Chapter 6
Thermochemistry

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Thermodynamics

- The study of energy and its transformations is known as thermodynamics
- The relationships between chemical reactions and energy changes that involve heat. This portion of thermodynamics is called thermochemistry

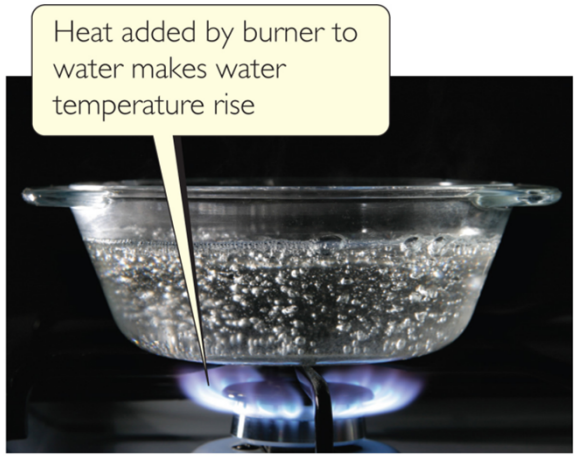
Energy

- Energy is the capacity to do work or transfer heat
- Work is the energy used to cause an object to move against a force

$$\textbf{Work} = \text{force} \times \text{distance}$$

- Heat is the energy used to cause the temperature of an object to increase. Heat passes spontaneously from the region of higher temperature to the region of lower temperature

(a)



(b)

Kinetic Energy and Potential Energy

- Kinetic energy (E_k) is energy an object possesses by virtue of its motion:

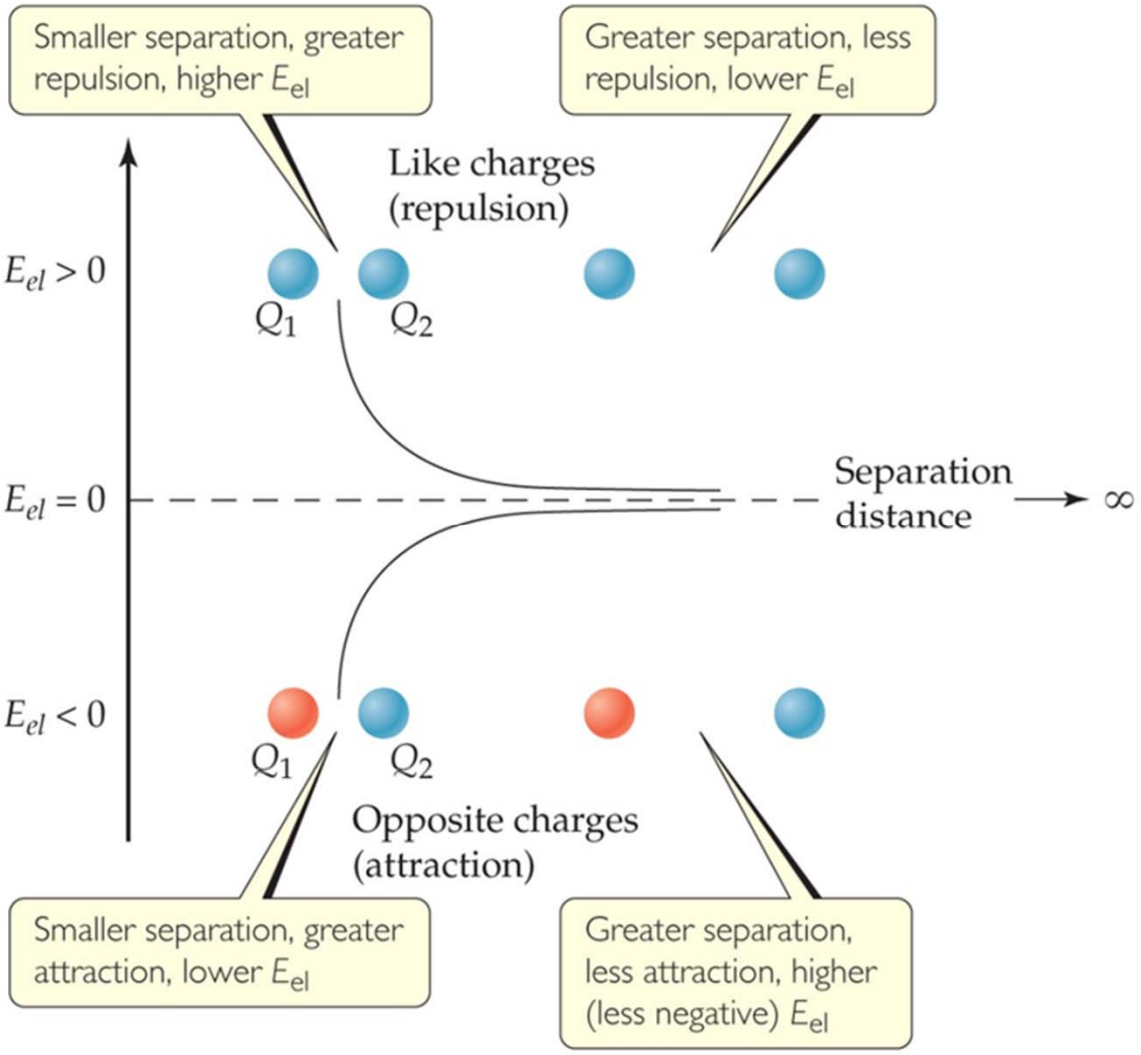
$$E_k = \tfrac{1}{2} mv^2$$

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

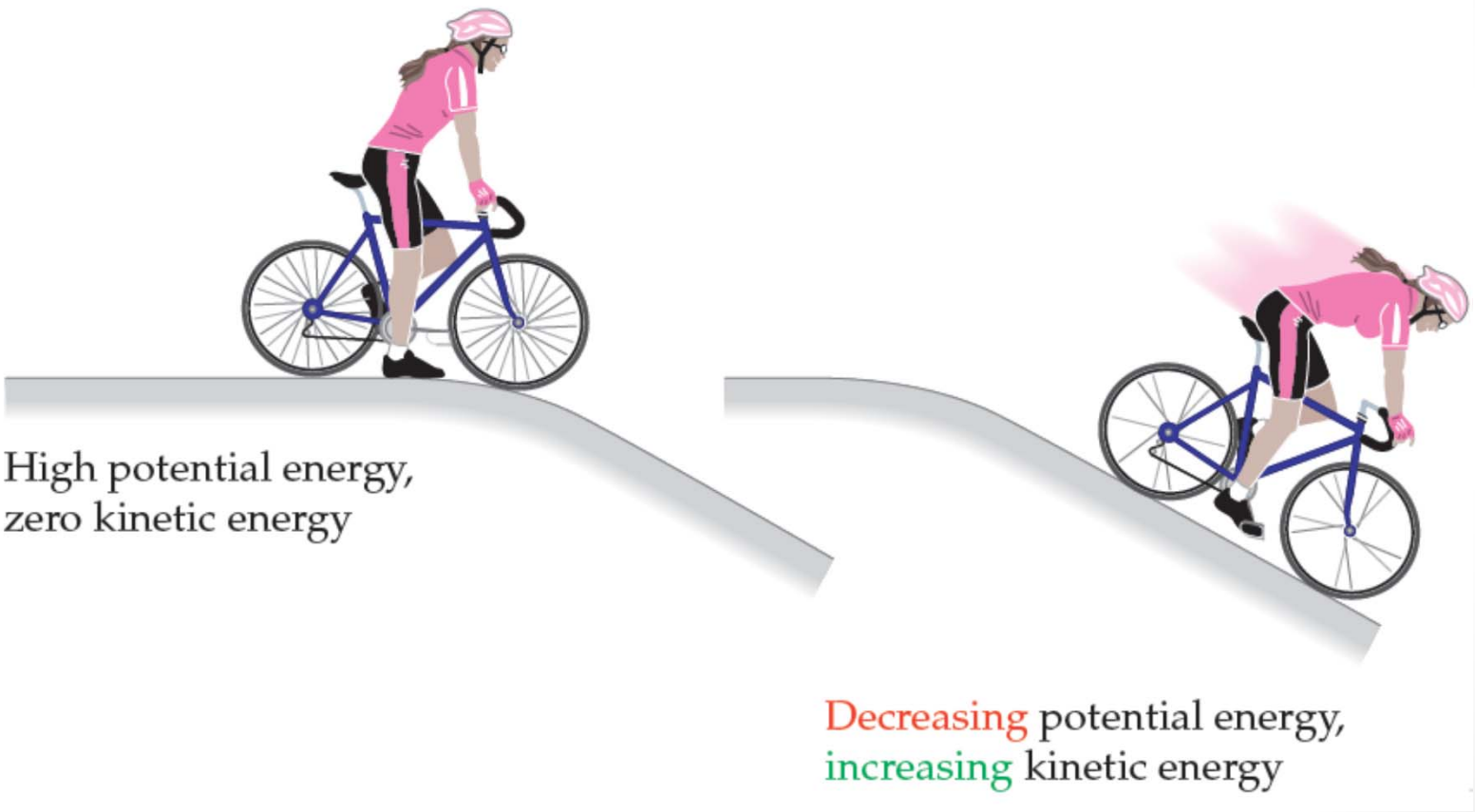
  - The most important form of potential energy in molecules is electrostatic potential energy, E_{el}:

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

Potential Energy



Kinetic Energy and Potential Energy



Units of Energy

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

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

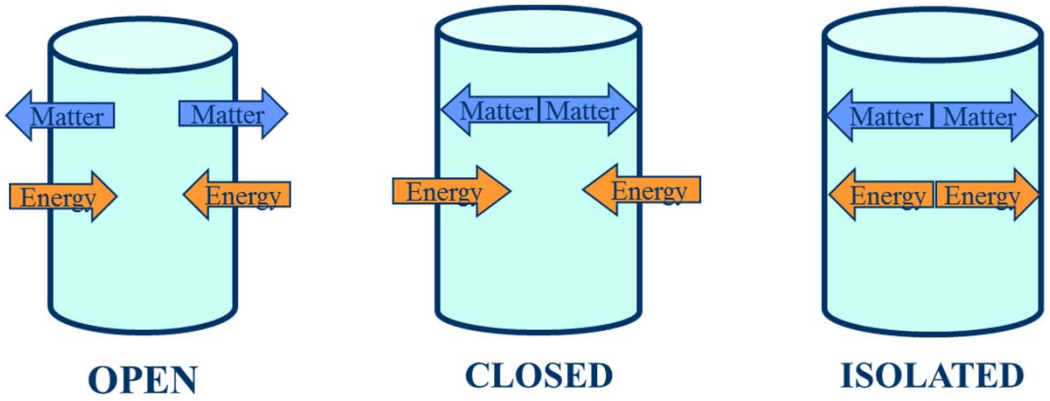
- An older, non-SI unit is still in widespread use, the calorie (cal):
- 1 cal = 4.184 J
- (Note: this is not the same as the calorie of foods; the food calorie is 1 kcal!)

System and Surroundings

- The system includes the molecules we want to study

  Types of Systems:

  - Open system: energy and matter can be exchanged with the surroundings.
  - Closed system: energy can be exchanged with the surroundings, matter cannot.
  - Isolated system: neither energy nor matter can be exchanged with the surroundings

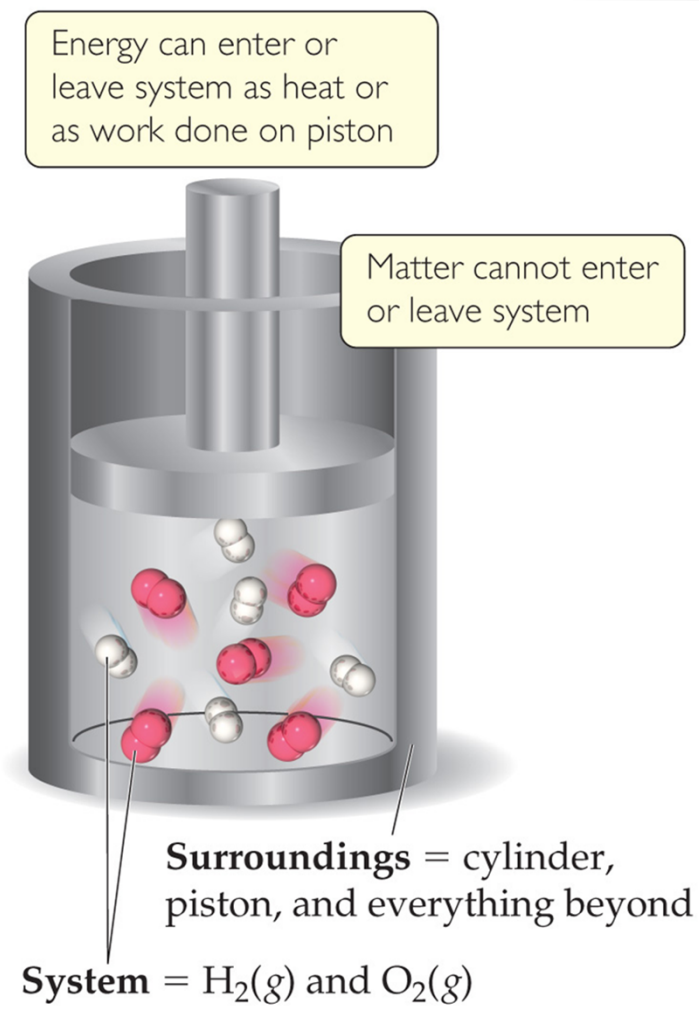


- The surroundings are everything else

Closed system

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

- It can exchange energy with its surroundings in the form of work and heat



First Law of Thermodynamics

- Energy can be neither created nor destroyed.
  - Any energy that is lost by a system must be gained by the surroundings, and vice versa.

Energy is conserved—is known as the first law of thermodynamics.

Internal Energy

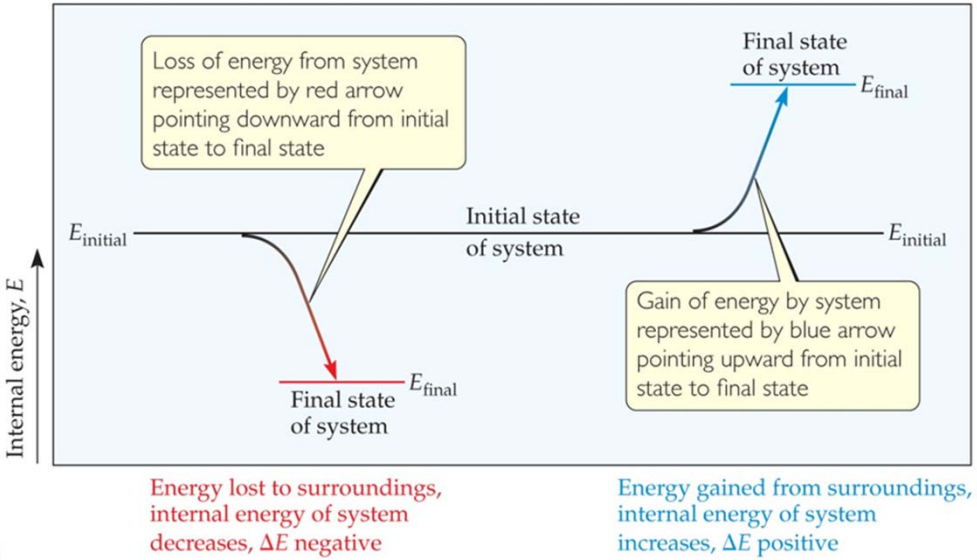
- The internal energy, E, of a system is the sum of all the kinetic and potential energies of the components of the system.
- We generally do not know the numerical value of a system's internal energy.
- In thermodynamics, we are mainly concerned with the change in E (and, as we shall see, changes in other quantities as well) that accompanies a change in the system.

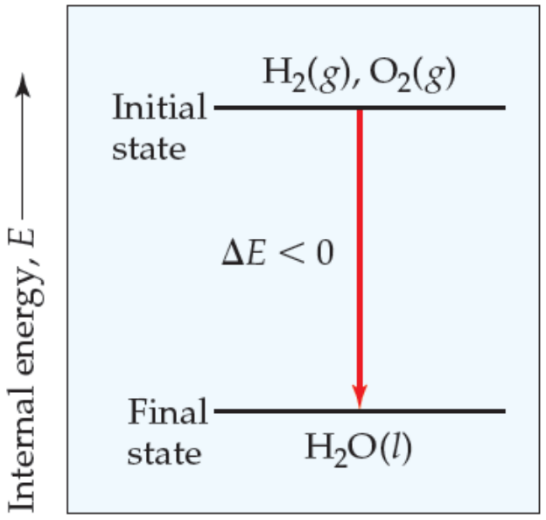
The change in internal energy:

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

Internal Energy

- A positive value of ΔE results when $E_{final} > E_{initial}$, indicating that the system has gained energy from its surroundings.
- A negative value of ΔE results when $E_{final} < E_{initial}$, indicating that the system has lost energy from its surroundings.





Relating E to Heat and Work

- When a system undergoes any chemical or physical change, the accompanying change in internal energy, ΔE, is the sum of the heat added to or liberated from the system, q, and the work done on or by the system, w:

$$\Delta E = q + w$$

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

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

Ex:

- A gas does 135 J of work while expanding, and at the same time it absorbs 156 J of heat. What is the change in internal energy?

Sol:

Heat is *absorbed by* the system; this means *q* is a *positive* quantity

$$\therefore q = +156 \text{ J}$$

Work is *done by* the system; this means *w* is a *negative* quantity

$$\therefore w = -135 \text{ J}$$

$$\therefore \Delta E = q + w = +156 \text{ J} + (-135 \text{ J}) = +21 \text{ J}$$

Work

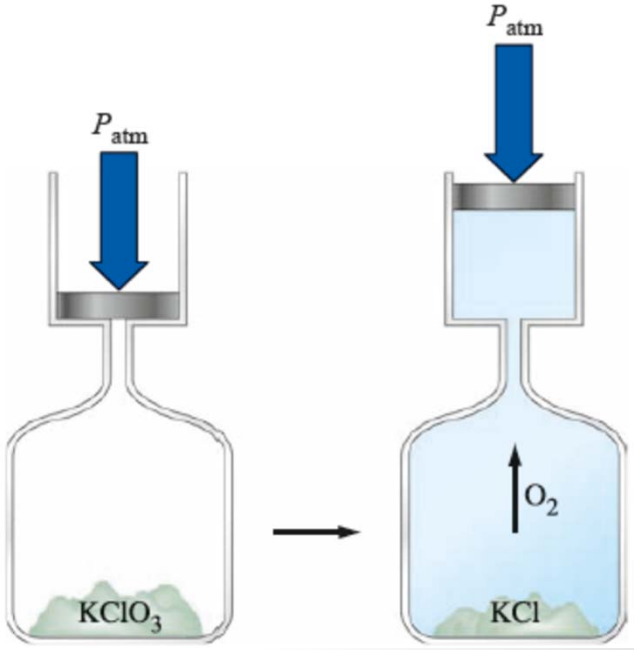
- Like heat, work is an energy transfer between a system and its surroundings.
- Unlike heat, work is caused by a force moving through a distance (heat is caused by a temperature difference).
- Calculating Work for gas

We will consider only pressure-volume work.

work (w) = $-P\triangle V$

- When a gas expands, $\triangle V$ is positive and the work is negative (system loses energy).
- When a gas is compressed, $\triangle V$ is negative and w is positive, signifying that energy (as work) enters the system. (system gains energy).

1 bar L = 100 J 1 atm L = 101.325 J



Sample Exercise 5.3

- A fuel is burned in a cylinder equipped with a piston. The initial volume of the cylinder is 0.250 L, and the final volume is 0.980 L. If the piston expands against a constant pressure of 1.35 atm, how much work (in J) is done?

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 0.980\ \text{L} - 0.250\ \text{L} = 0.730\ \text{L}$$

$$w = -P\Delta V = -(1.35\ \text{atm})(0.730\ \text{L}) = -0.9855\ \text{L-atm}$$

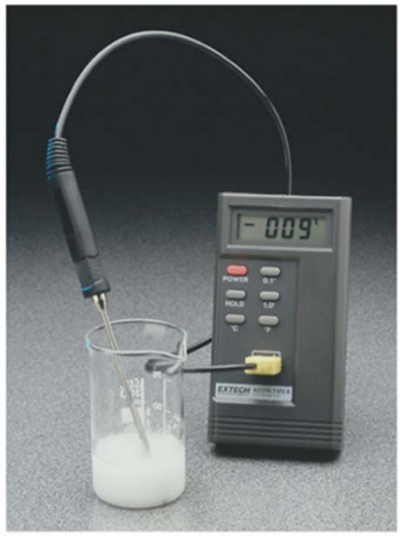
$$-(0.9855\ \cancel{\text{L-atm}})\left(\frac{101.3\ \text{J}}{1\ \cancel{\text{L-atm}}}\right) = -99.8\ \text{J}$$

Endothermic and Exothermic Processes

- When a process occurs in which the system absorbs heat, the process is called endothermic.
- A process in which the system loses heat is called exothermic.

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

System: reactants + products

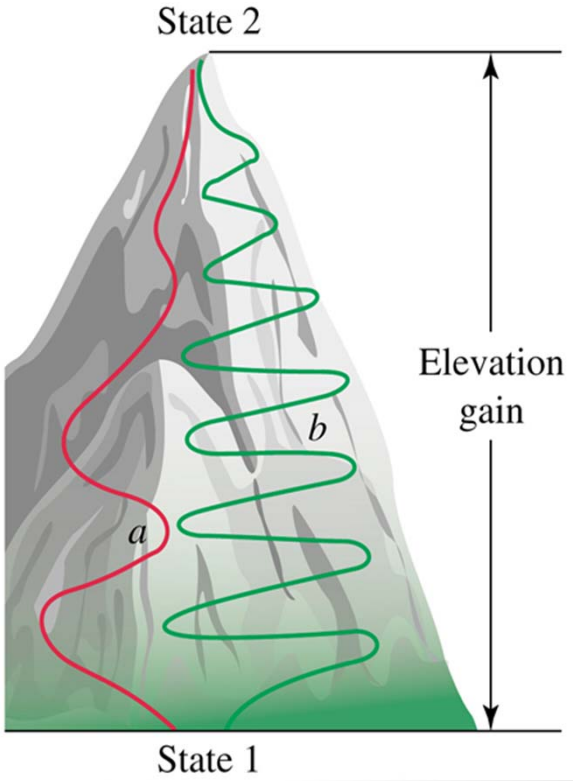
Surroundings: air around reactants

(b) An exothermic reaction

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

State function

- The value of a state function depends only on the present state of the system, not on the path the system took to reach that state.
- q and w are not state functions.
- ΔE is not state functions.



Enthalpy

- Under conditions of constant pressure, a thermodynamic quantity called enthalpy
- Enthalpy, which we denote by the symbol H, is defined as the internal energy plus the product of the pressure, P, and volume, V, of the system:

$$H = E + PV$$

- Like internal energy E, both P and V are state functions. H
- Enthalpy (H) is also state function

Enthalpy Change

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

$$\Delta H = \Delta(E + PV) = \Delta E + P\Delta V \text{ (constant pressure)}$$

$$\Delta E = q + w = q - P\Delta V \quad [w = -P V \text{ (at constant pressure)}]$$

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

The change in enthalpy equals the heat q_P gained or lost at constant pressure.

- When H is positive (that is, when q_P is positive), the system has gained heat from the surroundings, which means the process is endothermic.
- When H is negative, the system has released heat to the surroundings, which means the process is exothermic.

Enthalpies of Reaction

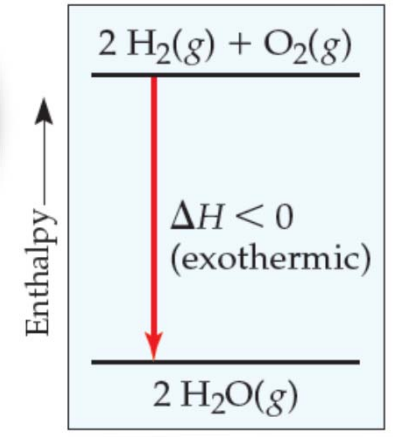
- Because $\Delta H = H_{final} - H_{initial}$, the enthalpy change for a chemical reaction is given by

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

- ΔH is called enthalpy of reaction or the heat of reaction and is sometimes written ΔH_{rxn}

EX: $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad \Delta H = -483.6\,kJ$

- Balanced chemical equations that show the associated enthalpy change in this way are called thermochemical equations.
- $\Delta H<0$ tells us that this reaction is exothermic.



Guidelines for Enthalpy

- Enthalpy is an extensive property.
  - When reaction is multiplied by a factor, ΔH_{rxn} is multiplied by that factor

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$

$$2\ C(s) + 2\ O_2(g) \rightarrow 2\ CO_2(g) \qquad \Delta H = 2(-393.5 \text{ kJ}) = -787.0 \text{ kJ}$$

- If a reaction is reversed, then the sign of ΔH is changed.

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$

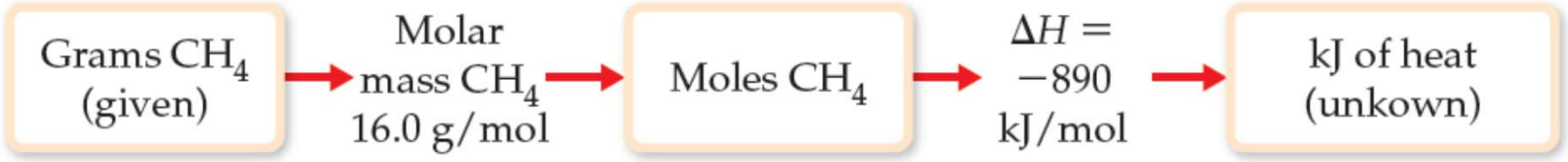
$$CO_2(g) \rightarrow C(s) + O_2(g) \quad \Delta H = +393.5 \text{ kJ}$$

Exercise 5.5

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

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

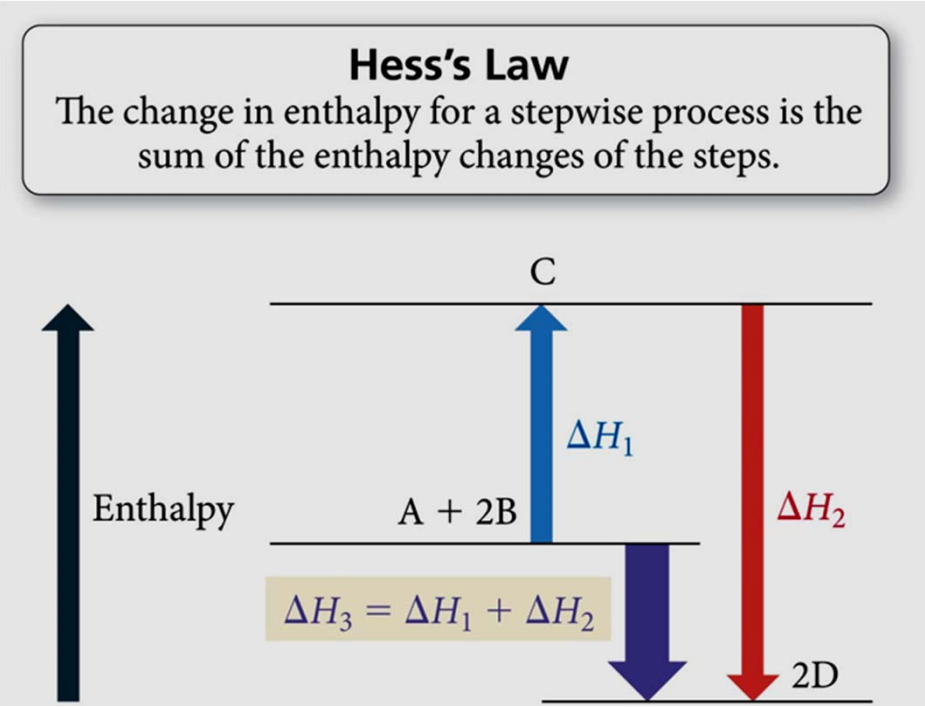
Sol:



$$\text{Heat} = (4.50\ \text{g}\,\cancel{CH_4})\left(\frac{1\ \text{mol}\,\cancel{CH_4}}{16.0\ \text{g}\,\cancel{CH_4}}\right)\left(\frac{-890\ \text{kJ}}{1\ \text{mol}\,\cancel{CH_4}}\right) = -250\ \text{kJ}$$

Guidelines for Enthalpy

- ΔH is state function. Hence, if a reaction can be expressed as a series of steps, then the ΔH_{rxn} for the overall reaction is the sum of the heats of reaction for each step. (Hess's Law)



Exercise 5.10

Calculate ΔH for the reaction

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

given the following chemical equations and their respective enthalpy changes:

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

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

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8\ \text{kJ}$$

Sol:

$$2\,\cancel{CO_2(g)} + H_2O(l) \longrightarrow C_2H_2(g) + \cancel{\tfrac{5}{2}O_2(g)} \qquad \Delta H = 1299.6\ \text{kJ}$$

$$2\,C(s) + \cancel{2\,O_2(g)} \longrightarrow \cancel{2\,CO_2(g)} \qquad \Delta H = -787.0\ \text{kJ}$$

$$H_2(g) + \cancel{\tfrac{1}{2}O_2(g)} \longrightarrow H_2O(l) \qquad \Delta H = -285.8\ \text{kJ}$$

$$2\,C(s) + H_2(g) \longrightarrow C_2H_2(g) \qquad \Delta H = 226.8\ \text{kJ}$$

Calorimetry

- 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.
- The heat capacity (C) of a system is the quantity of heat required to change the temperature of the system by 1℃

$$C = q/\Delta T \text{ (units are J/}^{\circ}\text{C)}$$

- Molar heat capacity (C_m) is the heat capacity of one mole of a substance.
- The specific heat (C_s) is the heat capacity of one gram of a pure substance (or homogeneous mixture)

$$C_s = C/m = q/(m\Delta T)$$

$$q = C_s m \Delta T$$

- Water has a specific heat of 1 cal/(g℃).
- 4.184 J = 1 cal

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)
$N_2(g)$	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

Exercise 5.6

- (a) How much heat is needed to warm 250 g of water (about 1 cup) from 22 °C (about room temperature) to 98 °C (near its boiling point)? (b) What is the molar heat capacity of water?

Sol:

(a) $\Delta T = 98\ ^\circ C - 22\ ^\circ C = 76\ ^\circ C = 76\ K$

$q = Csm\Delta T = (4.18\ J/gK)(250\ g)(76\ K) = 7.9 * 10^4\ J$

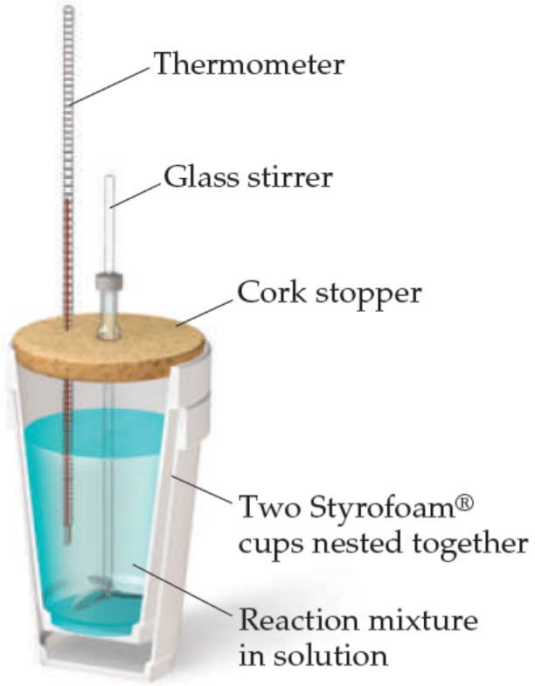
(b) Water has a specific heat of 1 cal/(gK), 4.184 J = 1 cal

$C_m = (18\ g/mole)[\ 4.18\ J/(gK)\ ] = 75.2\ J/mole\ K$

Coffee-cup calorimeter

- Reactions done in aqueous solution are at constant pressure.
- The calorimeter is often nested foam cups containing the solution.

$$q_{reaction} = - q_{solution} = -(mass_{solution} \times Cs, solution \times \Delta T)$$



Exercise 5.7

- 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 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/gK.

Sol

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

$$\Delta T = 27.5\ ^\circ\text{C} - 21.0\ ^\circ\text{C} = 6.5\ ^\circ\text{C} = 6.5\ \text{K}$$

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

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

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

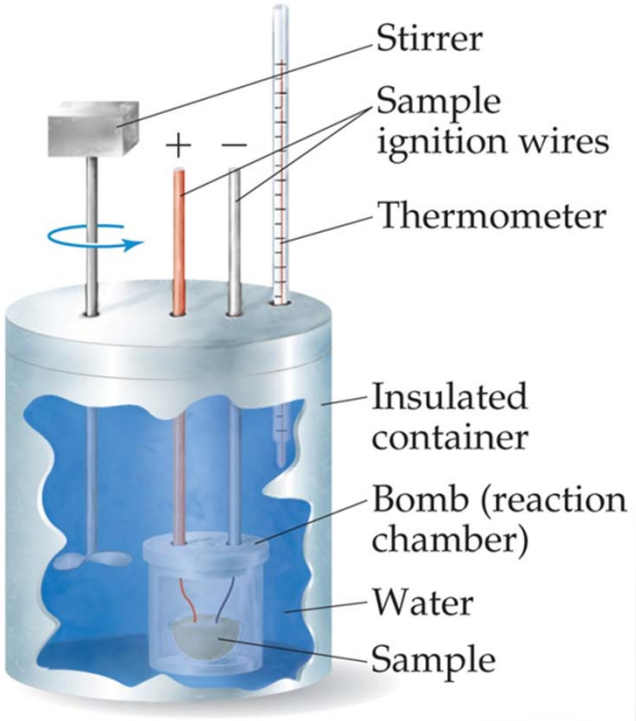
$$(0.050\ \text{L})(1.0\ \text{mol/L}) = 0.050\ \text{mol}$$

$$\Delta H = -2.7\ \text{kJ}/0.050\ \text{mol} = -54\ \text{kJ/mol}$$

Bomb Calorimeter

- 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.

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



Exercise 5.8

The combustion of methylhydrazine (CH_6N_2), a liquid rocket fuel, produces $N_2(g)$, $CO_2(g)$, and $H_2O(l)$:

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

When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 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.

Sol:

$$\Delta T = (39.50\,^\circ\text{C} - 25.00\,^\circ\text{C}) = 14.50\,^\circ\text{C}$$

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

$$\left(\frac{-113.0\,\text{kJ}}{4.00\,\text{g}\,\cancel{CH_6N_2}}\right) \times \left(\frac{46.1\,\text{g}\,\cancel{CH_6N_2}}{1\,\text{mol}\,CH_6N_2}\right) = -1.30 \times 10^3\,\text{kJ/mol}\,CH_6N_2$$

$$2\,CH_6N_2(l) + 5\,O_2(g) \longrightarrow 2\,N_2(g) + 2\,CO_2(g) + 6\,H_2O(l) \qquad \Delta H = -2.6 \times 10^3\ \text{KJ}$$

Standard enthalpy change

- The standard state is the state of a material at a defined set of conditions.
- Pure gas at exactly 1 atm pressure
- Pure solid or liquid in its most stable form at exactly 1 atm pressure and temperature of interest (Usually 25 $^{\circ}$C)
- Substance in a solution with concentration 1 M
- The standard enthalpy change, $\triangle H^{\circ}$, is the enthalpy change when all reactants and products are in their standard states.

Standard enthalpy of formation

- The standard enthalpy of formation, ΔH_f°, is the enthalpy change for the reaction forming 1 mole of a pure compound from its constituent elements.
- The elements must be in their standard states.
- The ΔH_f°, for a pure element in its standard state = 0 kJ/mol.

Calculating Standard Enthalpy Change for a Reaction

- The standard enthalpy of formation corresponds to the formation of a compound from its constituent elements in their standard states

$$\text{elements} \longrightarrow \text{compound} \qquad \Delta H_f^\circ$$

- The decomposition of a compound into its constituent elements in their standard states:

$$\text{compound} \longrightarrow \text{elements} \qquad -\Delta H_f^\circ$$

$$\begin{array}{lll} \text{reactants} \longrightarrow \text{elements} & \Delta H_1 = -\sum \Delta H_f^\circ(\text{reactants}) \\ \underline{\text{elements} \longrightarrow \text{products} \quad \Delta H_2 = +\sum \Delta H_f^\circ(\text{products})} \\ \text{reactants} \longrightarrow \text{products} & \Delta H_{rxn}^\circ = \Delta H_1 + \Delta H_2 \end{array}$$

Calculating Standard Enthalpy Change for a Reaction

- The ΔH° for the reaction is then the sum of the ΔH_f° for the component reactions.

- The ΔH° for the reaction is then the sum of the ΔH_f° for the component reactions.

$$\Delta H^\circ_{reaction} = \Sigma\, n\, \Delta H_f^\circ(products) - \Sigma\, n\, \Delta H_f^\circ(reactants)$$

Σ means sum.

n is the coefficient of the reaction.

Standard Enthalpies of Formation

Table 5.3 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

Using Enthalpies of Formation to Calculate Enthalpies of Reaction

EX:

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

$$C_3H_8(g) \longrightarrow 3\,C(s) + 4\,H_2(g) \qquad \Delta H_1 = -\Delta H_f^\circ[C_3H_8(g)] \qquad [5.26]$$

$$3\,C(s) + 3\,O_2(g) \longrightarrow 3\,CO_2(g) \qquad \Delta H_2 = 3\Delta H_f^\circ[CO_2(g)] \qquad [5.27]$$

$$4\,H_2(g) + 2\,O_2(g) \longrightarrow 4\,H_2O(l) \qquad \Delta H_3 = 4\Delta H_f^\circ[H_2O(l)] \qquad [5.28]$$

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H_{rxn}^\circ = \Delta H_1 + \Delta H_2 + \Delta H_3 \qquad [5.29]$$

Exercise 5.12

- (a) Calculate the standard enthalpy change for the combustion of 1 mol of benzene, $C_6H_6(\ell)$, to $CO_2(g)$ and $H_2O(\ell)$.

Sol:

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

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

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

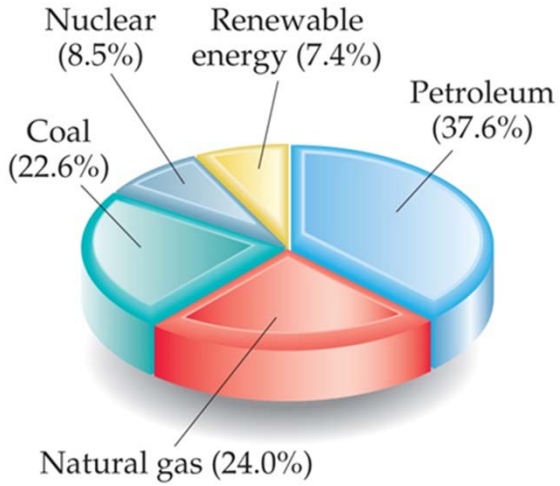
	Approximate Composition (% by Mass)			Fuel Value	
	Carbohydrate	Fat	Protein	kJ/g	kcal/g (Cal/g)
Carbohydrate	100	—	—	17	4
Fat	—	100	—	38	9
Protein	—	—	100	17	4
Apples	13	0.5	0.4	2.5	0.59
Beer[a]	1.2	—	0.3	1.8	0.42
Bread	52	3	9	12	2.8
Cheese	4	37	28	20	4.7
Eggs	0.7	10	13	6.0	1.4
Fudge	81	11	2	18	4.4
Green 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

[a]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 %)			
	C	H	O	Fuel Value (kJ/g)
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



Other Energy Sources

- Nuclear fission produces 8.5% of the U.S. energy needs.
- Renewable energy sources, like solar, wind, geothermal, hydroelectric, and biomass sources produce 7.4% of the U.S. energy needs.