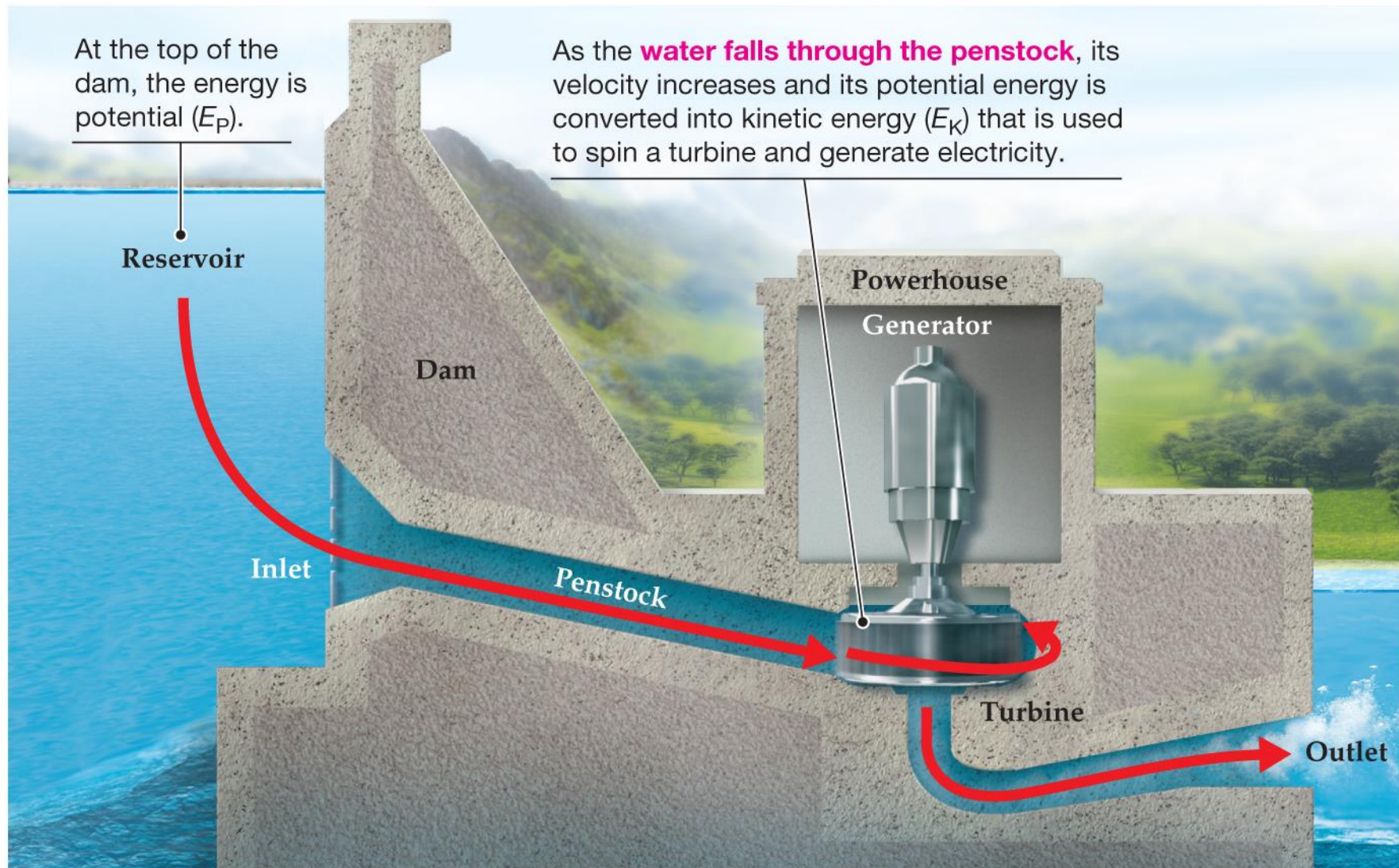Lecture Presentation

Chapter 9

Thermochemistry: Chemical Energy

John E. McMurry
Robert C. Fay

Energy and Its Conservation

Conservation of Energy Law: Energy cannot be created or destroyed; it can only be converted from one form to another.

Energy and Its Conservation

At the top of the dam, the energy is potential (E_P).

As the **water falls through the penstock**, its velocity increases and its potential energy is converted into kinetic energy (E_K) that is used to spin a turbine and generate electricity.

Reservoir

Dam

Inlet

Penstock

Powerhouse

Generator

Turbine

Outlet

Energy and Its Conservation

Thermal Energy: The kinetic energy of molecular motion. It is measured by finding the *temperature* of an object.

Heat: The amount of thermal energy transferred from one object to another as the result of a *temperature difference* between the two
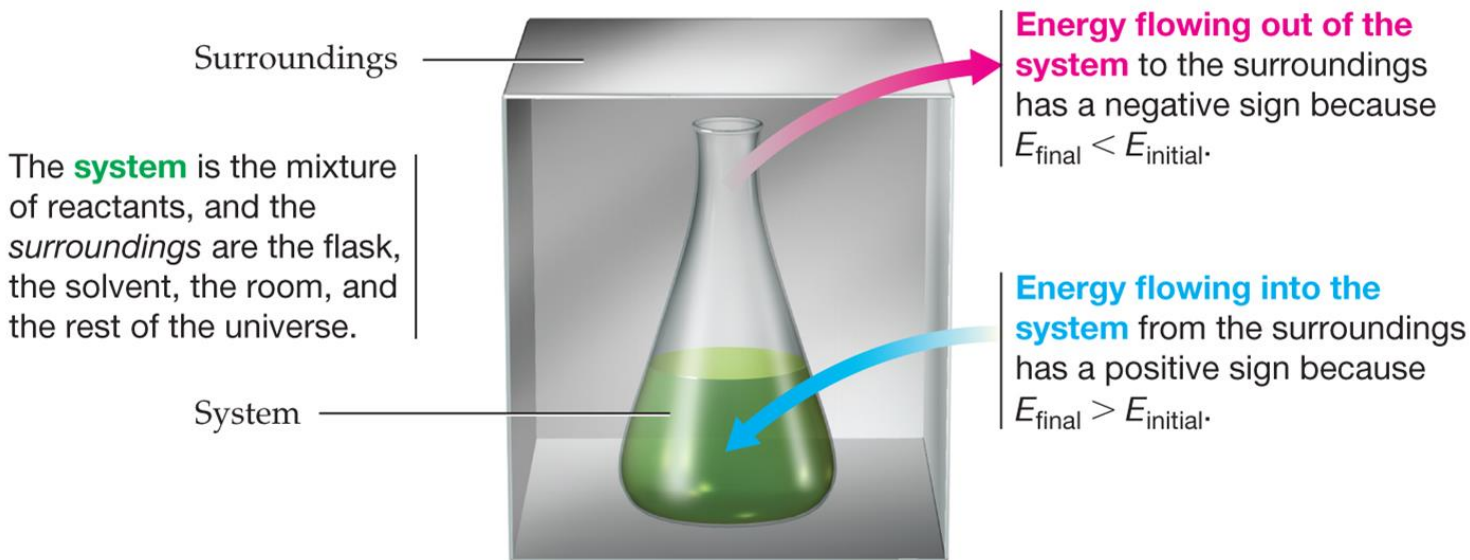
Internal Energy and State Functions

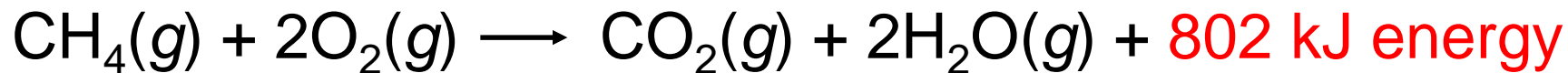**First Law of Thermodynamics**: The total internal energy E of an isolated system is constant.

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

The energy change is the difference between final and initial states.

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

Surroundings

The **system** is the mixture of reactants, and the *surroundings* are the flask, the solvent, the room, and the rest of the universe.

System

Energy flowing out of the system to the surroundings has a negative sign because $E_{final} < E_{initial}$.

Energy flowing into the system from the surroundings has a positive sign because $E_{final} > E_{initial}$.

Internal Energy and State Functions

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{802 kJ energy}$$

$$\Delta E = E_{final} - E_{initial} = -802 \text{ kJ}$$

802 kJ is released when 1 mol of methane, CH_4, reacts with 2 mol of oxygen to produce 1 mol of carbon dioxide and 2 mol of water.
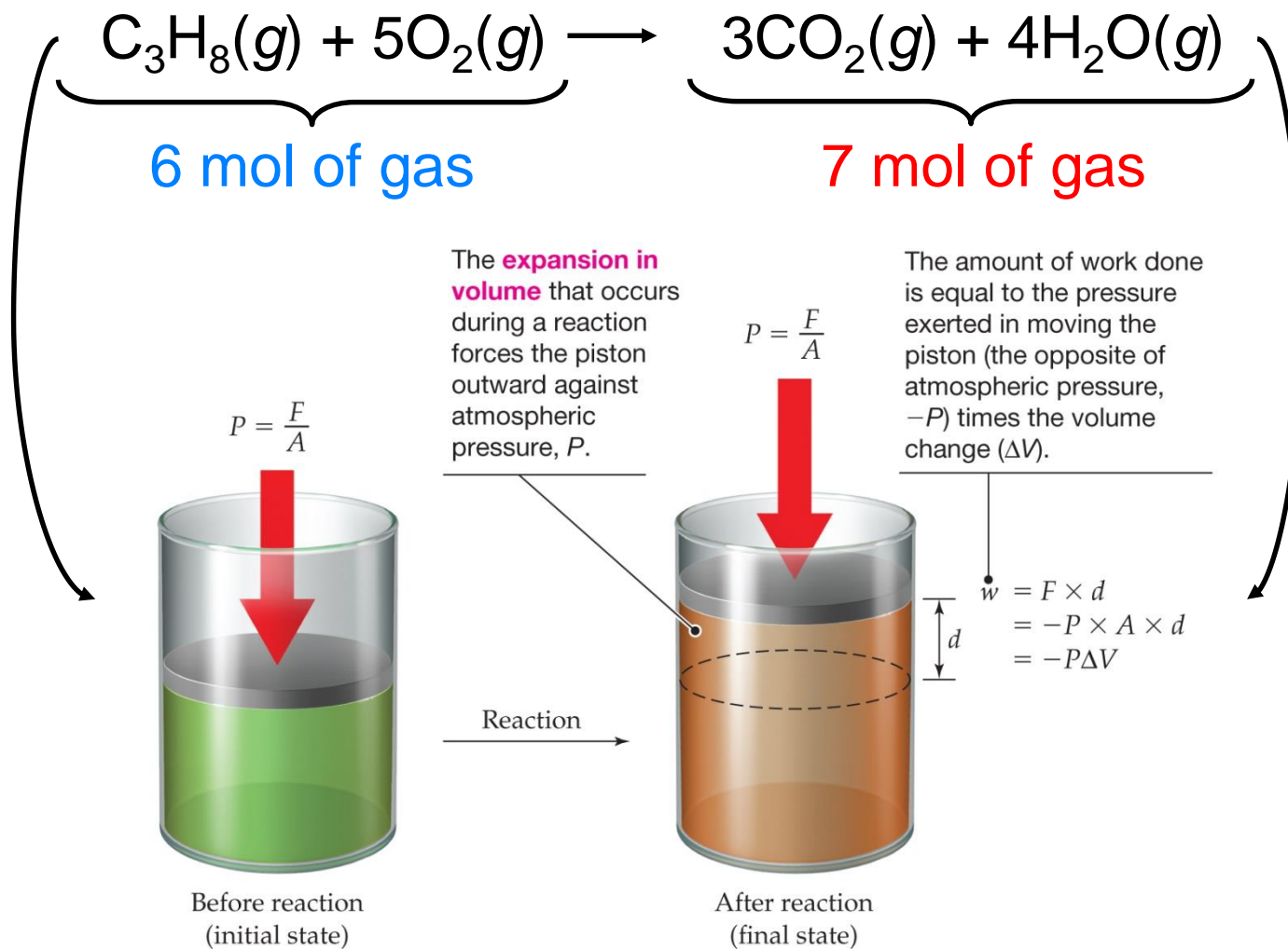
Balancing Chemical Equations

State Function: A function or property whose value depends only on the present state, or condition, of the system, not on the path used to arrive at that state
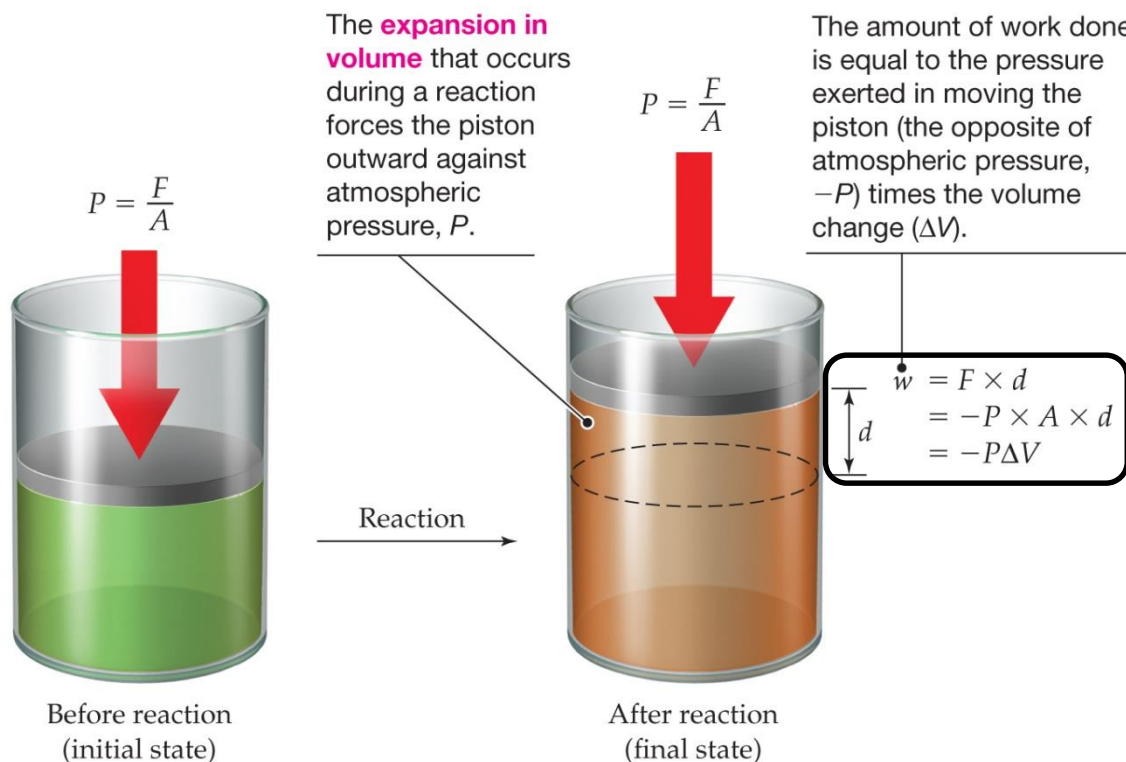

State function
Position

Nonstate functions
Work expended
Money spent

Expansion Work

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

6 mol of gas   7 mol of gas

The **expansion in volume** that occurs during a reaction forces the piston outward against atmospheric pressure, P.

$P = \dfrac{F}{A}$

The amount of work done is equal to the pressure exerted in moving the piston (the opposite of atmospheric pressure, $-P$) times the volume change (ΔV).

$P = \dfrac{F}{A}$

$P = \dfrac{F}{A}$

$$\begin{aligned} w &= F \times d \\ &= -P \times A \times d \\ &= -P\Delta V \end{aligned}$$

Reaction

Before reaction
(initial state)

After reaction
(final state)

Expansion Work

Expansion Work: Work done as the result of a volume change in the system

The **expansion in volume** that occurs during a reaction forces the piston outward against atmospheric pressure, P.

$P = \frac{F}{A}$

The amount of work done is equal to the pressure exerted in moving the piston (the opposite of atmospheric pressure, $-P$) times the volume change (ΔV).

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

$P = \frac{F}{A}$

Before reaction (initial state)

Reaction

After reaction (final state)

Energy and Enthalpy

$$\Delta E = q + w$$

q = heat transferred w = work = $-P\Delta V$

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

Constant Volume ($\Delta V = 0$): $q_v = \Delta E$

Constant Pressure: $q_p = \Delta E + P\Delta V$

Energy and Enthalpy

$$q_{p} = \Delta E + P\Delta V = \boldsymbol{\Delta H}$$

Enthalpy change
or
Heat of reaction (at constant pressure)

Enthalpy is a state function whose value depends only on the current state of the system, not on the path taken to arrive at that state.

$$\Delta H = H_{final} - H_{initial}$$

$$= H_{products} - H_{reactants}$$

Thermochemical Equations and the Thermodynamic Standard State

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

$\Delta H = -2044 \text{ kJ}$

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$
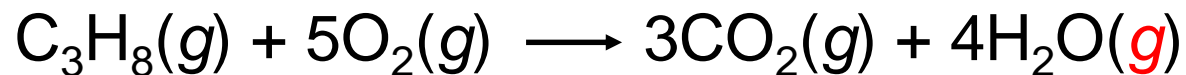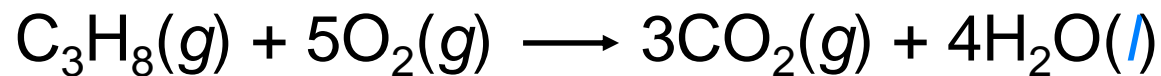
$\Delta H = -2220 \text{ kJ}$

Thermochemical Equations and the Thermodynamic Standard State

Thermodynamic Standard State: Most stable form of a substance at 1 atm pressure and at a specified temperature, usually 25 °C; 1 M concentration for all substances in solution

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$
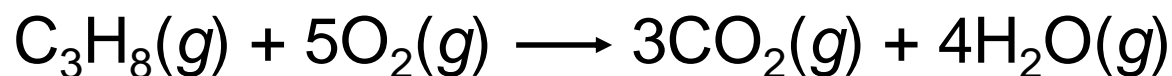
$$\Delta H° = -2044 \text{ kJ}$$

Enthalpies of Physical and Chemical Change

Enthalpy of Fusion (ΔH_{fusion}): The amount of heat necessary to melt a substance without changing its temperature

Enthalpy of Vaporization (ΔH_{vap}): The amount of heat required to vaporize a substance without changing its temperature

Enthalpy of Sublimation (ΔH_{subl}): The amount of heat required to convert a substance from a solid to a gas without going through a liquid phase
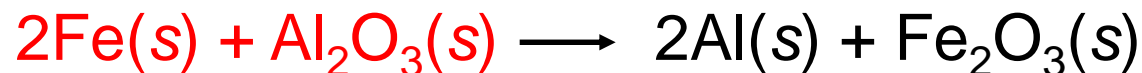
Enthalpies of Physical and Chemical Change

At constant temperature,
$$\Delta H_{subl} = \Delta H_{fusion} + \Delta H_{vap}$$

ΔH_{subl}

ΔH_{vap}

ΔH_{fusion}

Vapor

Liquid

Solid

Enthalpies of Physical and Chemical Change

$2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$
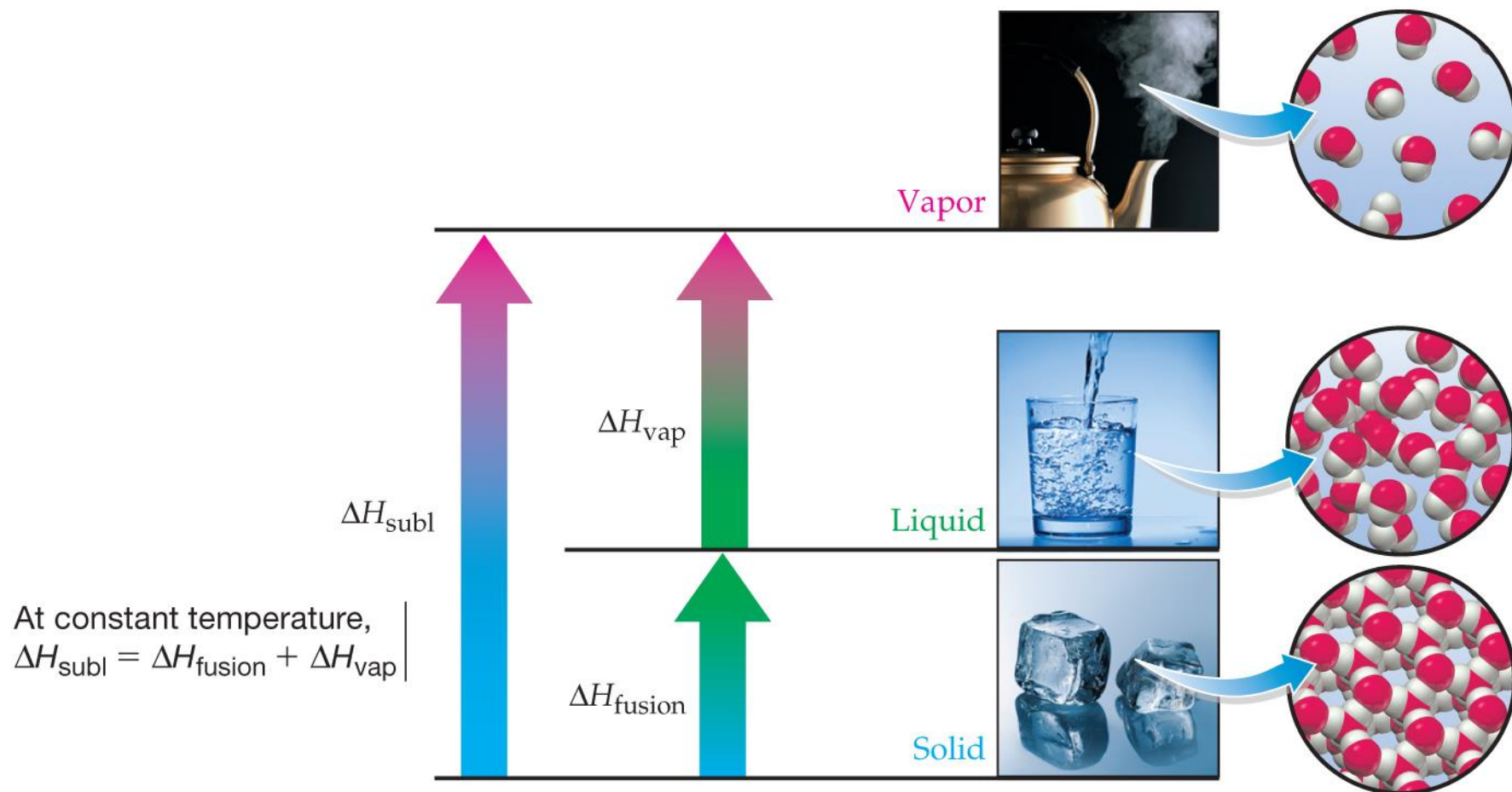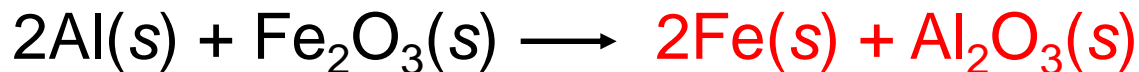
$$\Delta H° = -852 \text{ kJ}$$

Exothermic

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

$$\Delta H° = +852 \text{ kJ}$$

Endothermic

Calorimetry and Heat Capacity

Measure the heat flow at *constant pressure* (**ΔH**).

The reaction takes place inside an insulated vessel outfitted with a loose-fitting top, a thermometer, and a stirrer.

Thermometer

Stirrer

Insulated vessel

Reaction mixture
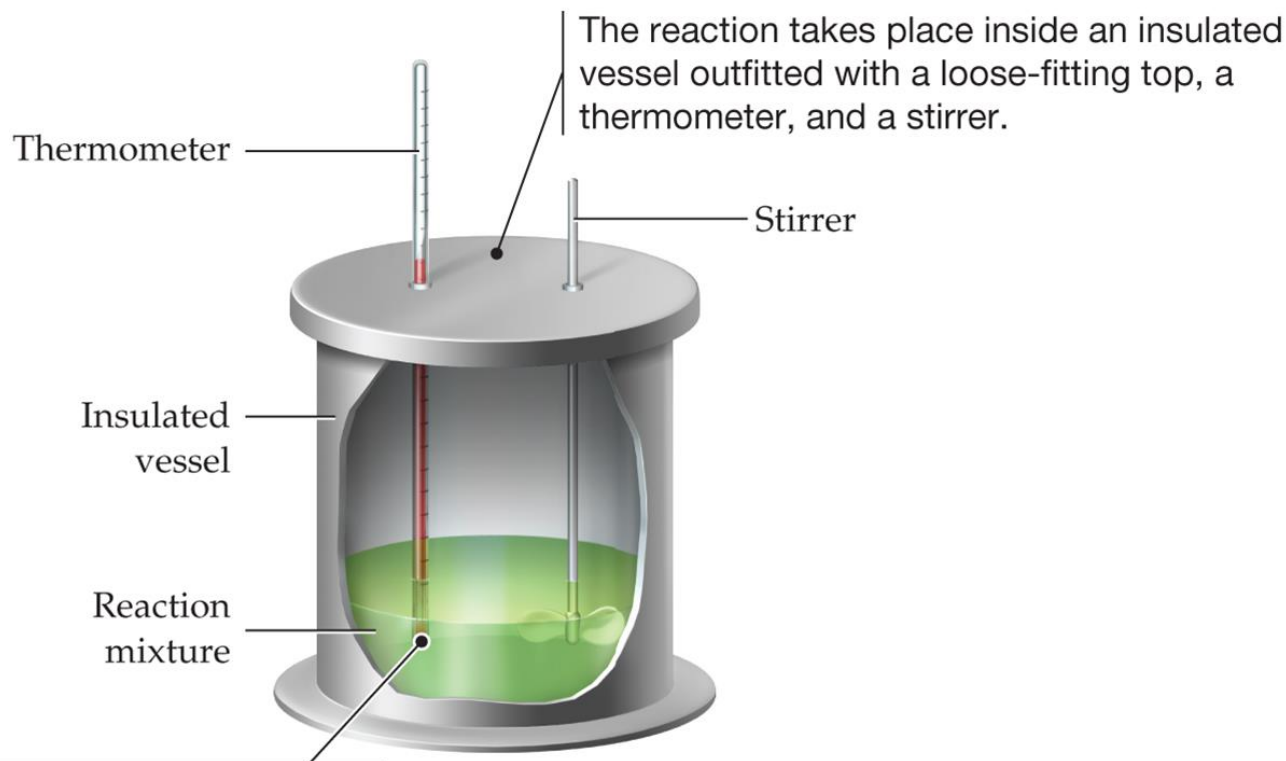
Measuring the **temperature change** that accompanies the reaction makes it possible to calculate ΔH.

Calorimetry and Heat Capacity

Measure the heat flow at *constant volume* (**ΔE**).

Thermometer — Stirrer — Ignition wires — Oxygen atmosphere — Water — Sample in cup
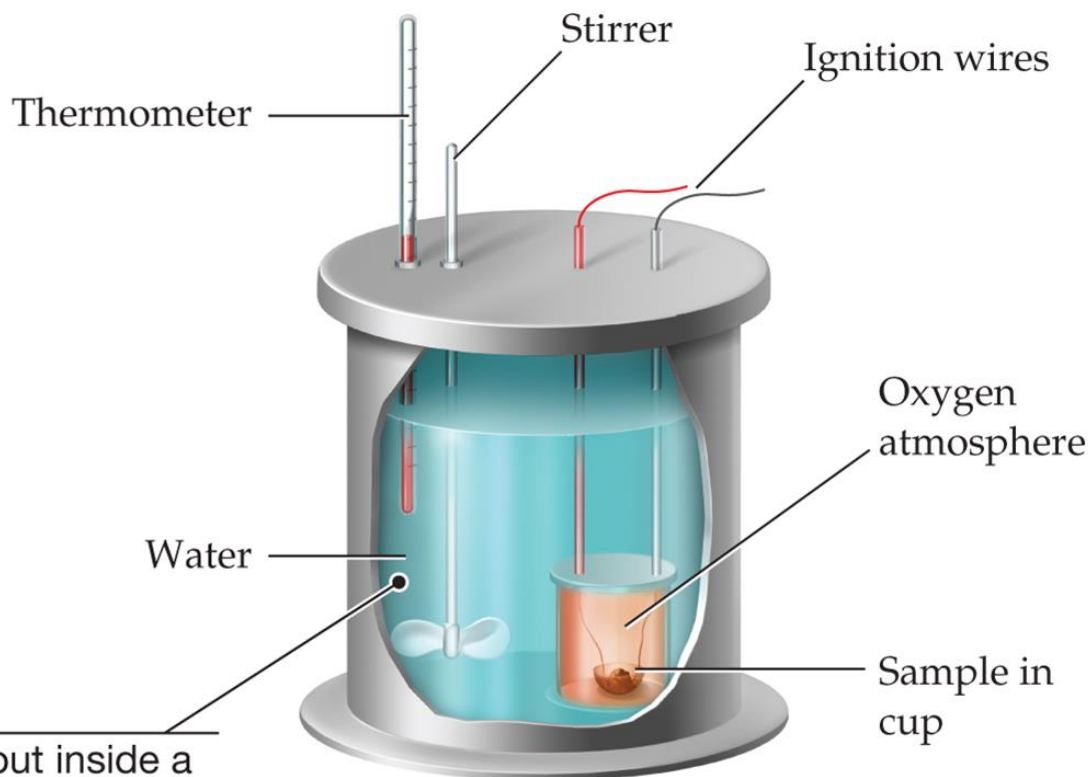
The reaction is carried out inside a steel bomb, and the heat evolved is transferred to the bomb and surrounding water, where the **temperature rise** is measured.

Calorimetry and Heat Capacity

Heat Capacity (C): The amount of heat necessary to raise the temperature of an object or substance a given amount

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

Specific Heat (Capacity): The amount of heat required to raise the temperature of 1 g of a substance by 1 °C

$$q = (\text{Specific heat}) \times (\text{Mass of substance}) \times \Delta T$$

Calorimetry and Heat Capacity

Molar Heat Capacity (C_m): The amount of heat necessary to raise the temperature of 1 mol of a substance by 1 °C

$$q = C_m \times \text{Moles of substance} \times \Delta T$$

Calorimetry and Heat Capacity

TABLE 9.1 Specific Heats and Molar Heat Capacities for Some Common Substances at 25 °C

Substance	Specific Heat (c) J/(g · °C)	Molar Heat Capacity (C_m) J/(mol · °C)
Air (dry)	1.01	29.1
Aluminum	0.897	24.2
Copper	0.385	24.4
Gold	0.129	25.4
Iron	0.449	25.1
Mercury	0.140	28.0
NaCl	0.859	50.2
Water(s)[a]	2.03	36.6
Water(l)	4.179	75.3

[a]At −11°C

Calorimetry and Heat Capacity

Assuming that a can of soda has the same specific heat as water, calculate the amount of heat (in kilojoules) transferred when one can (about 350 g) is cooled from 25 °C to 3 °C.

q = (Specific heat) × (Mass of substance) × ΔT

Specific heat = 4.18 $\dfrac{J}{g \ °C}$

Mass = 350 g

Temperature change = 3 °C – 25 °C = –22 °C

Calorimetry and Heat Capacity

Calculate the amount of heat transferred.

Heat evolved = $\dfrac{4.18 \text{ J}}{\text{g }°\text{C}} \times 350 \text{ g} \times -22 °\text{C} = -32\,000 \text{ J}$

$-32\,000 \text{ J} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}} = \boxed{-32 \text{ kJ}}$

Hess's Law

Hess's Law: The overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for the individual steps in the reaction.
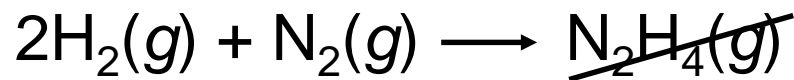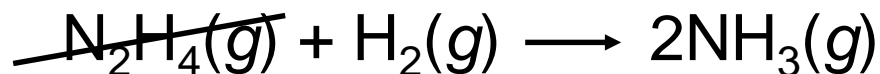
Haber Process
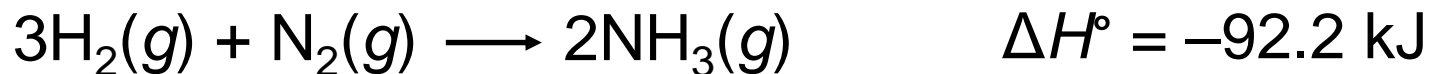
$$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H° = -92.2 \text{ kJ}$$

Hess's Law

Hess's Law: The overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for the individual steps in the reaction.
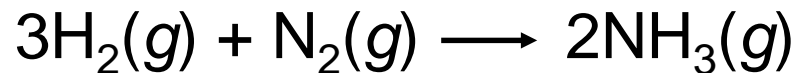
Multiple-Step Process

$$2H_2(g) + N_2(g) \longrightarrow N_2H_4(g) \qquad \Delta H^\circ_1 = \text{?}$$

$$N_2H_4(g) + H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H^\circ_2 = -187.6 \text{ kJ}$$

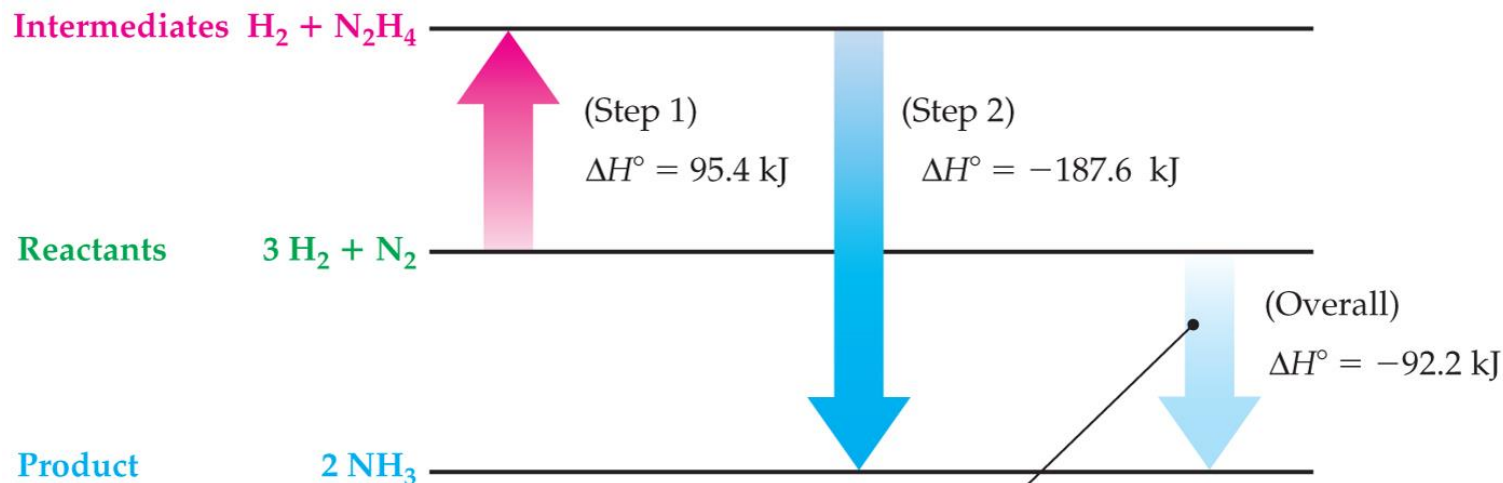$$\overline{3H_2(g) + N_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H^\circ_{1+2} = \quad -92.2 \text{ kJ}}$$

Hess's Law

$$\Delta H^{\circ}_{1} + \Delta H^{\circ}_{2} = \Delta H^{\circ}_{1+2}$$

$$\Delta H^{\circ}_{1} = \Delta H^{\circ}_{1+2} - \Delta H^{\circ}_{2}$$

$$= -92.2 \text{ kJ} - (-187.6 \text{ kJ}) = +95.4 \text{ kJ}$$

Intermediates $H_2 + N_2H_4$

(Step 1)
$\Delta H^{\circ} = 95.4$ kJ

(Step 2)
$\Delta H^{\circ} = -187.6$ kJ

Reactants $3 H_2 + N_2$

(Overall)
$\Delta H^{\circ} = -92.2$ kJ

Product $2 NH_3$

The enthalpy change for the **overall reaction** equals the sum of the enthalpy changes for the individual Steps **1** and **2**, a statement known as Hess's law.

Standard Heats of Formation

Standard Heat of Formation (ΔH°_f): The enthalpy change for the formation of 1 mol of a substance in its standard state from its constituent elements in their standard states

Standard states

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H^\circ_f = -74.8 \text{ kJ}$$

1 mol of a substance
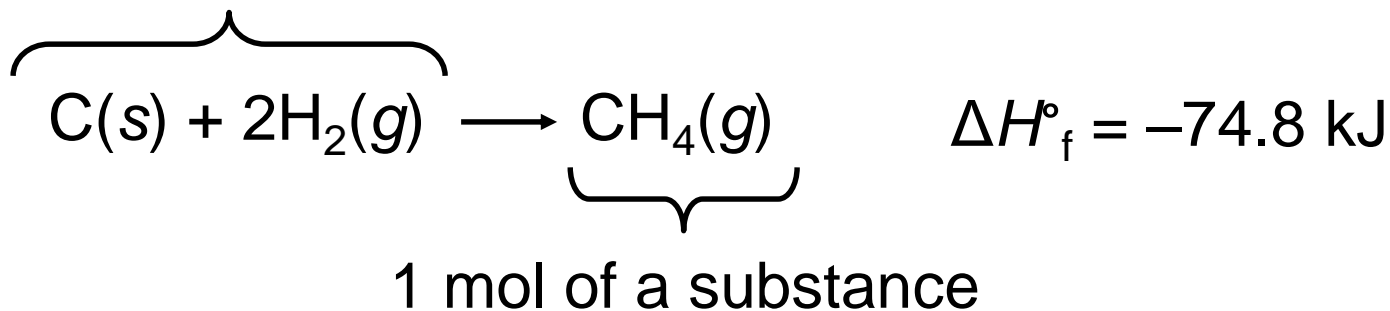
Standard Heats of Formation

TABLE 9.2 Standard Heats of Formation for Some Common Substances at 25 °C

Substance	Formula	$\Delta H°_f$ (kJ/mol)	Substance	Formula	$\Delta H°_f$ (kJ/mol)
Acetylene	$C_2H_2(g)$	227.4	Hydrogen chloride	$HCl(g)$	−92.3
Ammonia	$NH_3(g)$	−46.1	Iron(III) oxide	$Fe_2O_3(s)$	−824.2
Carbon dioxide	$CO_2(g)$	−393.5	Magnesium carbonate	$MgCO_3(s)$	−1095.8
Carbon monoxide	$CO(g)$	−110.5	Methane	$CH_4(g)$	−74.8
Ethanol	$C_2H_5OH(l)$	−277.7	Nitric oxide	$NO(g)$	91.3
Ethylene	$C_2H_4(g)$	52.3	Water (g)	$H_2O(g)$	−241.8
Glucose	$C_6H_{12}O_6(s)$	1273.3	Water (l)	$H_2O(l)$	−285.8

Standard Heats of Formation

$$\Delta H° = \Delta H°_f \text{ (Products)} - \Delta H°_f \text{ (Reactants)}$$

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$
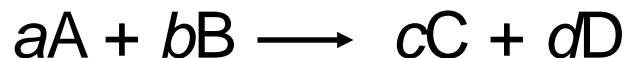
$$\Delta H° = [c\,\Delta H°_f\,(\text{C}) + d\,\Delta H°_f\,(\text{D})] - [a\,\Delta H°_f\,(\text{A}) + b\,\Delta H°_f\,(\text{B})]$$
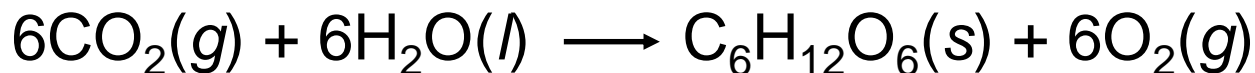
Products Reactants

Standard Heats of Formation

Using standard heats of formation, calculate the standard enthalpy of reaction for the photosynthesis of glucose ($C_6H_{12}O_6$) and O_2 from CO_2 and liquid H_2O.

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

$$\Delta H° = \text{?}$$

Standard Heats of Formation

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$$
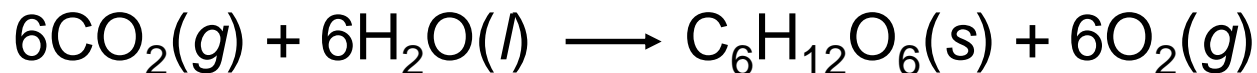
$$\Delta H° = \text{?}$$

$$\Delta H° = [\Delta H°_f \ (C_6H_{12}O_6(s))] -$$

$$[6 \ \Delta H°_f \ (CO_2(g)) + 6 \ \Delta H°_f \ (H_2O(l))]$$

$$\Delta H° = [(1 \ \text{mol})(-1260 \ \text{kJ/mol})] -$$

$$[(6 \ \text{mol})(-393.5 \ \text{kJ/mol}) + (6 \ \text{mol})(-285.8 \ \text{kJ/mol})]$$

$$\Delta H° = \boxed{2816 \ \text{kJ}}$$

Bond Dissociation Energies

Bond dissociation energies are standard enthalpy changes for the corresponding bond-breaking reactions.

| TABLE 7.2	Average Bond Dissociation Energies, D (kJ/mol)								
H—H	436[a]	C—H	410	N—H	390	O—F	180	I—I	151[a]
H—C	410	C—C	350	N—C	300	O—Cl	200	S—F	310
H—F	570[a]	C—F	450	N—F	270	O—Br	210	S—Cl	250
H—Cl	432[a]	C—Cl	330	N—Cl	200	O—I	220	S—Br	210
H—Br	366[a]	C—Br	270	N—Br	240	O—N	200	S—S	225
H—I	298[a]	C—I	240	N—N	240	O—O	180		
H—N	390	C—N	300	N—O	200	F—F	159[a]		
H—O	460	C—O	350	O—H	460	Cl—Cl	243[a]		
H—S	340	C—S	260	O—C	350	Br—Br	193[a]		

Multiple covalent bonds[b]

C=C	728	C≡C	965	C=O	732	O=O	498[a]	N≡N	945[a]

[a]Exact value.

[b]We'll discuss multiple covalent bonds in Section 7.5.

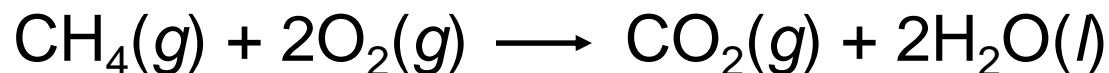© 2016 Pearson Education, Inc.

Bond Dissociation Energies

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
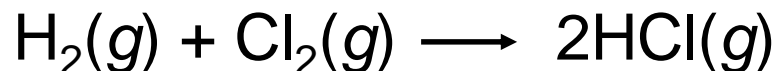
$$\Delta H° = D(\text{Reactant bonds}) - D(\text{Product bonds})$$

$$\Delta H° = (D_{H-H} + D_{Cl-Cl}) - (2D_{H-Cl})$$

$$\Delta H° = [(1 \text{ mol})(436 \text{ kJ/mol}) + (1 \text{ mol})(243 \text{ kJ/mol})] -$$

$$(2 \text{ mol})(432 \text{ kJ/mol})$$

$$\Delta H° = \boxed{-185 \text{ kJ}}$$

Fossil Fuels, Fuel Efficiency, and Heats of Combustion

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H° = [\Delta H°_f (CO_2(g)) + 2\,\Delta H°_f (H_2O(l))] - [\Delta H°_f (CH_4(g))]$$

$$\Delta H° = [(1\text{ mol})(-393.5\text{ kJ/mol}) + (2\text{ mol})(-285.8\text{ kJ/mol})] -$$

$$[(1\text{ mol})(-74.8\text{ kJ/mol})]$$

$$\Delta H° = \boxed{-890.3\text{ kJ}}$$
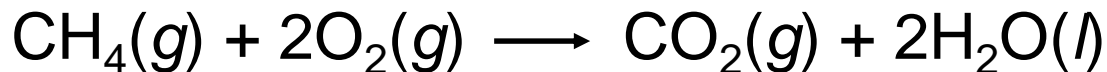
Fossil Fuels, Fuel Efficiency, and Heats of Combustion

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

TABLE 9.3 Thermochemical Properties of Some Fuels

Fuel	Combustion Enthalpy		
	kJ/mol	kJ/g	kJ/mL
Hydrogen, $H_2(l)$	−285.8	−141.8	−9.9[a]
Ethanol, $C_2H_5OH(l)$	−1366.8	−29.7	−23.4
Graphite, $C(s)$	−393.5	−32.8	−73.8
Methane, $CH_4(g)$	−890.3	−55.5	−30.8[a]
Methanol, $CH_3OH(l)$	−725.9	−22.7	−17.9
Octane, $C_8H_{18}(l)$	−5470	−47.9	−33.6
Toluene, $C_7H_8(l)$	−3910	−42.3	−36.7

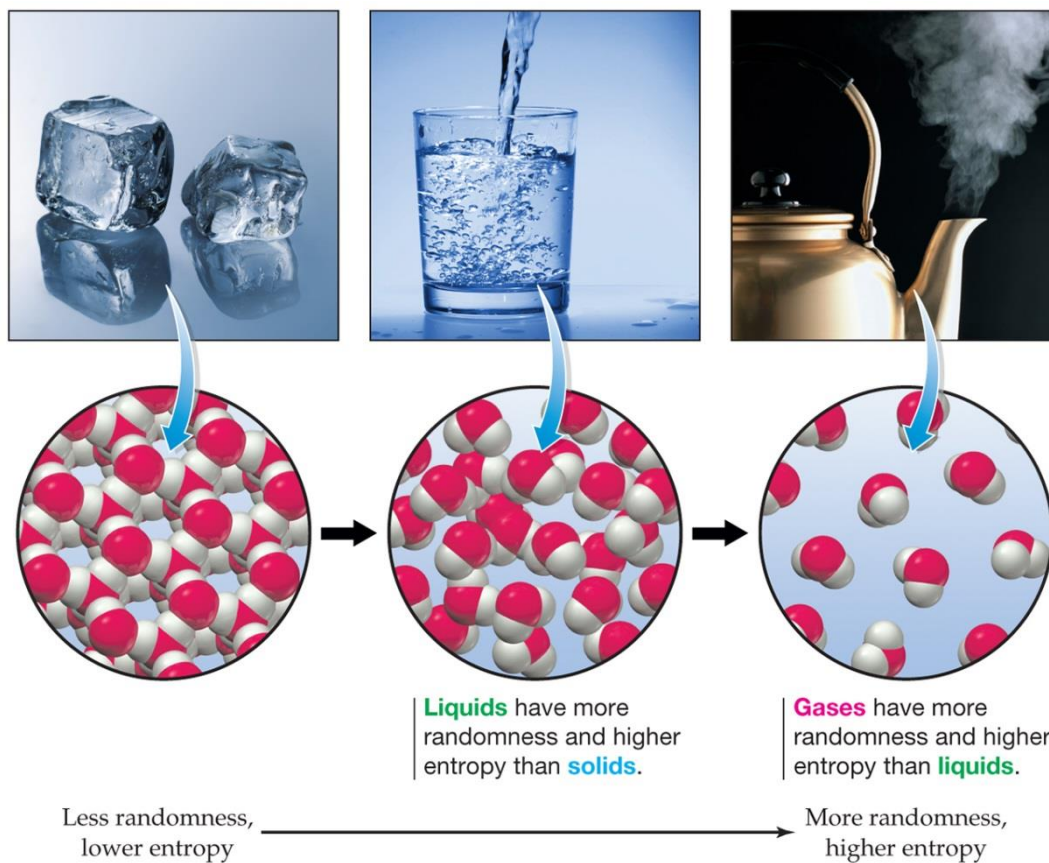[a]Calculated for the compressed liquid at 0 °C

An Introduction to Entropy

Spontaneous Process: A process that, once started, proceeds on its own without a continuous external influence

An Introduction to Entropy

Entropy (*S*): The amount of molecular randomness in a system

Liquids have more randomness and higher entropy than **solids**.

Gases have more randomness and higher entropy than **liquids**.

Less randomness, lower entropy ⟶ More randomness, higher entropy

An Introduction to Entropy

Spontaneous processes are
- favored by a decrease in H (negative ΔH).
- favored by an increase in S (positive ΔS).

Nonspontaneous processes are
- favored by an increase in H (positive ΔH).
- favored by a decrease in S (negative ΔS).

An Introduction to Free Energy

Gibbs Free-Energy Change (ΔG)

$$\Delta G = \Delta H - \text{T} \, \Delta S$$

Enthalpy of reaction   Temperature (in kelvin)   Entropy change
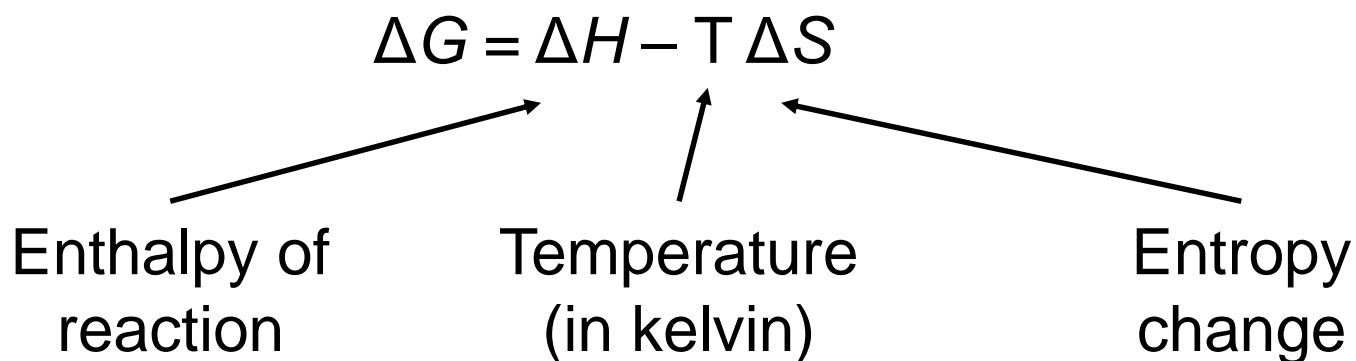
An Introduction to Free Energy

Gibbs Free-Energy Change (Δ*G*)

$$\Delta G = \Delta H - T\,\Delta S$$

Δ*G* < 0   Process is spontaneous.

Δ*G* = 0   Process is at equilibrium
(neither spontaneous nor nonspontaneous).

Δ*G* > 0   Process is nonspontaneous.

An Introduction to Free Energy

$\Delta S° = +22.0 \, \text{J}/(\text{K} \cdot \text{mol})$ **(Entropy increases)**

$\Delta H° = +6.01 \, \text{kJ/mol}$ **(Endothermic)**

Spontaneous above 0 °C

Spontaneous below 0 °C

$\Delta S° = -22.0 \, \text{J}/(\text{K} \cdot \text{mol})$ **(Entropy decreases)**

$\Delta H° = -6.01 \, \text{kJ/mol}$ **(Exothermic)**

Solid water

Liquid water

Below 0 °C, the enthalpy term ΔH dominates the entropy term $T\Delta S$ in the Gibbs free-energy equation, so **freezing** is spontaneous.

At 0 °C the entropy and enthalpy terms are exactly balanced.

Above 0 °C, the entropy term dominates the enthalpy term, so **melting** is spontaneous.