl—F	253
C—N	293	N—F	272	O—F	190	Cl—Cl	242
C—O	358	N—Cl	200	O—Cl	203		
C=O	799	N—Br	243	O—I	234	Br—F	237
C—F	485					Br—Cl	218
C—Cl	328	H—H	436			Br—Br	193
C—Br	276	H—F	567				
C—I	240	H—Cl	431			I—Cl	208
		H—Br	366			I—Br	175
		H—I	299			I—I	151

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## Bond Enthalpies and Enthalpy of Reaction

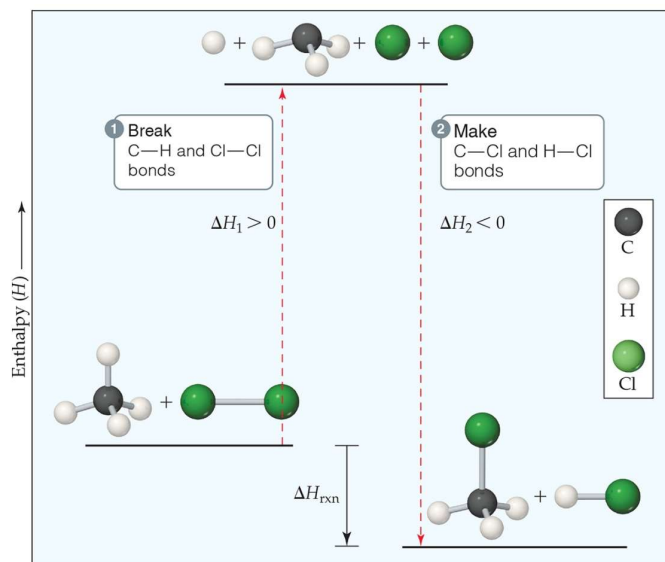
To obtain an estimate of  $\Delta H$ ,

- Sum the bond enthalpies for all bonds broken and subtract the sum of the bond enthalpies for all bonds formed.

$$H_{\text{rxn}} = (\text{bond enthalpies of bonds broken}) - (\text{bond enthalpies of bonds formed})$$

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Predict whether a chemical reaction will be endothermic or exothermic using bond enthalpies.



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## Energy in Foods

The energy released when one gram of food is combusted is its **fuel value**.

TABLE 5.5 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>a</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>a</sup> Beer typically contains 3.5% ethanol, which has fuel value.



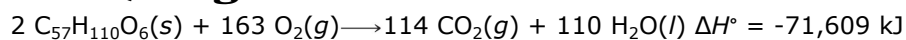
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•Most of the energy in foods comes from carbohydrates, fats, and proteins.

•Carbohydrates (17kJ/g):



•Fats (38kJ/g):



•Proteins produce 17kJ/g (same as carbohydrates):

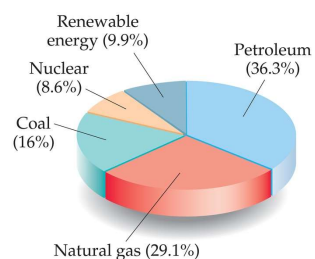
However, their chemical reaction in the body is NOT the same as in a calorimeter

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## Fuels

TABLE 5.6 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



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



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