So you have a 25-minute quiz today

For offline class:

What are allowed?

- A pen
- A periodic table
- An A4-sized sheet of hand written notes
- A calculator

No other devices are allowed!

GENERAL CHEMISTRY I

Chapter 5
Thermochemistry

Contents

5-1 The Nature of Chemical Energy

5-2 The First Law of Thermodynamics

5-3 Enthalpy

5-4 Enthalpy of Reaction

5-5 Calorimetry

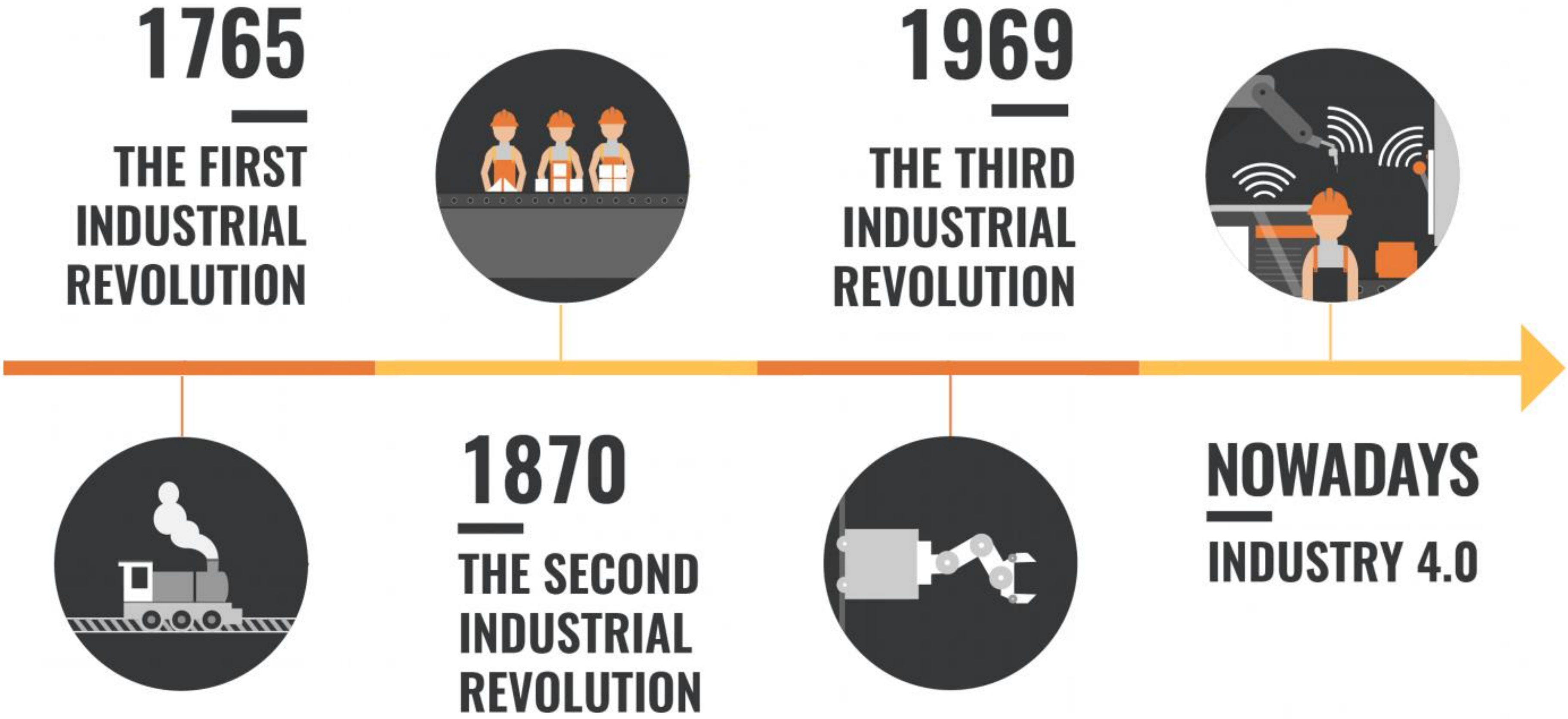
5-6 Hess’s Law

5-7 Enthalpies of Formation

5-8 Bond Enthalpy

5-9 Foods anf Fuels

Industrial Revolutions



1765

THE FIRST INDUSTRIAL REVOLUTION

1870

THE SECOND INDUSTRIAL REVOLUTION

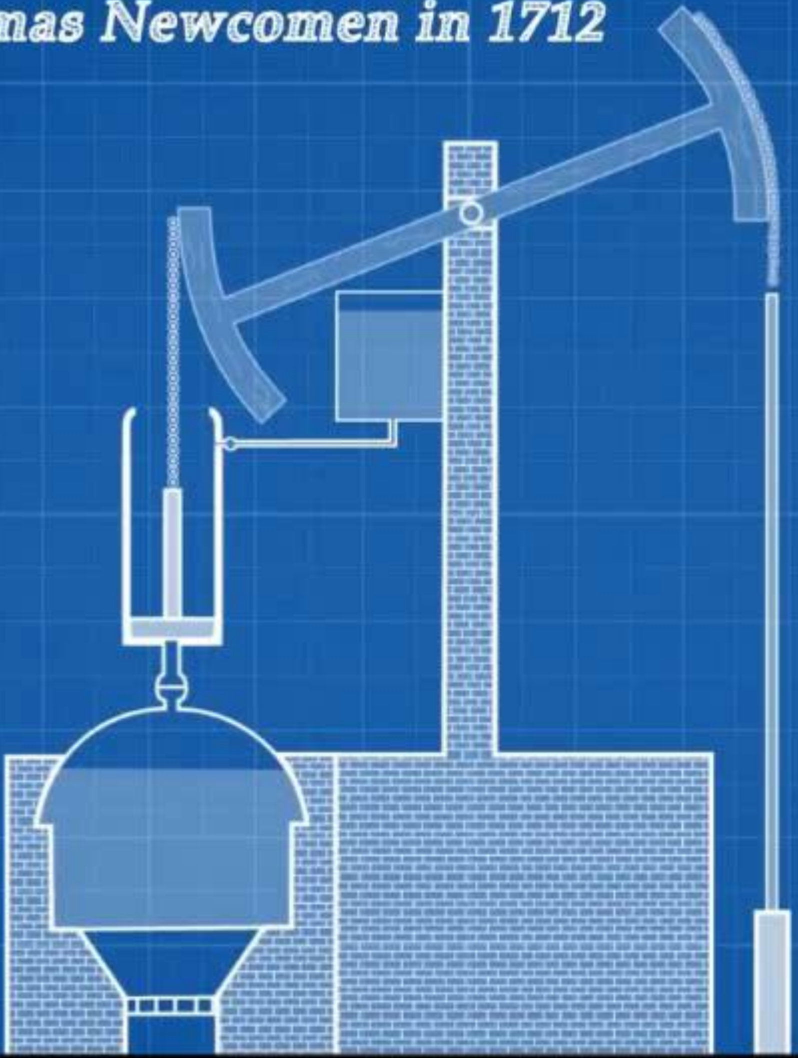
1969

THE THIRD INDUSTRIAL REVOLUTION

NOWADAYS

INDUSTRY 4.0

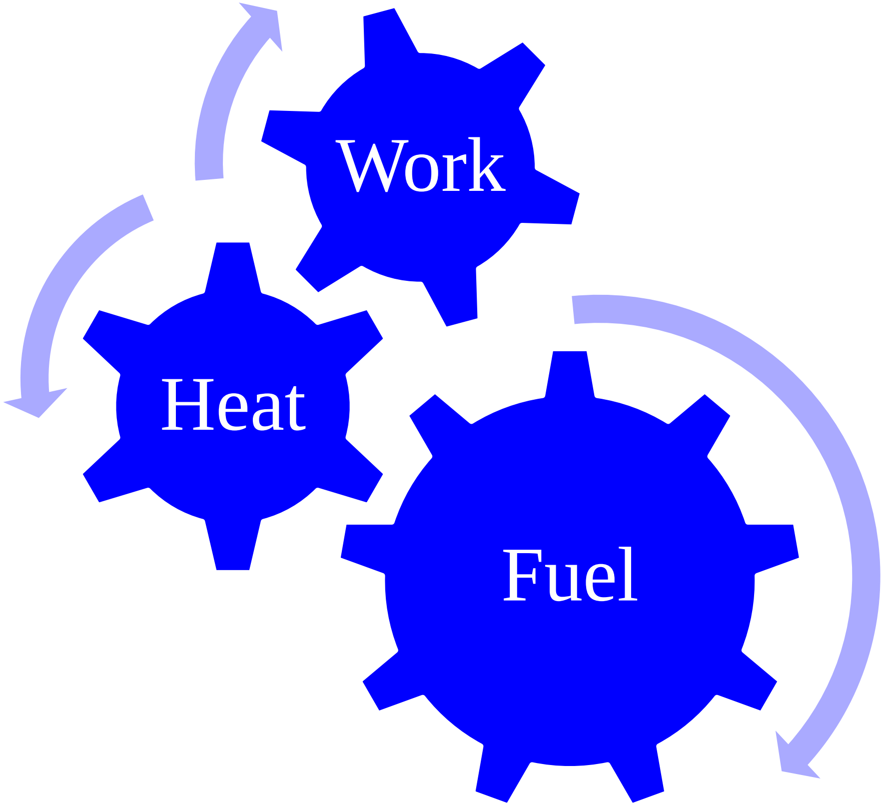
Invented by Thomas Newcomen in 1712



Getting Started: Some Terminology

- Thermodynamics (Greek: *thérme*-, "heat"; *dy'namis*, "power")

  This area of study began during the ***1st Industrial Revolution*** *in order to develop the relationships among* ***heat, work, and fuels in steam engines***



5-1 The Nature of Chemical Energy

Chemical reactions that do work

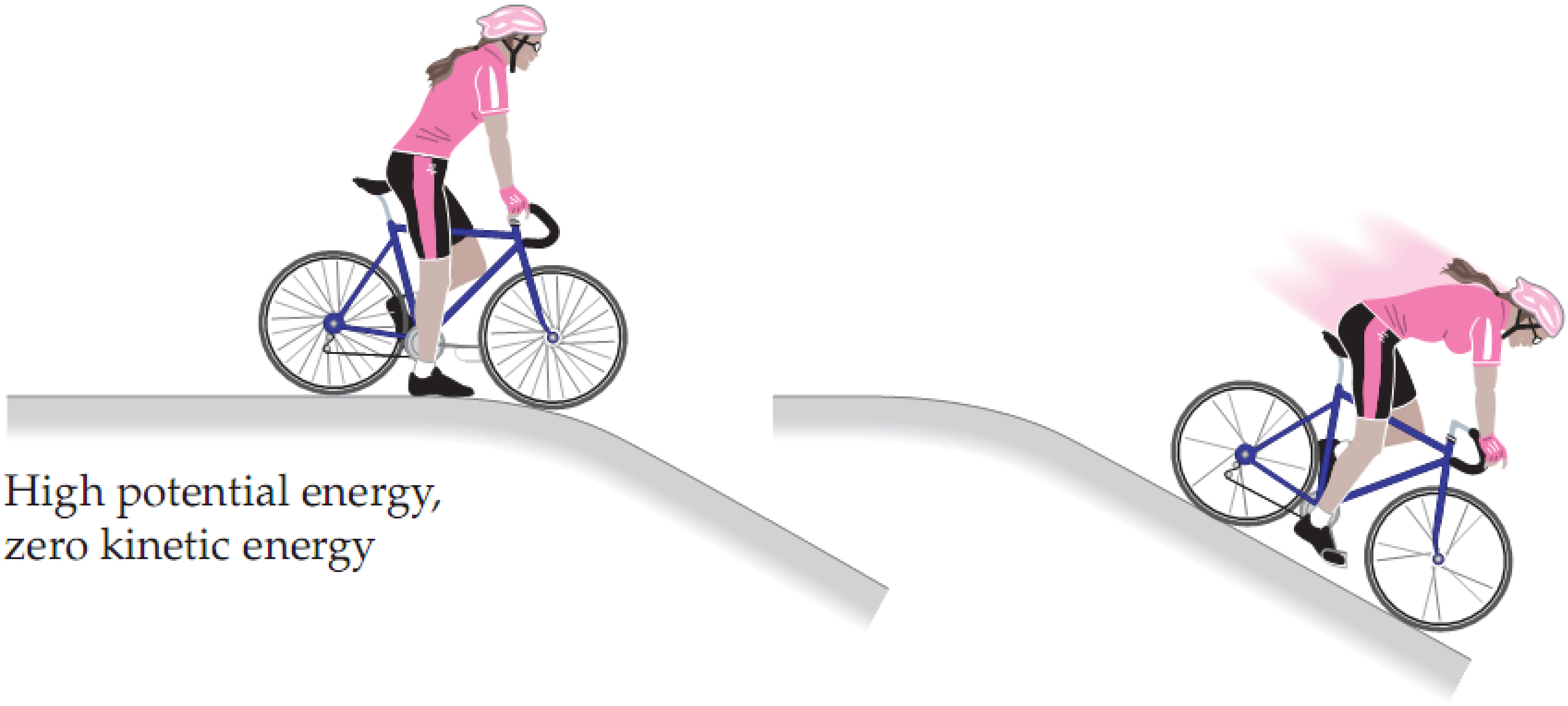
Chemical reactions that release heat

- Work, w, is force acting through a distance.
  - $w = F \times d$
- Energy, E, is the capacity to do work.
  - Potential Energy
  - Kinetic Energy

Kinetic Energy and Potential Energy

- Kinetic Energy
  - The energy of motion.
- Potential Energy
  - Energy due to condition, position, or composition.
  - Associated with forces of attraction or repulsion between objects.
  - The energy that originates from chemical reactions is associated mainly with changes in potential energy
- Energy can change from potential to kinetic.

Kinetic Energy and Potential Energy



High potential energy,
zero kinetic energy

Decreasing potential energy,
increasing kinetic energy

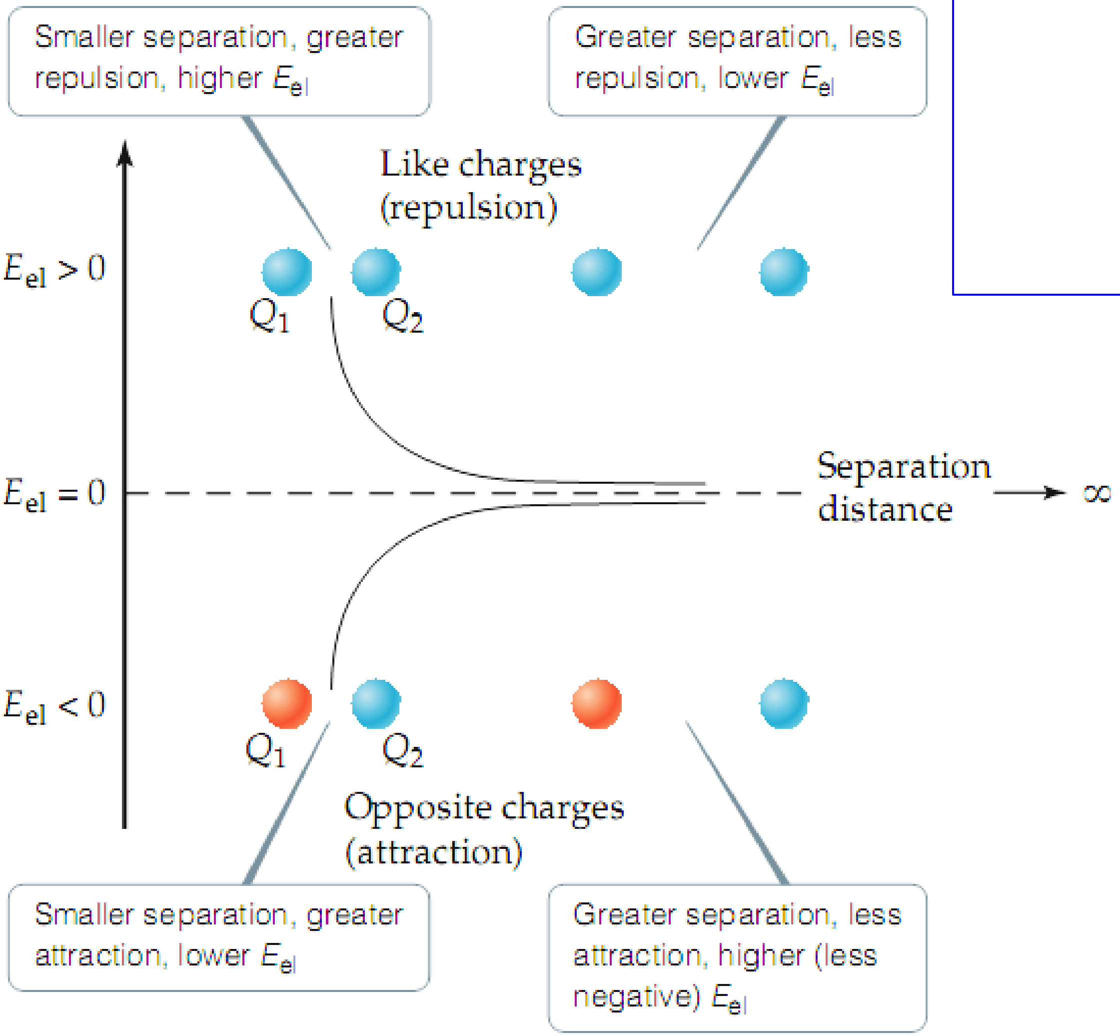
Electrostatic Potential Energy

Electrostatic potential energy, E_{el}

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

$k = 8.99 \times 10^9$ J.m/C^2

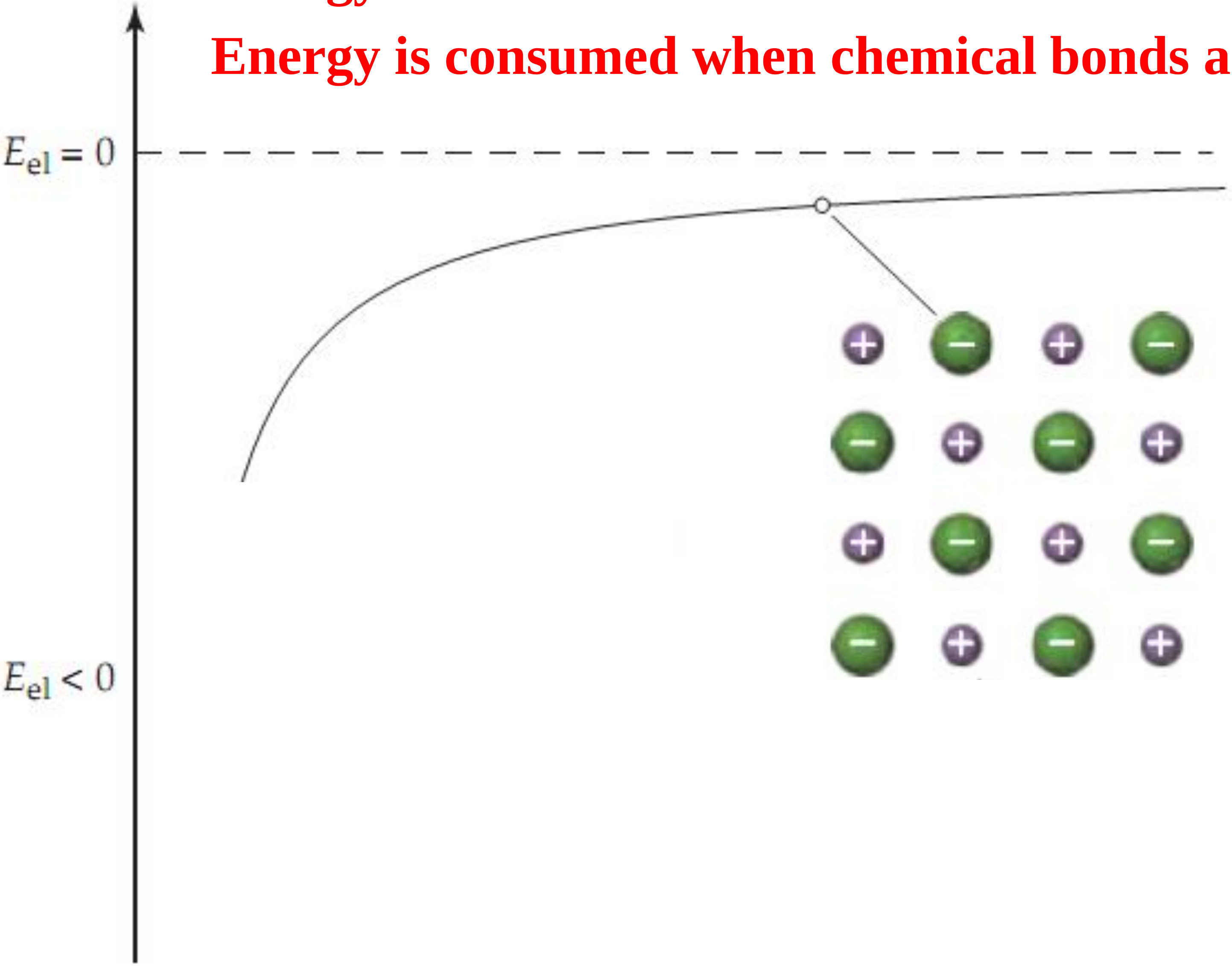
Q_1, Q_2: charges of the particles



If the ions in the figure were released and allowed to move, would they move closer together or farther apart?

Energy is released when chemical bonds are formed;

Energy is consumed when chemical bonds are broken



Units of Energy

- Work

$$w = Fd \qquad [w] = \left(\frac{\text{kg m}}{\text{s}^2}\right)\text{m} = \text{J}$$

- Kinetic Energy

$$E_k = \frac{1}{2}mv^2 \qquad [E_k] = \text{kg}\left(\frac{\text{m}}{\text{s}}\right)^2 = \text{J}$$

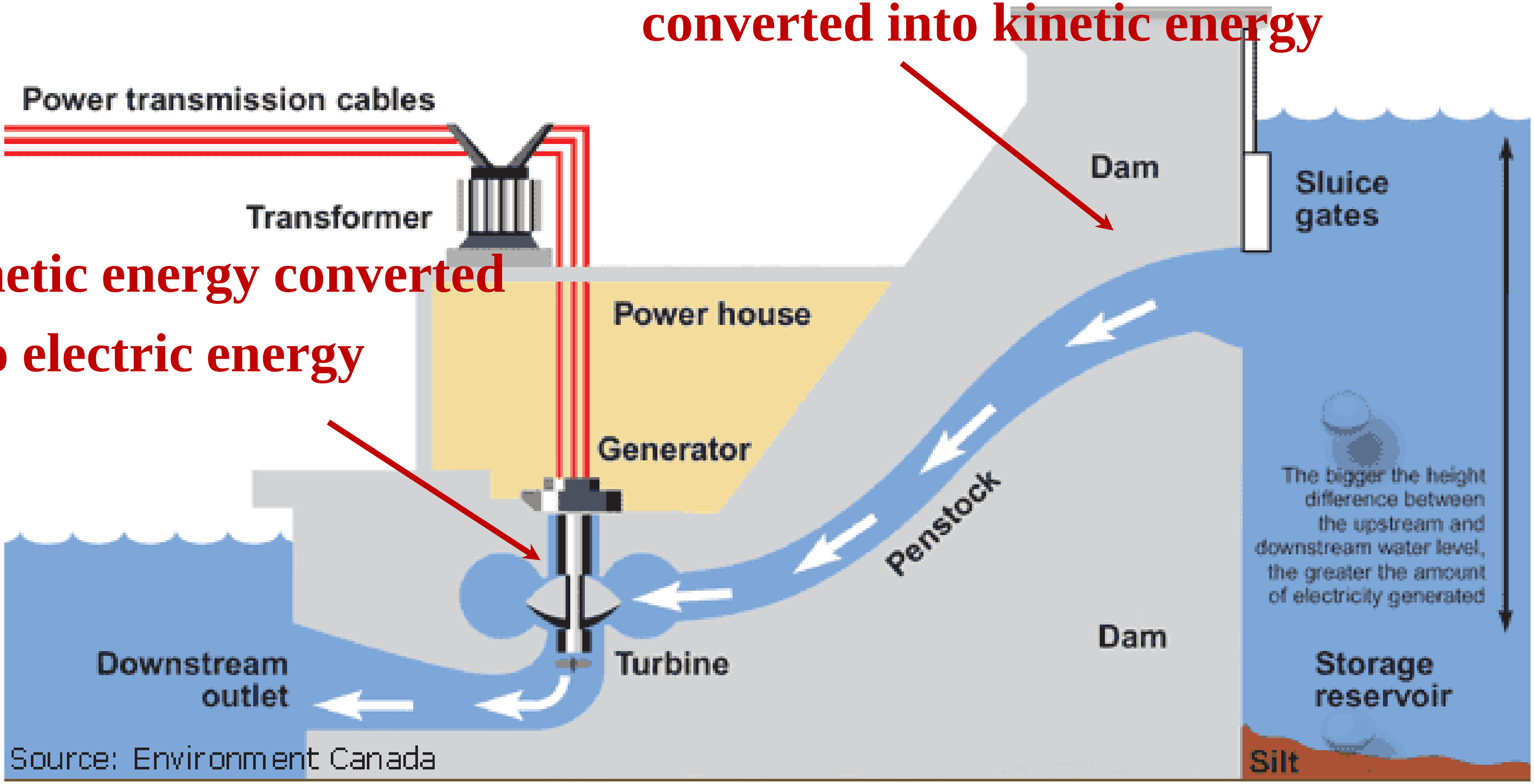
1 cal = 4.184 J (exactly)

Energy and Temperature

- Thermal Energy
  - Kinetic energy associated with random molecular motion.
  - In general proportional to temperature.
  - An intensive property.
- Heat and Work
  - q and w.
  - Energy changes.

5-2 The First Law of Thermodynamics

Energy can be converted from one form to another, but it is neither created nor destroyed.



Gravitational potential energy converted into kinetic energy

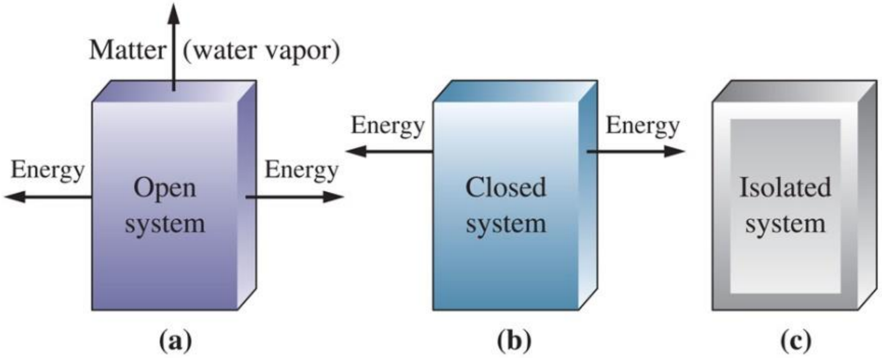
Kinetic energy converted into electric energy

Source: Environment Canada

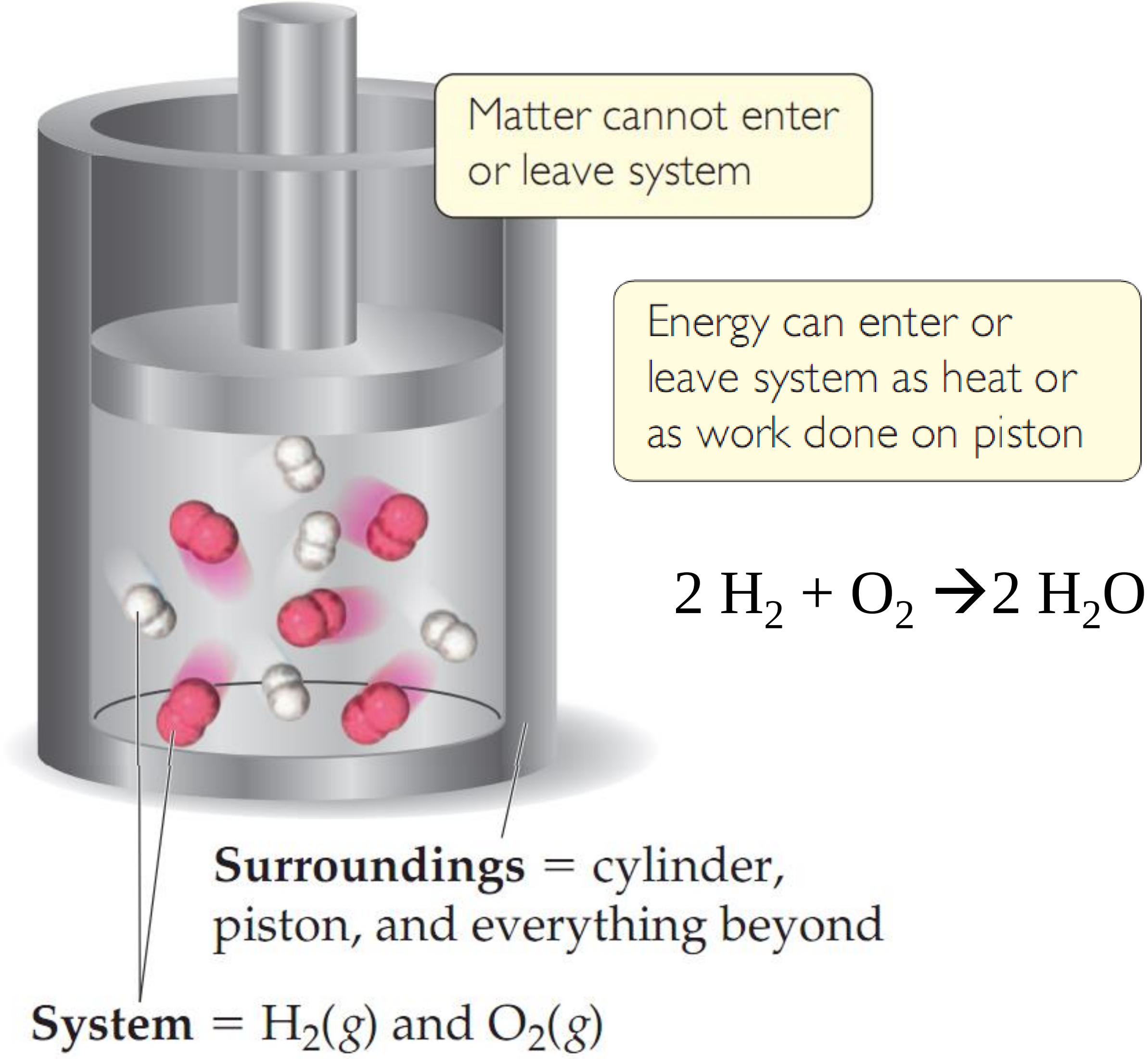
Lake Berryessa is 4' OVER
the Glory Hole Spillway for the
First Time in 20 Years!
2-27-19 Lake Berryessa News Drone Report
Napa County, California

System and Surroundings

- System
- Surroundings



If the H_2 and O_2 molecules in the cylinder react to form H_2O, will the number of molecules in the cylinder change? Will the mass in the cylinder change?



$$2\ H_2 + O_2 \rightarrow 2\ H_2O + \text{energy}$$

EXAMPLE

What is the kinetic energy, in J, of

(a) an Ar atom moving at a speed of 650 m/s,

(b) a mole of Ar atoms moving at 650 m/s?

(Hint: 1 amu = 1.66 x 10^{-27} kg.)

$$E_{k1atom} = \frac{1}{2}mv^2 = \frac{1}{2} \times (39.948amu \times 1.66 \times 10^{-27}\frac{kg}{amu}) \times \left(650\frac{m}{s}\right)^2$$

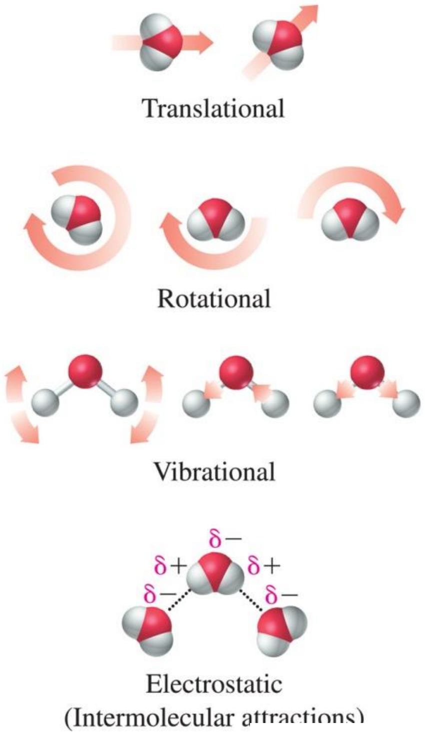
$$= 1.40 \times 10^{-20}\ J$$

$$E_{k1mole} = \frac{1}{2}mv^2 = \frac{1}{2} \times (39.948g \times 10^{-3}\frac{kg}{g}) \times \left(650\frac{m}{s}\right)^2$$

$$= 8.44 \times 10^{3} J$$

Internal Energy

- Internal Energy, E.
  - Total energy (potential and kinetic) in a system.



- Translational kinetic energy.
- Molecular rotation.
- Bond vibration.
- Intermolecular attractions.
- Chemical bonds.
- Electrons.
- The total quantity of matter in the system

Change in Internal Energy

- A system contains *only* internal energy.
  - A system does not contain heat or work.
  - These only occur during a *change* in the system.

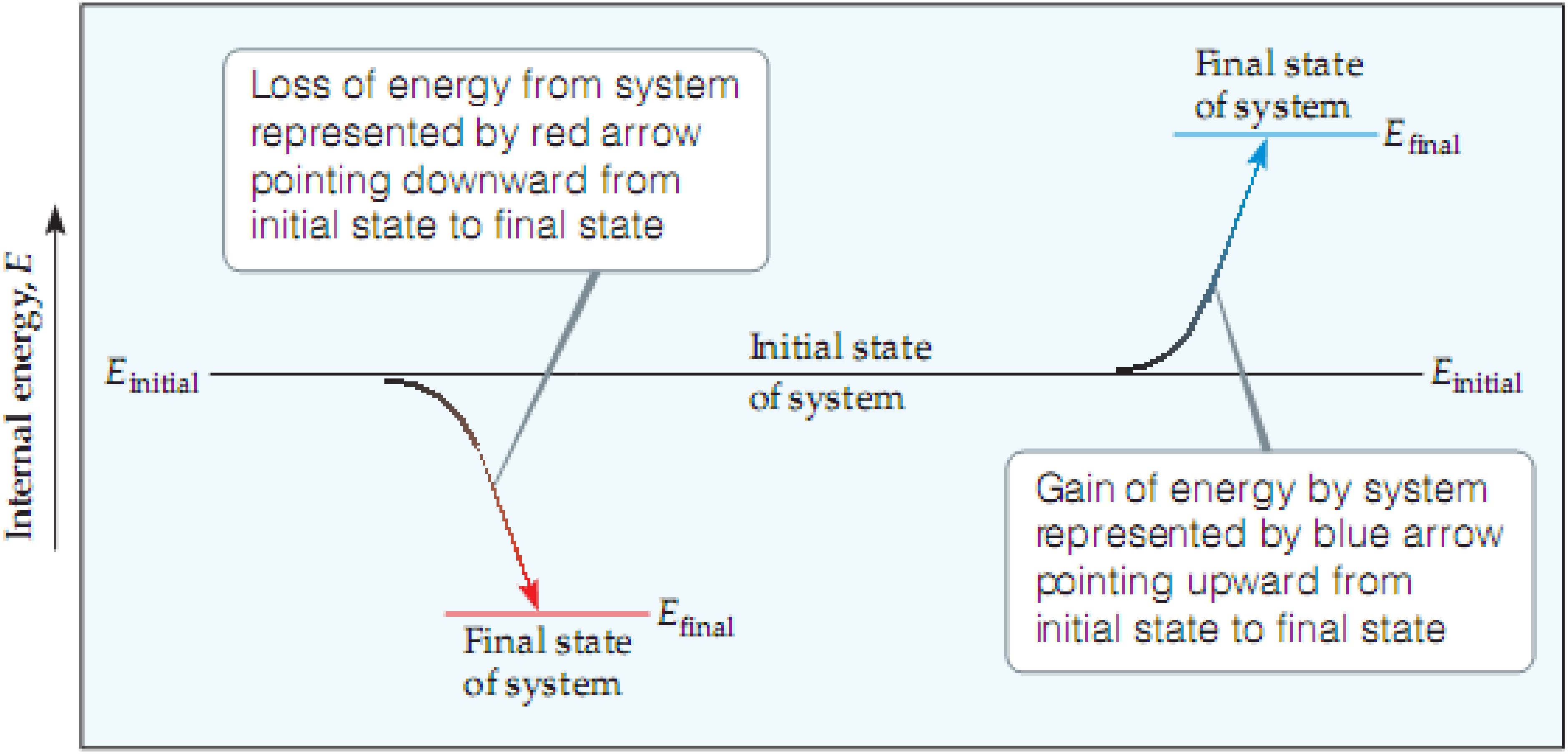
- Law of Conservation of Energy
  - The energy of an isolated system is constant

- Change in internal energy, ΔE
  - $\Delta E = E_{\text{final}} - E_{\text{initial}}$

    a number

    a unit

    a sign



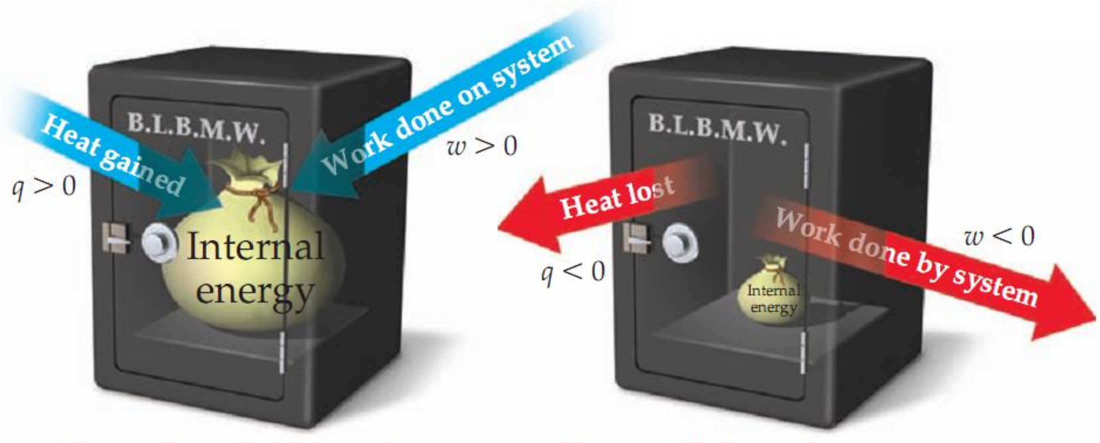
Energy lost to surroundings, internal energy of system decreases, ΔE negative

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

Relating ΔE to Heat and Work

- A system may exchange energy with its surroundings in two general ways: as heat, **q**, or as work, **w**.

System is interior of vault



Energy deposited into system $\Delta E > 0$

Energy withdrawn from system $\Delta E < 0$

$$\Delta E = q + w$$

EXAMPLE

Gases A(g) and B(g) are confined in a cylinder-and-piston arrangement and react to form a solid product C(s). As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

Lose 1150 J as heat: q = -1150 J

480 J as work done on the system by the surroundings : w = + 480

$\Delta E = q + w = (-1150\text{ J}) + (+ 480\text{ J}) = -670\text{ J}$

➔ Energy has been transferred from the system to the surroundings

PRACTICE

1. Calculate the change in the internal energy for a process in which a system absorbs 140 J of heat from the surroundings and does 85 J of work on the surroundings.

Absorb 140 J as heat: $q = +140$ J

85 J as work done on the surroundings by the system: $w = -85$ J

$\Delta E = q + w = (+140\text{ J}) + (-85\text{J}) = 55\text{ J}$

➔ Energy has been transferred from the surroundings to the system

PRACTICE

2. A mixture of gases A_2 and B_2 are introduced to a slender metal cylinder that has one end closed and the other fitted with a piston that makes a gas-tight seal so that the gases are a closed system. The cylinder is submerged in a large beaker of water whose temperature is 25 °C, and a spark is used to trigger a reaction in the cylinder. At the completion of the reaction, the piston has moved downward, and the temperature of the water bath has increased to 28 °C. If we define the system as the gases inside the cylinder, which of the following best describes the signs of q, w, and ΔE for this reaction?

(a) $q < 0$, $w < 0$, $\Delta E < 0$

(b) $q < 0$, $w > 0$, $\Delta E < 0$

[✓ (c)] $q < 0$, $w > 0$, the sign of ΔE cannot be determined from the information given

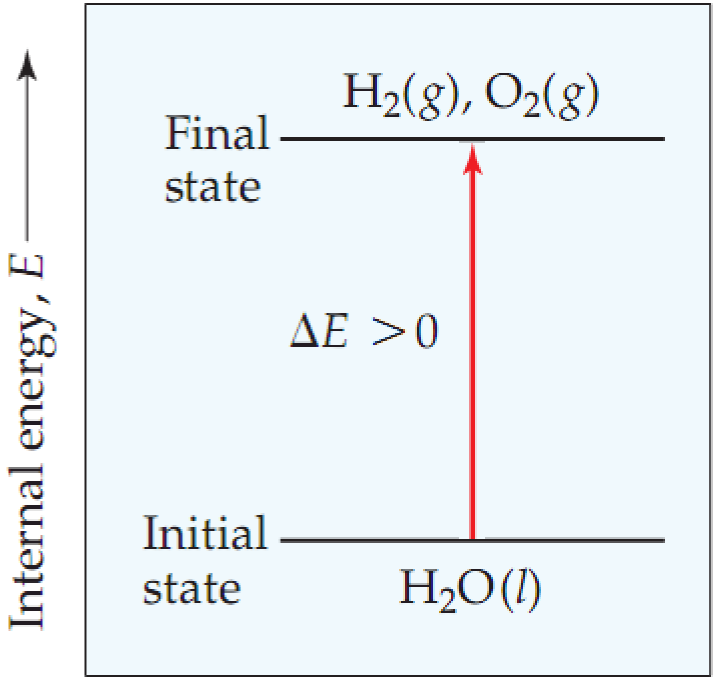
(d) $q > 0$, $w > 0$, $\Delta E > 0$

(e) $q > 0$, $w < 0$, the sign of ΔE cannot be determined from the information given

Endothermic and Exothermic Processes

endo- means "*into*" exo- means "*out of*"

- Exothermic processes.
  - Produces heat, q < 0.
- Endothermic processes.
  - Consumes heat, q > 0.



Is this reaction exothermic or endothermic?

$E_{initial}$ lower than E_{final} therefore, energy is consumed by the system during reaction.

This is a endothermic reaction

State Functions

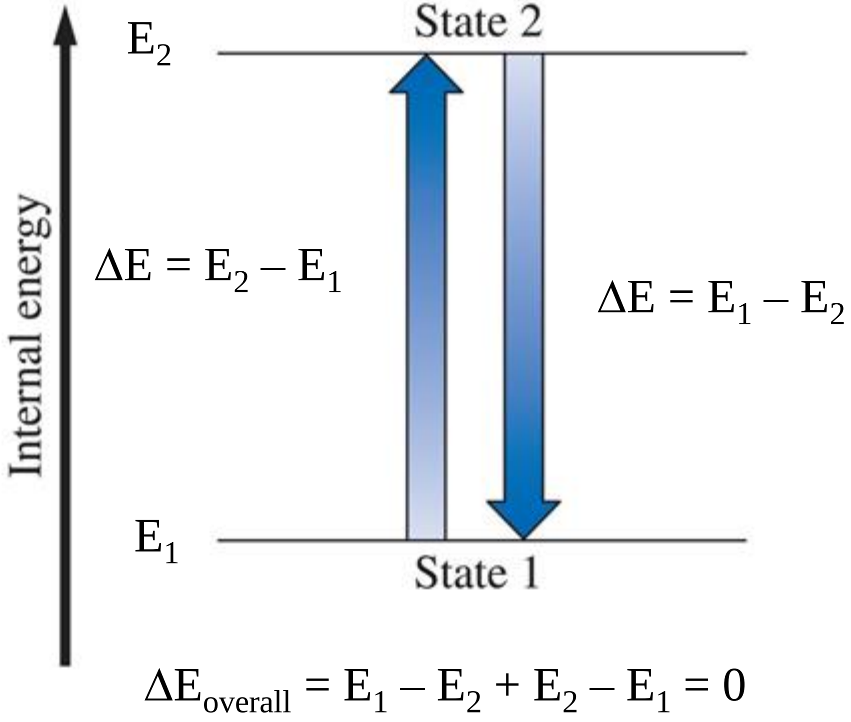
- Any property that has a unique value for a specified state of a system is said to be a State Function.
  - Water at 293.15 K and 1.00 atm is in a specified state.
  - d = 0.99820 g/mL
  - This density is a unique function of the state.
  - It does not matter *how* the state was established.

State Functions

- E is an example of state function
  - Not easily measured.
  - An extensive property (proportional to the total quantity of matter in the system)
  - 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

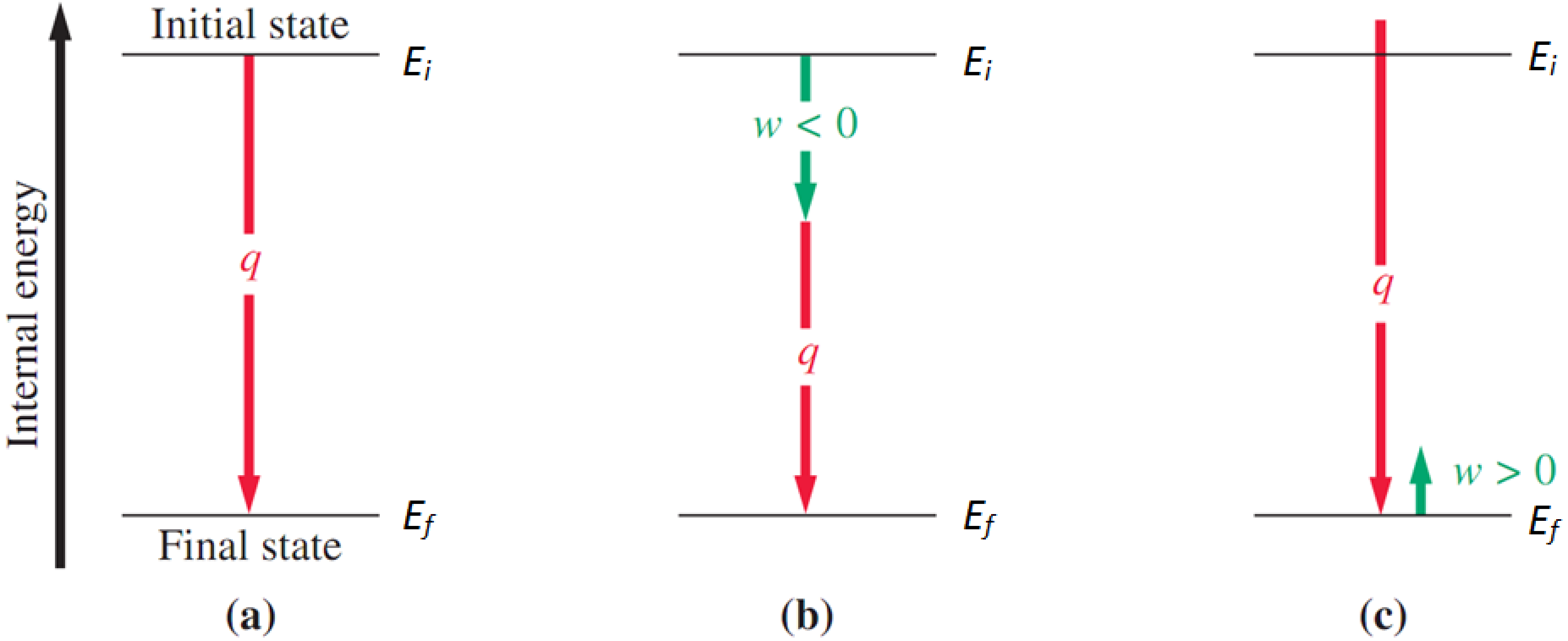
State Functions

- ΔE has a unique value between two states.
  - Is easily measured.
  - ΔE depends only on the initial and final states of the system, not on how the change occurs.



Path Dependent Functions

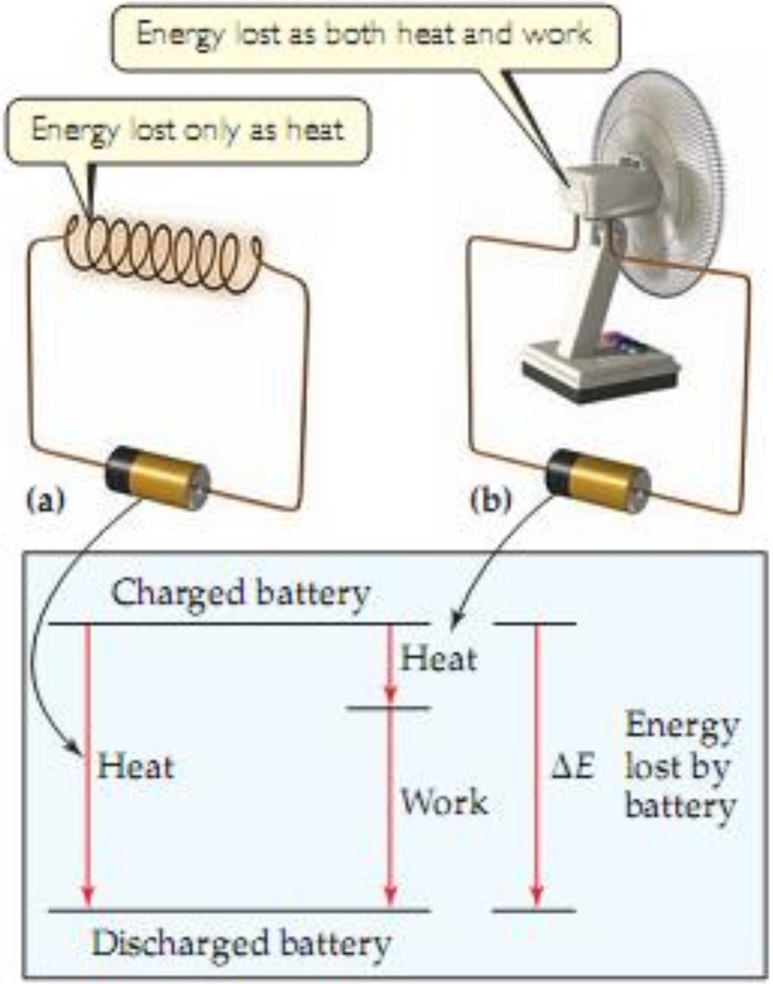
- Heat (q) and work (w) are not functions of state
  - Their values depend on the path of change



no work is done
$\Delta E = q$

work is done by the system
$(w < 0)$

the surroundings do work
on the system $(w > 0)$


Energy lost as both heat and work
Energy lost only as heat
(a)
(b)
Charged battery
Heat
Heat
Work
ΔE
Energy lost by battery
Discharged battery

5-3 Enthalpy

enthalpy (Greek: *enthalpein*, “to warm”)

Enthalpy, H, is the internal energy plus the product of the pressure, P, and volume, V, of the system:

$$H = E + PV$$

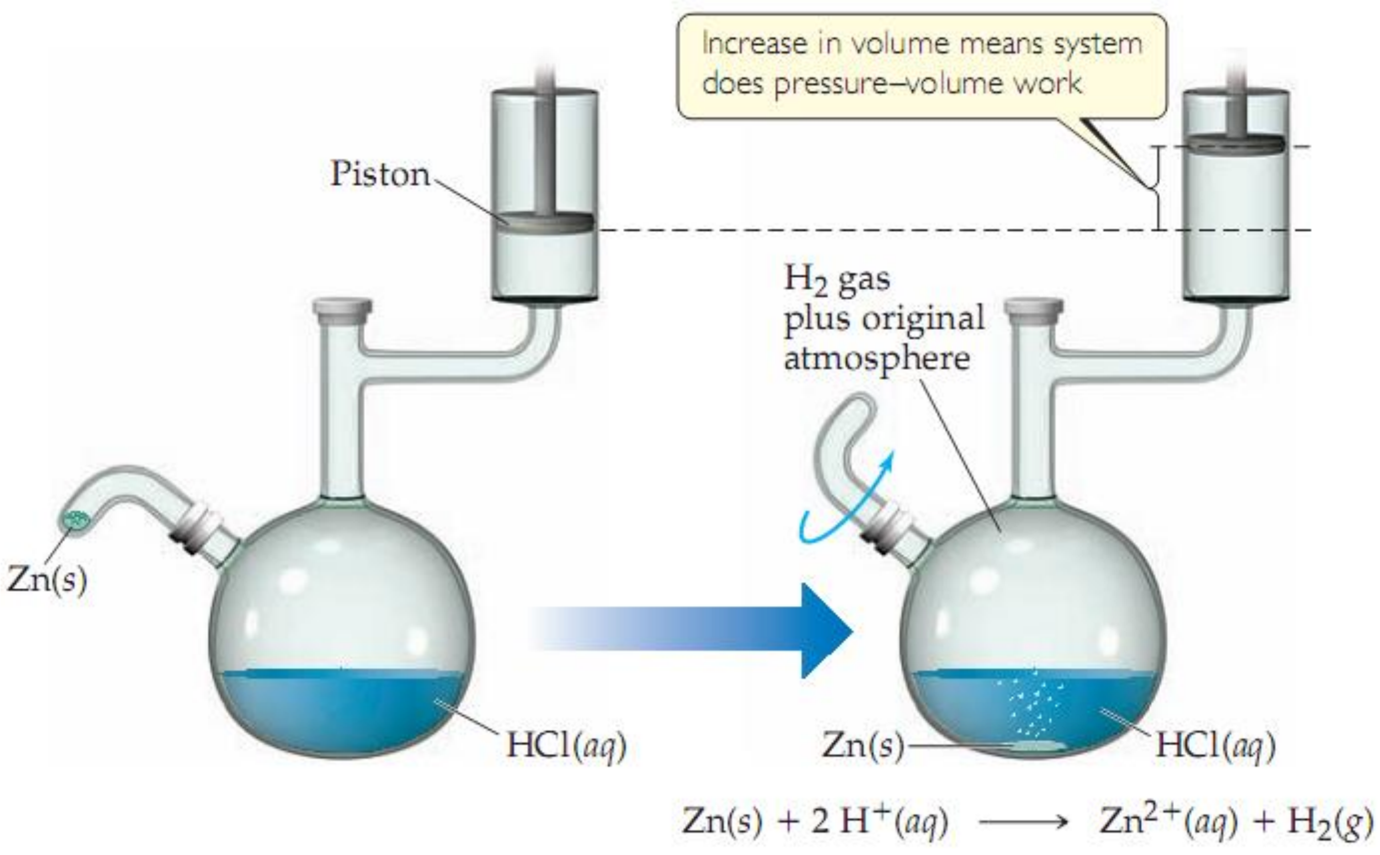
E is a state function

P and V are state functions, they depend only on the current state of the system and not on the path taken to that state.

➔ **H is a state function**

Pressure–Volume Work

- Most commonly, the work produced by chemical or physical changes open to the atmosphere is the mechanical work associated with a change in volume



$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

pressure-volume work

(P–V work)

$w = -P\,\Delta V$

$\Delta V = V_{final} - V_{initial}$

EXAMPLE

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? (1 L.atm = 101.3 J)

$w = -P\,\Delta V$

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

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

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

PRACTICE

1. If a balloon is expanded from 0.055 to 1.403 L against an external pressure of 1.02 atm, how many L.atm of work is done?

(a) -0.056 L.atm,

[✓ (b)] -1.37 L.atm,

(c) 1.43 L.atm,

(d) 1.49 L.atm,

(e) 139 L.atm.

Expansion: work by the system.

$w = -P\,\Delta V = -(1.02\ \text{atm})\times(1.403\ \text{L} - 0.055\ \text{L}) = -1.37\ \text{L.atm}$

PRACTICE

2. Calculate the work, in J, if the volume of a system contracts from 1.55 to 0.85 L at a constant pressure of 0.985 atm.

Contraction: work done on the system by the surroundings.

$$\mathbf{w = -P\,\Delta V = -0.985atm \times (0.85\ L - 1.55\ L)\left(\frac{101.3\ J}{1\ L.atm}\right)}$$

$$\mathbf{= 69.8\ J}$$

Enthalpy Change

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

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

$$\Delta E = q + w$$

$$w = -P\,\Delta V \text{ (at constant pressure)}$$

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

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

- The difference in ΔH and ΔE is often small because P ΔV is small

Under a constant pressure ΔH is the amount of heat that flows into or out of the system

(a) An endothermic reaction **(b)** An exothermic reaction

Because H is a state function, ΔH (which equals qP) depends only on the initial and final states of the system, not on how the change occurs

EXAMPLE

Indicate the sign of the enthalpy change, ΔH, in the following processes carried out under atmospheric pressure and indicate whether each process is endothermic or exothermic:

(a) An ice cube melts;

(b) 1 g of butane (C_4H_{10}) is combusted in sufficient oxygen to give complete combustion to CO_2 and H_2O.

(a) the water that makes up the ice cube is the system. The ice cube absorbs heat from the surroundings as it melts, so ΔH is positive and the process is **endothermic**

(b) the system is the 1 g of butane and the oxygen required to combust it. The combustion of butane in oxygen gives off heat, so ΔH is negative and the process is **exothermic**

PRACTICE

1. A chemical reaction that gives off heat to its surroundings is said to be _____________ and has a _____________ value of ΔH.

(a) endothermic, positive

(b) endothermic, negative

(c) exothermic, positive

[✓ (d)] exothermic, negative

2. Molten gold poured into a mold solidifies at atmospheric pressure. With the gold defined as the system, is the solidification an [✓ exothermic] or endothermic process?

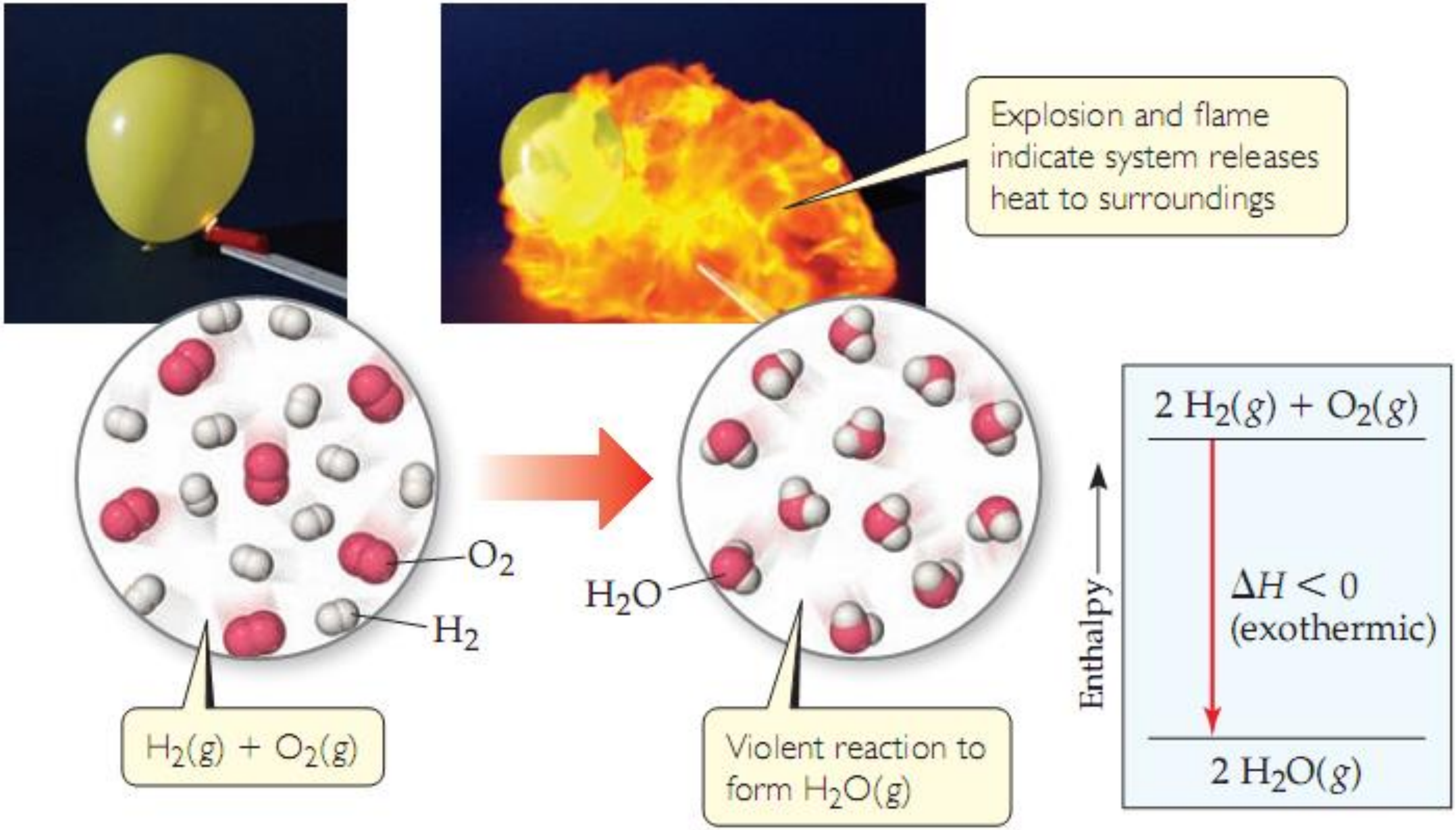
5-4 Enthalpies of Reaction

- $\Delta H = H_{final} - H_{initial}$
- $\Delta H_{reaction} = H_{products} - H_{reactants}$

For example, when 2 mol $H_2(g)$ burn to form 2 mol $H_2O(g)$ at a constant pressure, the system releases 483.6 kJ of heat.

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g) \quad \Delta H = -483.6\ kJ$$

The **negative sign** for ΔH tells us that this reaction is **exothermic**



Explosion and flame indicate system releases heat to surroundings

$H_2(g) + O_2(g)$

Violent reaction to form $H_2O(g)$

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

Thermochemical Equations and Enthalpy Diagrams

1. **Enthalpy is an extensive property**.

Example: 1 mol of CH_4 *is burned in a constant-pressure system:*

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \quad \Delta H = -890\ kJ$$

$$2\ CH_4(g) + 4\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(l) \quad \Delta H = -1780\ kJ$$

2. **The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction**.

$$CO_2(g) + 2\ H_2O(l) \rightarrow CH_4(g) + 2\ O_2(g)\ \Delta H = +890\ kJ$$

3. **The enthalpy change for a reaction depends on the states of the reactants and products**.

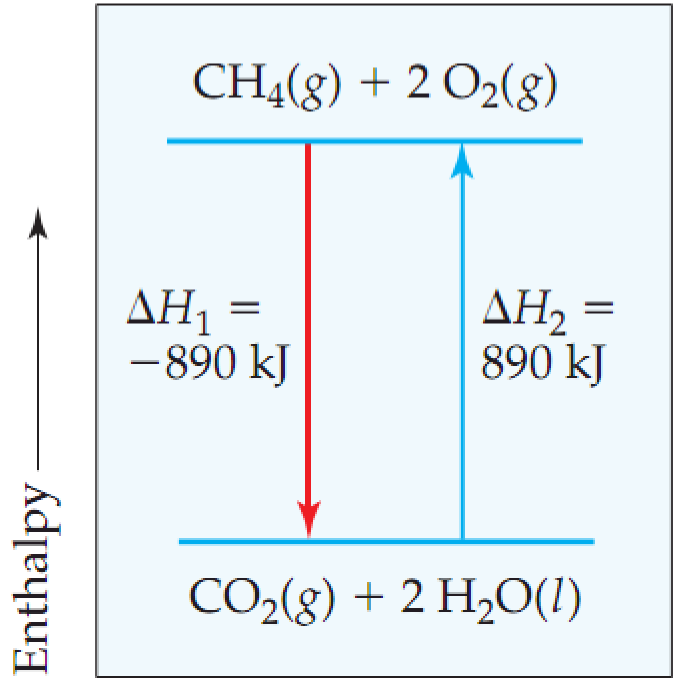
$$H_2O(l) \rightarrow H_2O(g)\ \Delta H = +44\ kJ$$

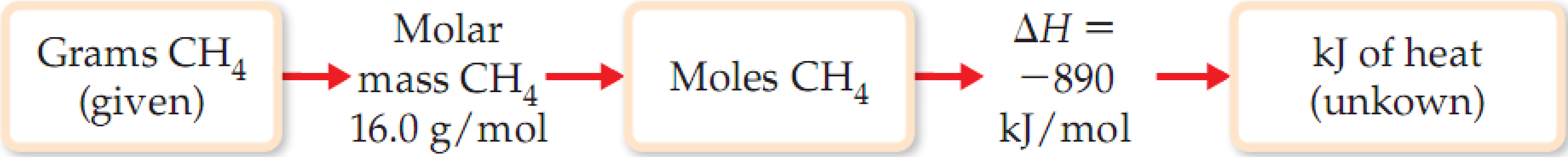
$$2\ H_2O(l) \rightarrow 2\ H_2O(g)\ \Delta H = +88\ kJ$$

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O\mathbf{(g)} \quad \Delta H = \mathbf{-802\ kJ}$$

EXAMPLE

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





Grams CH_4 (given) → Molar mass CH_4 16.0 g/mol → Moles CH_4 → $\Delta H =$ −890 kJ/mol → kJ of heat (unkown)

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

PRACTICE

1. The complete combustion of ethanol, C_2H_5OH (FW = 46.0 g/mol), proceeds as follows:

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3\,H_2O(l) \qquad \Delta H = -555\text{ kJ}$

What is the enthalpy change for combustion of 15.0 g of ethanol?

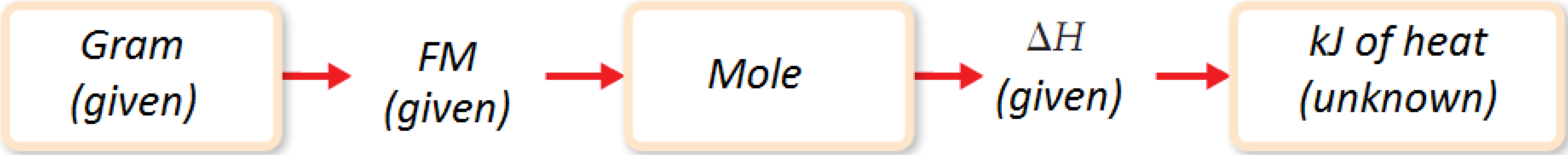
(a) -12.1 kJ

[✓ (b)] -181 kJ

(c) -422 kJ

(d) -555 kJ

(e) -1700 kJ



Gram (given) → FM (given) → Mole → ΔH (given) → kJ of heat (unknown)

$$\text{Heat} = (15.0\text{ g } C_2H_5OH)\left(\frac{1mol\ C_2H_5OH}{46.0\ g\ C_2H_5OH}\right)\left(\frac{-555kJ}{mol\ C_2H_5OH}\right) = -181\text{ kJ}$$

PRACTICE

2. Hydrogen peroxide can decompose to water and oxygen by the reaction

$$2\ H_2O_2(l) \rightarrow 2\ H_2O(l) + O_2(g) \quad \Delta H = -196\ kJ$$

Calculate the quantity of heat released when 5.00 g of $H_2O_2(l)$ decomposes at constant pressure.

FW of H_2O_2 = 2 x 1.008 + 2 x 15.999 = 34.014

Heat = $(5.00\ g\ H_2O_2)\left(\frac{1 mol\ H_2O_2}{34.014\ g\ H_2O_2}\right)\left(\frac{-196 kJ}{2 mol\ H_2O_2}\right)$= **-14.4 kJ**

To be continued..

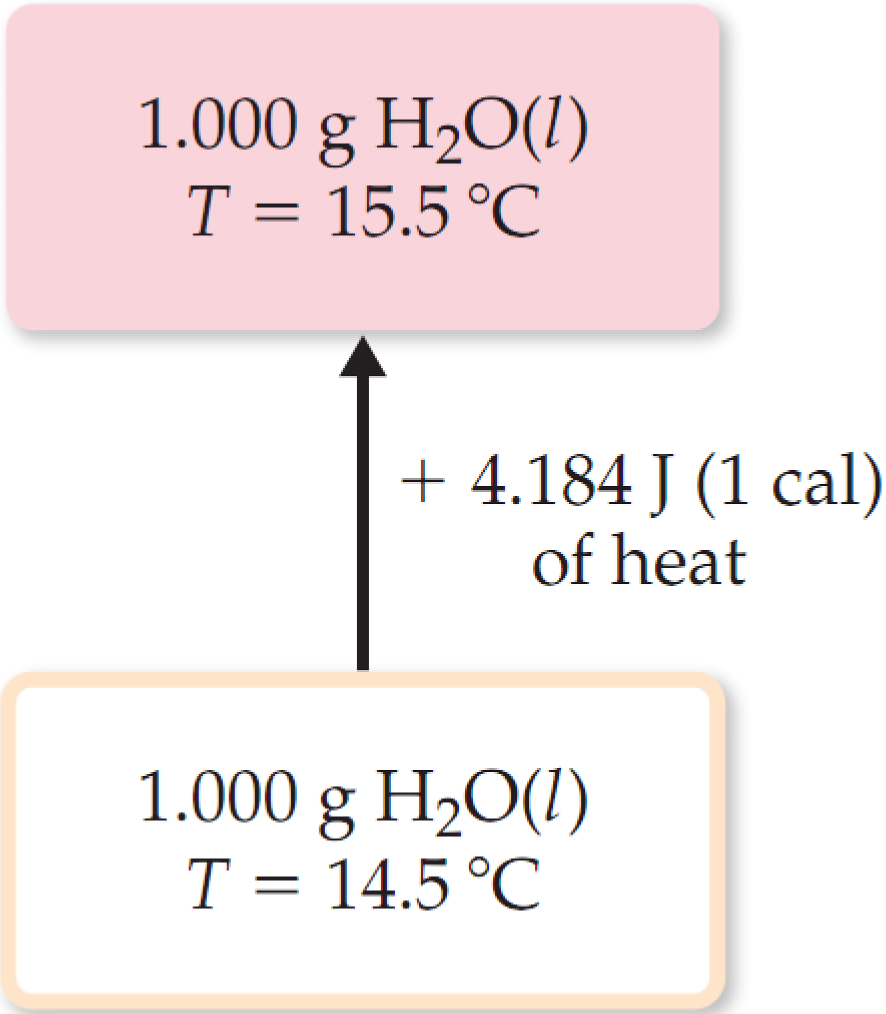
Last week

- 5-1 The Nature of Chemical Energy
- 5-2 The First Law of Thermodynamics
- 5-3 Enthalpy
- 5-4 Enthalpy of Reaction

This week

- 5-5 Calorimetry
- 5-6 Hess’s Law
- 5-7 Enthalpies of Formation
- 5-8 Bond Enthalpy
- 5-9 Foods anf Fuels

5-5 Calorimetry



1.000 g $H_2O(l)$
$T = 15.5\ ^\circ C$

$+ 4.184$ J (1 cal)
of heat

1.000 g $H_2O(l)$
$T = 14.5\ ^\circ C$

Heat Capacity and Specific Heat

Every object has its own **heat capacity**, C, the quantity of heat required to change its temperature by 1 K

$$C = \frac{q}{\Delta T} \qquad \text{[in units of } \frac{J}{K}\text{]}$$

- The heat capacity of one mole of a substance is called its **molar heat capacity**, C_m
- The heat capacity of one gram of a substance is called its **specific heat capacity**, or merely its specific heat, C_s

$$\text{specific heat} = \frac{\text{(quantity of heat transferred)}}{\text{(grams of substance)} \times \text{(temperature change)}}$$

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

EXAMPLE

209 J is required to increase the temperature of 50.0 g of water by 1.00 C. What is the specific heat of water?

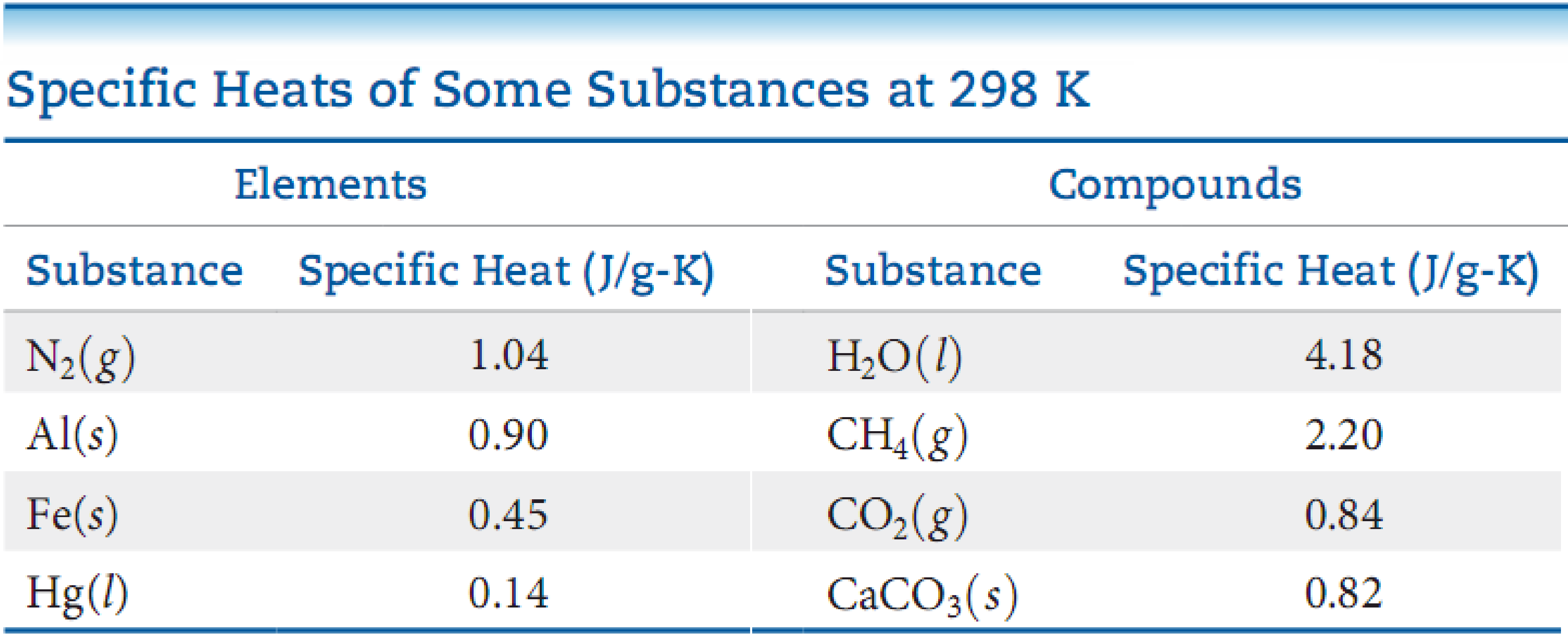
ΔT in Kelvin = ΔT in Celsius

$$C_s = \frac{q}{m \times \Delta T} = \frac{209J}{(50.0g) \times (1.00K)} = 4.18 \text{ J/g.K}$$

Note:

- ♦ 1 cal = 4.184 J exactly

The specific heat values for a given substance can vary slightly with temperature, the temperature is often precisely specified.



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

EXAMPLE

(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?

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

$$\Delta T = 98C - 22C = 76C = 76K$$

$$q = C_s \times m \times \Delta T = (\frac{4.18J}{g.K}) \times (250g) \times (76K) = 7.9 \times 10^4 J$$

1mol H_2O =18.0g H_2O

$$C_m = \left(\frac{4.14J}{gK}\right)\left(\frac{18.0g}{mol}\right) = 75.2\text{J/mol.K}$$

PRACTICE

1. Suppose you have equal masses of two substances, A and B. When the same amount of heat is added to samples of each, the temperature of A increases by 14 °C whereas that of B increases by 22 °C. Which of the following statements is true?

(a) The heat capacity of B is greater than that of A.

[✓ (b)] The specific heat of A is greater than that of B.

(c) The molar heat capacity of B is greater than that of A.

(d) The volume of A is greater than that of B.

(e) The molar mass of A is greater than that of B.

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

The larger the ΔT, the smaller the C_s

$$\Delta T_B > \Delta T_A \Rightarrow C_{s\_B} < C_{s\_A}$$

PRACTICE

2. (a) Large beds of rocks are used in some solar-heated homes to store heat. Assume that the specific heat of the rocks is 0.82 J/g.K. Calculate the quantity of heat absorbed by 50.0 kg of rocks if their temperature increases by 12.0 °C.

(b) What temperature change would these rocks undergo if they emitted 450 kJ of heat?

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

$$\Delta T = 12.0C = 12.0K$$

$$q = C_s \times m \times \Delta T = (\frac{0.82J}{g.K}) \times (50.0kg \times \frac{1000g}{1kg}) \times (12.0K) = 492 \times 10^3 J$$

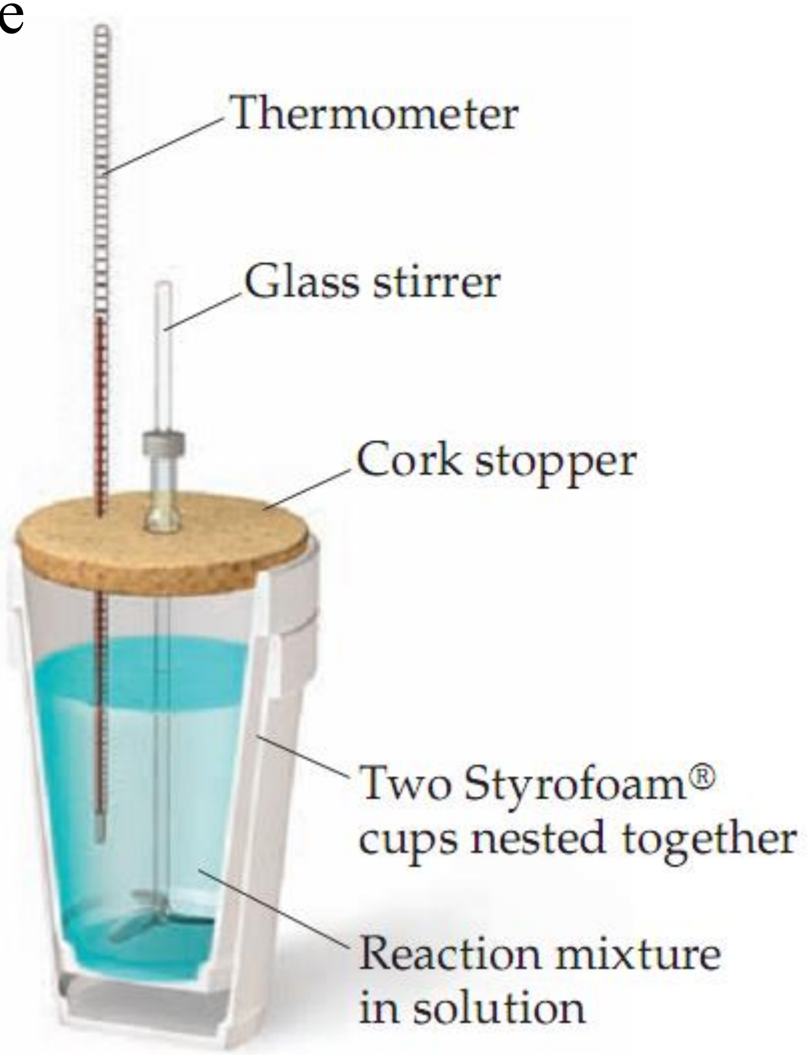
$$\Delta T = \frac{q}{m\times C_s} = \frac{(450\times10^3 J)}{(50.0kg\times\frac{1000g}{1kg})\times(\frac{0.82J}{gK})}$$ =11.0 K = 11.0 ^{o}C

Constant-Pressure Calorimetry

Exothermic reaction, heat is “lost” by the reaction and “gained” by the water in the solution, so the **temperature of the solution rises**.

For an **endothermic reaction**, heat is “gained” by the reaction and “lost” by the water in the solution, so the **temperature of the solution decreases**.

$q_{soln} = -q_{rxn}$.



EXAMPLE

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/g.K.

m = (100mL)x (1.0g/mL) = 100g

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

$$q_{rxn} = -C_s \times m \times \Delta T = -\left(\frac{4.18J}{g.K}\right) \times (100g) \times (6.5K) = -2.7 \times 10^3 J$$

$\Delta H = q_P = q_{rxn} = -2.7 \times 10^3 J = -2.7\ kJ$

(0.050mL)x (1.0mol/L) = 0.050 mol

ΔH = -2.7/0.050 = - 5.4 kJ/mol

PRACTICE

1. When 0.243 g of Mg metal is combined with enough HCl to make 100 mL of solution in a constant-pressure calorimeter, the following reaction occurs:

$$Mg(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

If the temperature of the solution increases from 23.0 to 34.1 °C as a result of this reaction, calculate ΔH in kJ/mol Mg. Assume that the solution has a specific heat of 4.18 J/g.°C and a density of 1.00 g/mL.

(a) -19.1 kJ/mol

(b) -111 kJ/mol

(c) -191 kJ/mol

[✓ (d)] -464 kJ/mol

(e) -961 kJ/mol

$$M = (100mL)(1.0g/mL) = 100g$$

$$\Delta T = 34.1\ {}^{o}C - 23.0\ {}^{o}C = 11.1\ {}^{o}C$$

$$\Delta H = q_P = q_{rxn} = -\left(\frac{4.18J}{g.{}^{o}C}\right) \times (100g) \times (11.1\ {}^{o}C) = -\ 4.64x10^3 J$$

$$\text{Mol of Mg} = \frac{1\ mol\ Mg}{24.3\ g\ Mg} \times 0.243g\ Mg = 0.01\ \text{mol}$$

$$\Delta H = -\ 4.64 \times 10^3 / 0.01 = -464 \times 10^3\ J = -464\ kJ$$

PRACTICE

2. When 50.0 mL of 0.100 M $AgNO_3$ and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30 to 23.11 °C. The temperature increase is caused by the following reaction:

$$AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$$

Calculate ΔH for this reaction in kJ/mol $AgNO_3$, assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g.°C

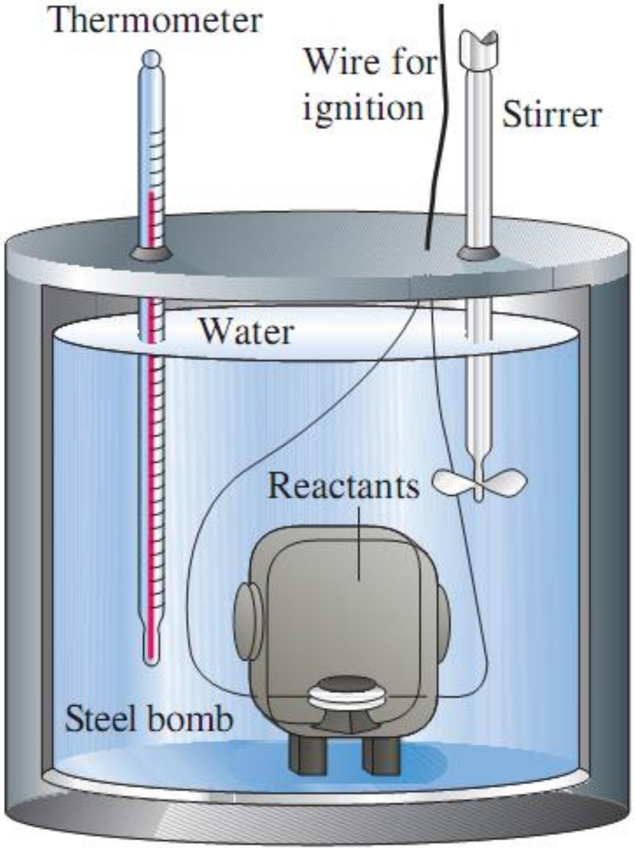
$\Delta T = 23.11\ ^{o}C - 22.30\ ^{o}C = 0.81\ ^{o}C$

$\Delta H = q_P = q_{rxn} = -\left(\frac{4.18 J}{g.\ ^{o}C}\right) \times (100 g\ ) \times (0.81\ ^{o}C) = -\ 339\ J$

$\text{Mol } AgNO_3 = (50.0 mL)\left(\frac{1L}{1000 mL}\right)(0.100 \text{mol/L}) = 0.005 \text{ mol}$

$\Delta H = \frac{-339\ J}{0.005\ mol} = -67.8 \times 10^3 J = -67.8\ kJ$

Bomb Calorimetry (Constant-Volume Calorimetry)



$q_{rxn} = - q_{cal}$

q_{rxn} : heat evolved in a combustion reaction

q_{cal} : heat absorbed by the calorimeter

where $q_{cal} = q_{bomb} + q_{water} + \dots$

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

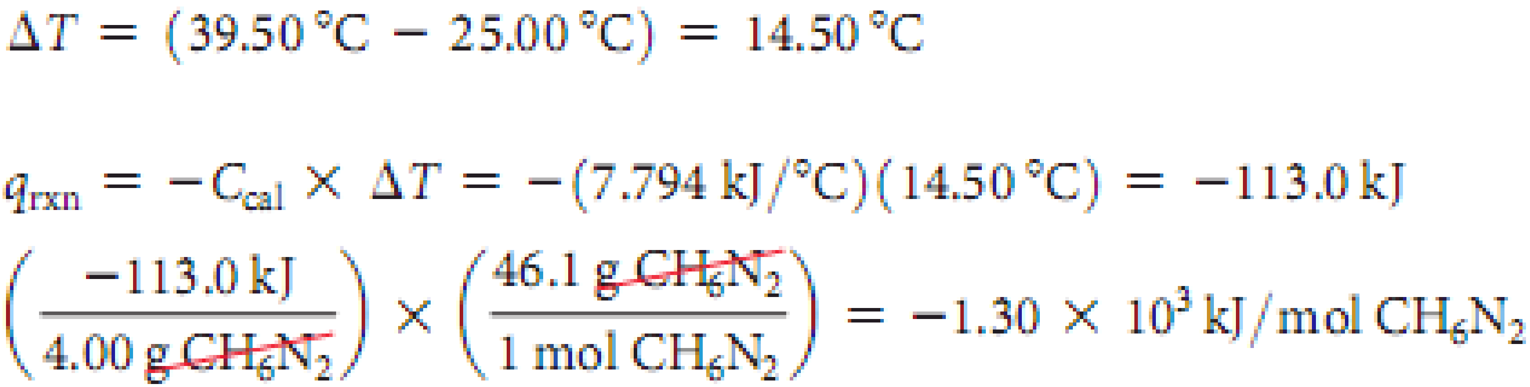
$q_{rxn} = - C_{cal} \times \Delta T$

EXAMPLE

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

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

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.



$$\Delta T = (39.50\,°\mathrm{C} - 25.00\,°\mathrm{C}) = 14.50\,°\mathrm{C}$$

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

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

PRACTICE

1. The combustion of exactly 1.000 g of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat. If the combustion of 0.550 g of benzoic acid causes the temperature of the calorimeter to increase from 22.01 to 24.27 °C, calculate the heat capacity of the calorimeter.

(a) 0.660 kJ/°C

[✓ (b)] 6.42 kJ/°C

(c) 14.5 kJ/°C

(d) 21.2 kJ/g.°C

(e) 32.7 kJ/°C

$$q_{rxn} = (0.550g)\frac{(-26.38kJ)}{1.000g} = -\ 14.51\ \text{kJ}$$

$$\Delta \text{T} = 24.27\ {}^{o}C - 22.01\ {}^{o}C = 2.26\ {}^{o}\text{C}$$

$$\text{C}_{\text{cal}} = -\ \frac{q_{rxn}}{\Delta T} = -\frac{(-14.51kJ)}{(2.26\ {}^{o}C)} = 6.42\ \text{kJ}/{}^{o}\text{C}$$

PRACTICE

2. A 0.5865-g sample of lactic acid, $HC_3H_5O_3$, is burned in a calorimeter whose heat capacity is 4.812 kJ/°C. The temperature increases from 23.10 to 24.95 °C. Calculate the heat of combustion of lactic acid

(a) Calculate the heat of combustion of lactic acid per gram

(b) Calculate the heat of combustion of lactic acid per mole.

$\Delta T = 24.95\ ^{o}C - 23.10\ ^{o}C = 1.85\ ^{o}C$

$q_{cal} = C_{cal} \times \Delta T = (4.812\ kJ/^{o}C)(1.85^{o}C) = 8.90\ kJ$

$q_{rxn} = -q_{cal} = -8.90\ kJ$

per gram:

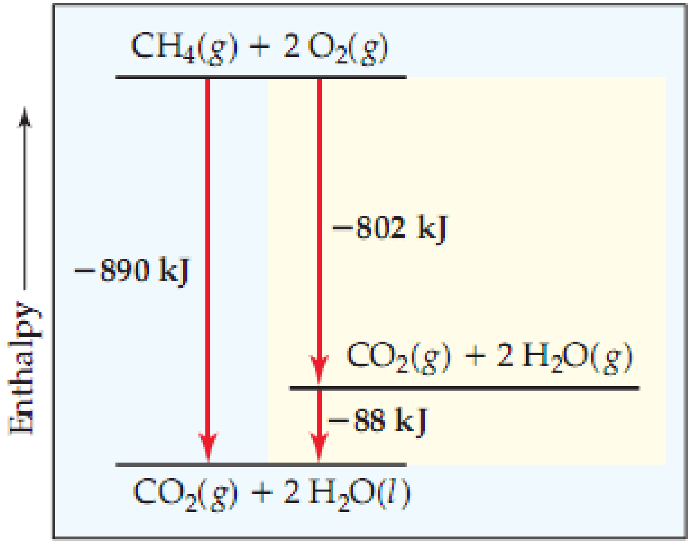
$$q_{rxn} = \frac{-8.90\ kJ}{0.5865 g} = -15.2\ kJ/g$$

per mole:

$$q_{rxn} = \frac{-8.90\ kJ}{0.5865 g} \times \frac{90.08}{1\ mol} = -1367\ kJ/mol$$

5-6 Hess' Law

If a reaction is carried out in a series of steps, ΔH for the overall reaction equals the sum of the enthalpy changes for the individual steps.



$$\begin{array}{lrcll} & CH_4(g) + 2\,O_2(g) & \longrightarrow & CO_2(g) + 2\,H_2O(g) & \Delta H = -802\ \mathrm{kJ} \\ \text{(Add)} & 2\,H_2O(g) & \longrightarrow & 2\,H_2O(l) & \Delta H = -88\ \mathrm{kJ} \\ \hline \multicolumn{2}{l}{CH_4(g) + 2\,O_2(g) + 2\,H_2O(g)} & \longrightarrow & CO_2(g) + 2\,H_2O(l) + 2\,H_2O(g) & \\ & & & & \Delta H = -890\ \mathrm{kJ} \end{array}$$

The net equation is

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

EXAMPLE

The enthalpy of reaction for the combustion of C to CO_2 is -393.5 kJ/mol C, and the enthalpy for the combustion of CO to CO_2 is - 283.0 kJ/mol CO. Using these data, calculate the enthalpy for the combustion of C to CO.

$$\begin{array}{lll}
C(s) + O_2(g) \longrightarrow CO_2(g) & & \Delta H = -393.5\,\text{kJ} \\
CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g) & & -\Delta H = 283.0\,\text{kJ} \\
\hline
C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) & & \Delta H = -110.5\,\text{kJ}
\end{array}$$

PRACTICE

Carbon occurs in two forms, graphite and diamond. The enthalpy of the combustion of graphite is -393.5 kJ/mol, and that of diamond is -395.4 kJ/mol:

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

$\mathrm{C(diamond)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}\quad \Delta H = -395.4\ \mathrm{kJ}$

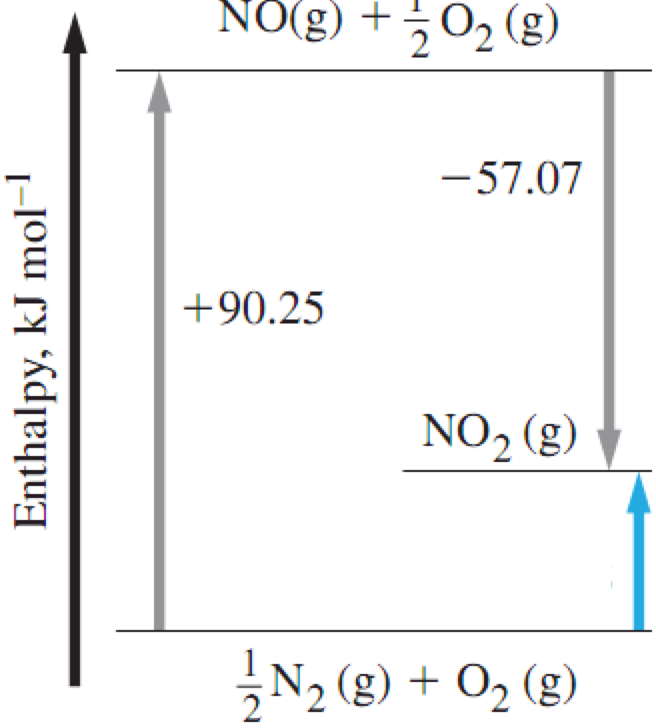
Calculate ΔH for the conversion of graphite to diamond:

$\mathrm{C(graphite)} \rightarrow \mathrm{C(diamond)}\ \Delta H = ?$

$$\begin{array}{l}
\mathrm{C(graphite)} + \cancel{\mathrm{O_2}}\mathrm{(g)} \rightarrow \cancel{\mathrm{CO_2}}\mathrm{(g)}\quad \Delta H = -393.5\ \mathrm{kJ} \\
\cancel{\mathrm{CO_2}}\mathrm{(g)} \rightarrow \mathrm{C(diamond)} + \cancel{\mathrm{O_2}}\mathrm{(g)}\ \Delta H = +\ 395.4\ \mathrm{kJ} \\
\hline
\mathrm{C(graphite)} \rightarrow \mathrm{C(diamond)}\ \Delta H = -393.5\ \mathrm{kJ} + 395.4\ \mathrm{kJ} = 1.9\ \mathrm{kJ}
\end{array}$$

PRACTICE

Calculate ΔH for $N_2 + 2O_2 \rightarrow 2NO_2$ using the following diagram



ΔH = 2 x 33.18 = 66.36 kJ

PRACTICE

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:

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

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

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

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

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

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

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

5-7 Enthalpies of Formation

The enthalpy of formation, ΔH^{o}_{f}, is the enthalpy change for the chemical equation when all the substances are in their standard states.

The standard state of a substance is its pure form at atmospheric pressure (1 atm) and the temperature of 298 K (25 °C)

$$\mathrm{C\ (graphite) + 2\ H_2\ (g) \rightarrow CH_4\ (g)} \qquad \Delta H^{o}_{f} = -74.9\,\mathrm{kJ}$$

When calculating ΔH^{o}_{f} remember:

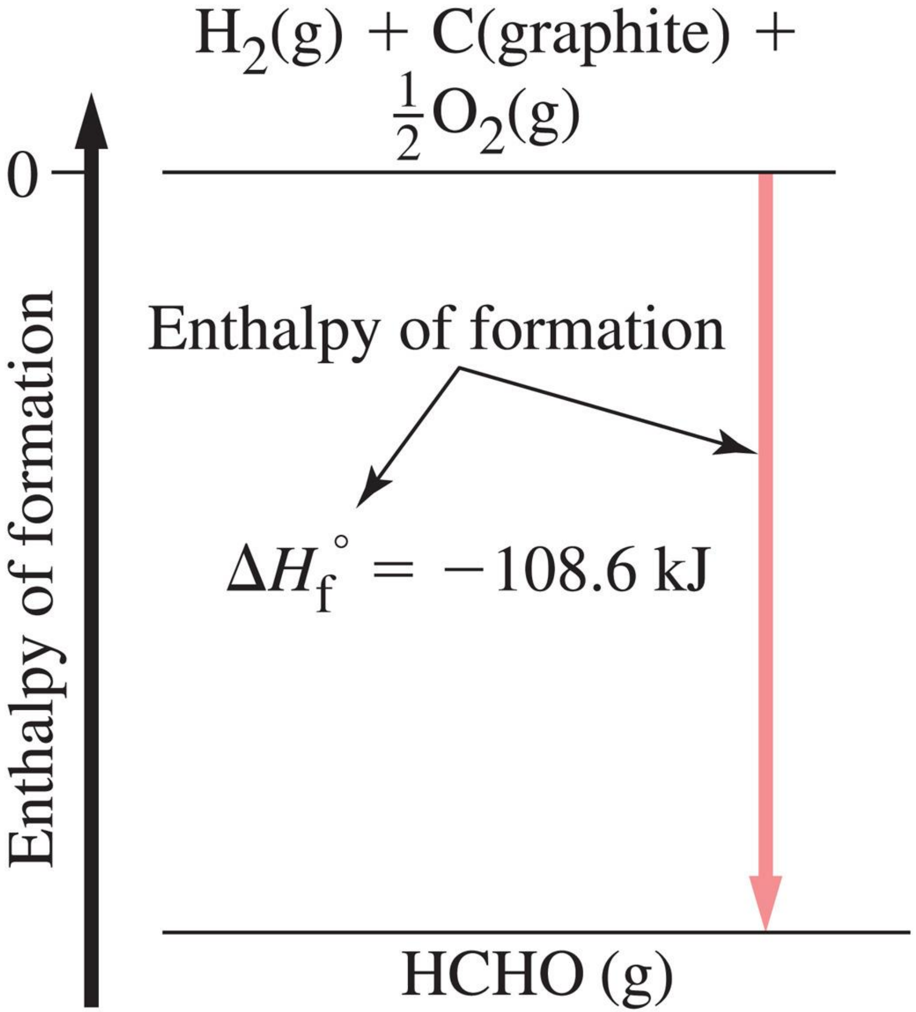
1. An element in its standard state is given an ΔH^{o}_{f} of zero.

   Ex: Na (s) P_4 (s) Cl_2 (g) S_8 (g)

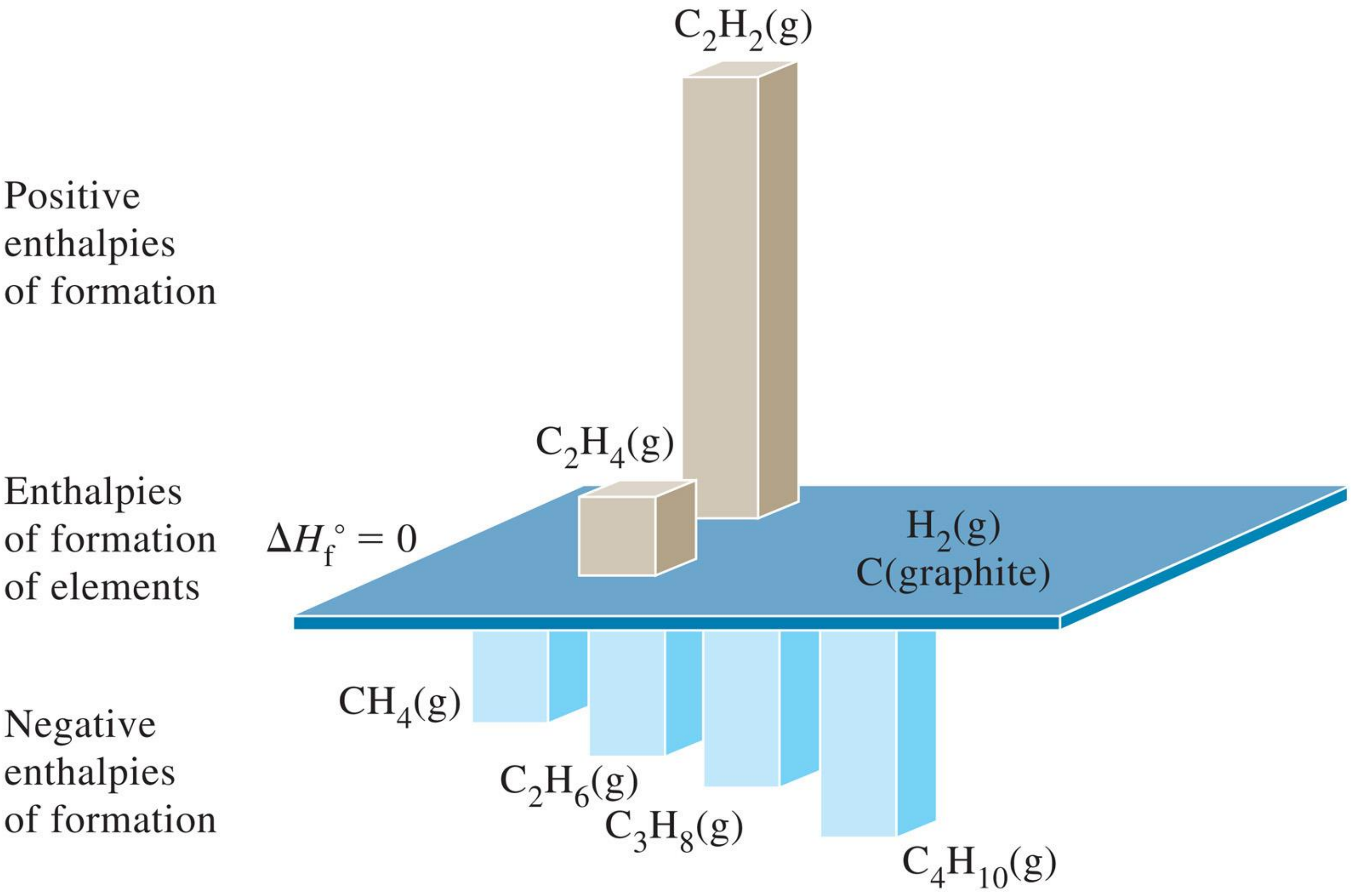
2. Most compounds have a negative ΔH^{o}_{f}
3. To find the ΔH_{rxn} use the following formula:

$$\Delta H^{o}_{rxn} = \Delta H^{o}_{f(products)} - \Delta H^{o}_{f(reactants)}$$

Standard Enthalpy of Formation



Standard Enthalpies of Formation



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

EXAMPLE

For which of these reactions at 25 °C does the enthalpy change represent a standard enthalpy of formation? For each that does not, what changes are needed to make it an equation whose ΔH is an enthalpy of formation?

(a) $2\,\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Na_2O}(s)$

(b) $2\,\mathrm{K}\enclose{circle}{(l)} + \mathrm{Cl_2}(g) \longrightarrow \enclose{circle}{2}\,\mathrm{KCl}(s)$

(c) $\mathrm{C_6H_{12}O_6}(s) \underset{\longleftarrow}{\longrightarrow} 6\,\mathrm{C}(\textit{diamond}) + 6\,\mathrm{H_2}(g) + 3\,\mathrm{O_2}(g)$

(a) 1 mol Na_2O is formed from the elements sodium and oxygen in their proper states, solid Na and O_2 gas, respectively. Therefore, the enthalpy change for reaction (a) corresponds to a standard enthalpy of formation.

$$\mathrm{K}(s) + \tfrac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{KCl}(s)$$

$$6\,\mathrm{C}(\textit{graphite}) + 6\,\mathrm{H_2}(g) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{C_6H_{12}O_6}(s)$$

PRACTICE

If the heat of formation of $H_2O(l)$ is -286 kJ/mol, which of the following thermochemical equations is correct?

(a) $2H(g)+O(g) \rightarrow H_2O(l)$ $\Delta H = -286\ \text{kJ}$

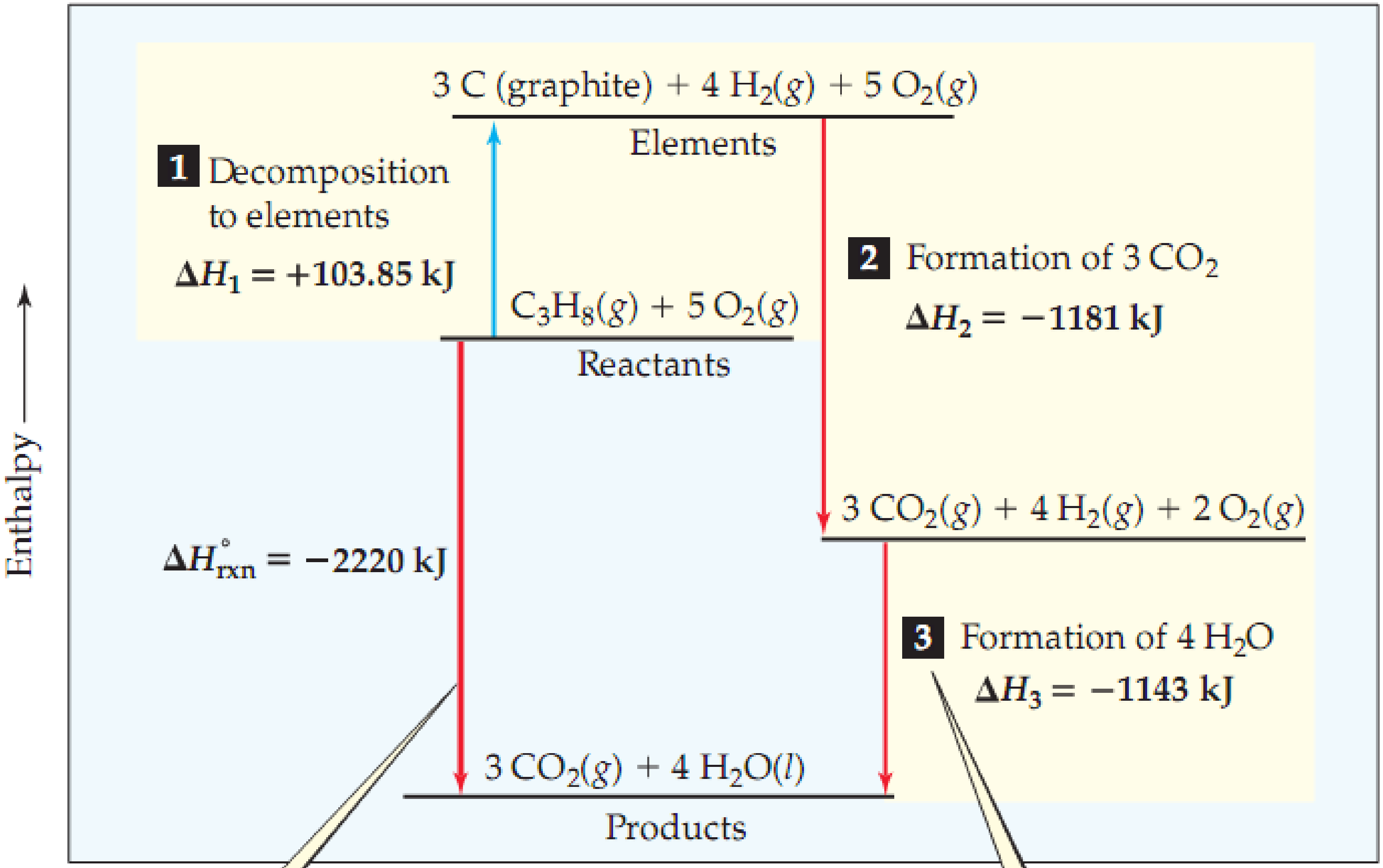
(b) $2H_2(g)+O_2(g) \rightarrow 2\ H_2O(l)$ $\Delta H = -286\ \text{kJ}$

[✓ (c)] $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286\ \text{kJ}$

(d) $H_2(g)+O(g) \rightarrow H_2O(l)$ $\Delta H = -286\ \text{kJ}$

(e) $H_2O(l) \rightarrow H_2(g) + 1/2\ O_2(g)$ $\Delta H = -286\ \text{kJ}$

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



$3\,C\,(\text{graphite}) + 4\,H_2(g) + 5\,O_2(g)$

Elements

1 Decomposition to elements

$\Delta H_1 = +103.85$ kJ

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

Reactants

2 Formation of 3 CO_2

$\Delta H_2 = -1181$ kJ

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

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

3 Formation of 4 H_2O

$\Delta H_3 = -1143$ kJ

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

Products

Enthalpy

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

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

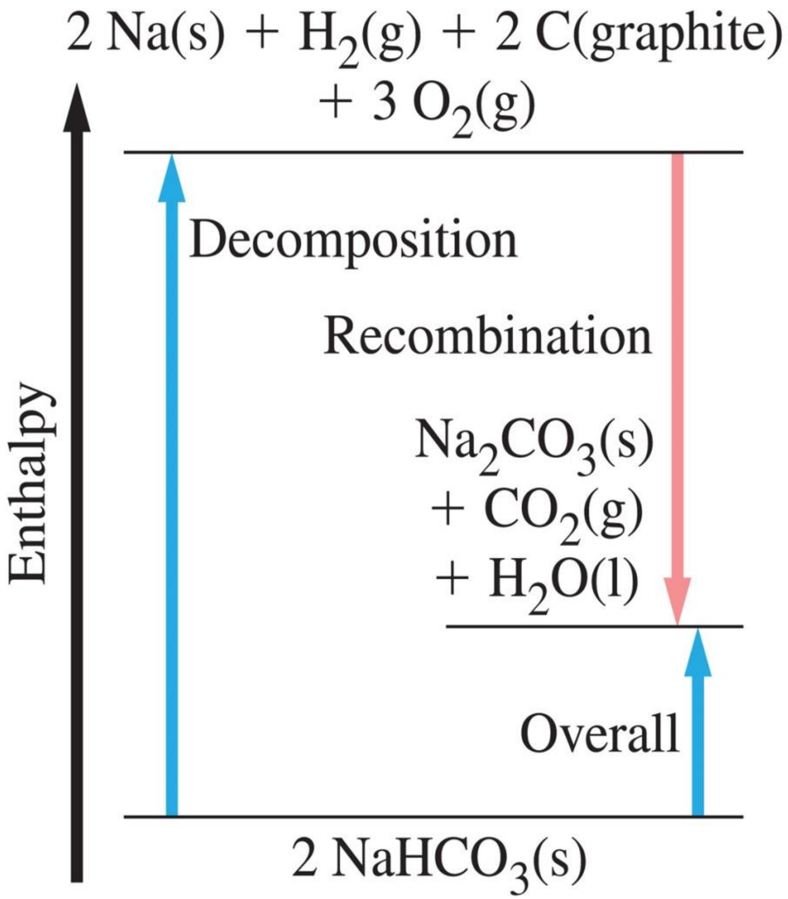
Calculate
Enthalpies of Reaction from Enthalpies of Formation

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

$$\begin{array}{rcll}
C_3H_8(g) & \longrightarrow & 3\,C(s) + 4\,H_2(g) & \Delta H_1 = -\Delta H_f^\circ[C_3H_8(g)] \\
3\,C(s) + 3\,O_2(g) & \longrightarrow & 3\,CO_2(g) & \Delta H_2 = 3\Delta H_f^\circ[CO_2(g)] \\
4\,H_2(g) + 2\,O_2(g) & \longrightarrow & 4\,H_2O(l) & \Delta H_3 = 4\Delta H_f^\circ[H_2O(l)] \\
\hline
C_3H_8(g) + 5\,O_2(g) & \longrightarrow & 3\,CO_2(g) + 4\,H_2O(l) & \Delta H^\circ_{\text{rxn}} = \Delta H_1 + \Delta H_2 + \Delta H_3
\end{array}$$

$$\begin{aligned}
\Delta H^\circ_{\text{rxn}} &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\
&= -\Delta H_f^\circ[C_3H_8(g)] + 3\Delta H_f^\circ[CO_2(g)] + \Delta 4H_f^\circ[H_2O(l)] \\
&= -(-103.85\ \text{kJ}) + 3(-393.5\ \text{kJ}) + 4(-285.8\ \text{kJ}) = -2220\ \text{kJ}
\end{aligned}$$

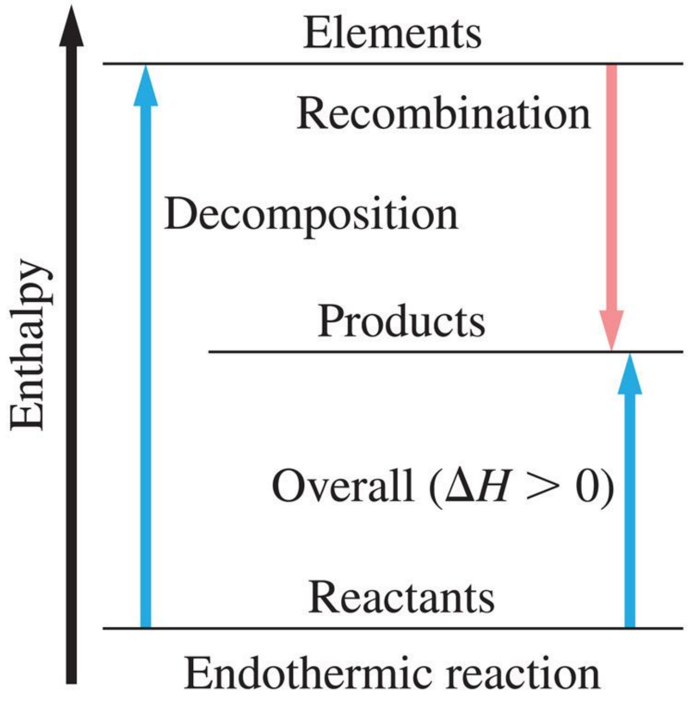
Standard Enthalpies of Reaction

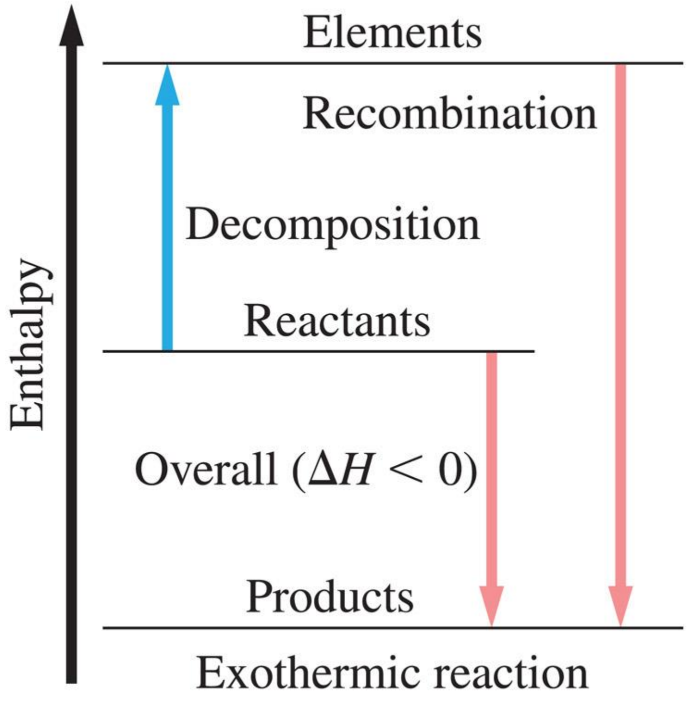


$$\Delta H_{\text{overall}} = -2\Delta H_f^\circ{}_{NaHCO_3} + \Delta H_f^\circ{}_{Na_2CO_3} + \Delta H_f^\circ{}_{CO_2} + \Delta H_f^\circ{}_{H_2O}$$

Enthalpy of Reaction

$$\Delta H_{rxn} = \Sigma n\Delta H_f^{\circ}{}_{products} - \Sigma m\Delta H_f^{\circ}{}_{reactants}$$





EXAMPLE

1. The combustion of benzene, C_6H_6(l) produce CO_2(g) and H_2O(l).

(a) Calculate the standard enthalpy change for the combustion of 1 mol of benzen

(b) Compare the quantity of heat produced by combustion of 1.00 g propane with that produced by 1.00 g benzene.

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

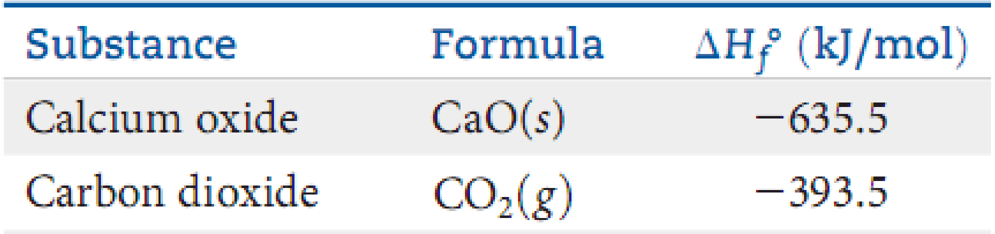
$$\begin{aligned}
\Delta H^\circ_{\text{rxn}} &= [6\Delta H_f^\circ(CO_2) + 3\Delta H_f^\circ(H_2O)] - [\Delta H_f^\circ(C_6H_6) + \tfrac{15}{2}\Delta H_f^\circ(O_2)] \\
&= [6(-393.5\text{ kJ}) + 3(-285.8\text{ kJ})] - [(49.0\text{ kJ}) + \tfrac{15}{2}(0\text{ kJ})] \\
&= (-2361 - 857.4 - 49.0)\text{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

$$C_3H_8(g):\quad (-2220\text{ kJ/mol})(1\text{ mol}/44.1\text{ g}) = -50.3\text{ kJ/g}$$

$$C_6H_6(l):\quad (-3267\text{ kJ/mol})(1\text{ mol}/78.1\text{ g}) = -41.8\text{ kJ/g}$$

EXAMPLE

2. The standard enthalpy change for the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ is 178.1 kJ. Calculate the standard enthalpy of formation of $CaCO_3(c)$



Substance	Formula	ΔH_f° (kJ/mol)
Calcium oxide	$CaO(s)$	−635.5
Carbon dioxide	$CO_2(g)$	−393.5

$$\Delta H^\circ_{\mathrm{rxn}} = \Delta H_f^\circ \mathrm{CaO}) + \Delta H_f^\circ(\mathrm{CO_2}) - \Delta \mathrm{H}_f^\circ(\mathrm{CaCO_3})$$

$$178.1 = -635.5\ \mathrm{kJ} - 393.5\ \mathrm{kJ} - \Delta \mathrm{H}_f^\circ(\mathrm{CaCO_3})$$

$$\Delta H_f^\circ(\mathrm{CaCO_3}) = -1207.1\ \mathrm{kJ/mol}$$

PRACTICE

1. Given 2 $SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$, which of the following equations is correct?

(a) $\Delta H^o_f\ (SO_3) = \Delta H°_{rxn} - \Delta H^o_f\ (SO_2)$

(b) $\Delta H^o_f\ (SO_3) = \Delta H°_{rxn} + \Delta H^o_f\ (SO_2)$

[✓ (c)] $2\ \Delta H^o_f\ (SO_3) = \Delta H°_{rxn} + 2\ \Delta H^o_f\ (SO_2)$

(d) $2\ \Delta H^o_f\ (SO_3) = \Delta H°_{rxn} - 2\ \Delta H^o_f\ (SO_2)$

(e) $2\ \Delta H^o_f\ (SO_3) = 2\ \Delta H^o_f\ (SO_2) - \Delta H°_{rxn}$

$$\Delta H°_{rxn} = \sum n\Delta H^o_f\ (\text{products}) - \sum m\Delta H^o_f\ (\text{reactants})$$

$$\Delta H°_{rxn} = 2\Delta H^o_f\ (SO_3) - (\cancel{\Delta H^o_f\ (O_2)} + 2\Delta H^o_f\ (SO_2))$$

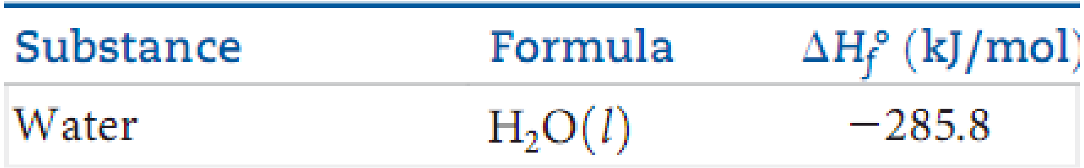
$$\Delta H°_{rxn} = 2\Delta H^o_f\ (SO_3) - 2\Delta H^o_f\ (SO_2)$$

$$2\Delta H^o_f\ (SO_3) = 2\Delta H^o_f\ (SO_2) + \Delta H°_{rxn}$$

PRACTICE

2. Given the following standard enthalpy change, calculate the standard enthalpy of formation of CuO(s):

$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l) \quad \Delta H° = –129.7\ kJ$



Substance	Formula	$\Delta H_f°$ (kJ/mol)
Water	$H_2O(l)$	−285.8

$$\Delta H°_{rxn} = \sum n\Delta H^o_f\,(\text{products}) - \sum m\Delta H^o_f\,(\text{reactants})$$

$$= (\cancel{\Delta H^o_f\,(Cu)} + \Delta H^o_f\,(H_2O)) - (\Delta H^o_f\,(CuO) + \cancel{\Delta H^o_f\,(H_2)})$$

$$= \Delta H^o_f\,(H_2O) - \Delta H^o_f\,(CuO)$$

$$\Delta H^o_f\,(CuO) = \Delta H^o_f\,(H_2O) – \Delta H°_{rxn} = –285.8 – (–129.7) = –156.1\ kJ$$

Changes of State of Matter

Molar enthalpy of vaporization:

$H_2O\,(l) \rightarrow H_2O(g)$ $\Delta H = 44.0$ kJ at 298 K

Molar enthalpy of fusion:

$H_2O\,(s) \rightarrow H_2O(l)$ $\Delta H = 6.01$ kJ at 273.15 K

EXAMPLE

Enthalpy Changes Accompanying Changes in States of Matter. Calculate ΔH for the process in which 50.0 g of water is converted from liquid at 10.0°C to vapor at 25.0°C.

Break the problem into two steps: Raise the temperature of the liquid first then completely vaporize it. The total enthalpy change is the sum of the changes in each step.

Set up the equation and calculate:

$$q_P = mc_{H_2O}\Delta T + n\Delta H_{vap}$$

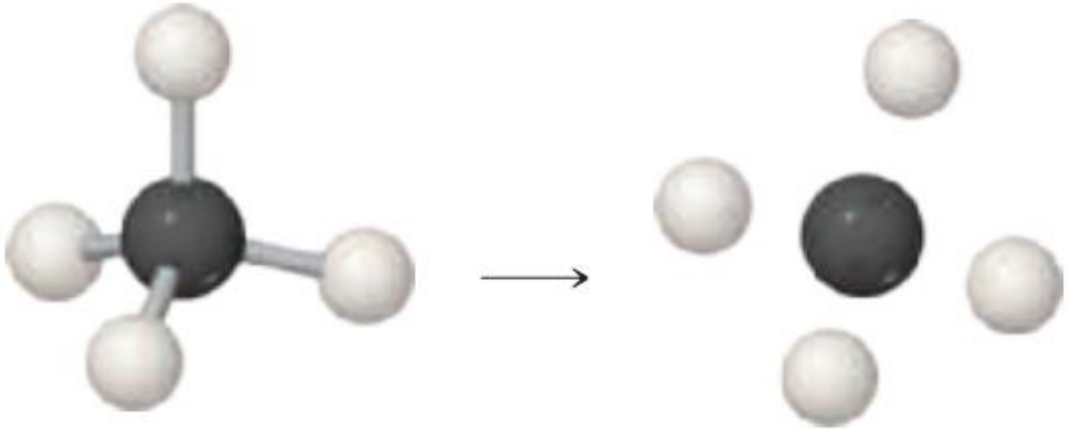
$$= (50.0\ \text{g})(4.184\ \text{J/g °C})(25.0\text{-}10.0)\text{°C} + \frac{50.0\ \text{g}}{18.0\ \text{g/mol}}\ 44.0\ \text{kJ/mol}$$

$$= 3.14\ \text{kJ} + 122\ \text{kJ} = 125\ \text{kJ}$$

5-8 Bond Enthalpies

The ***bond enthalpy*** is the enthalpy change, ΔH, for the breaking of a particular bond in one mole of a gaseous substance

$$CH_4(g) \longrightarrow C(g) + 4\,H(g) \qquad \Delta H = 1660\text{ kJ}$$



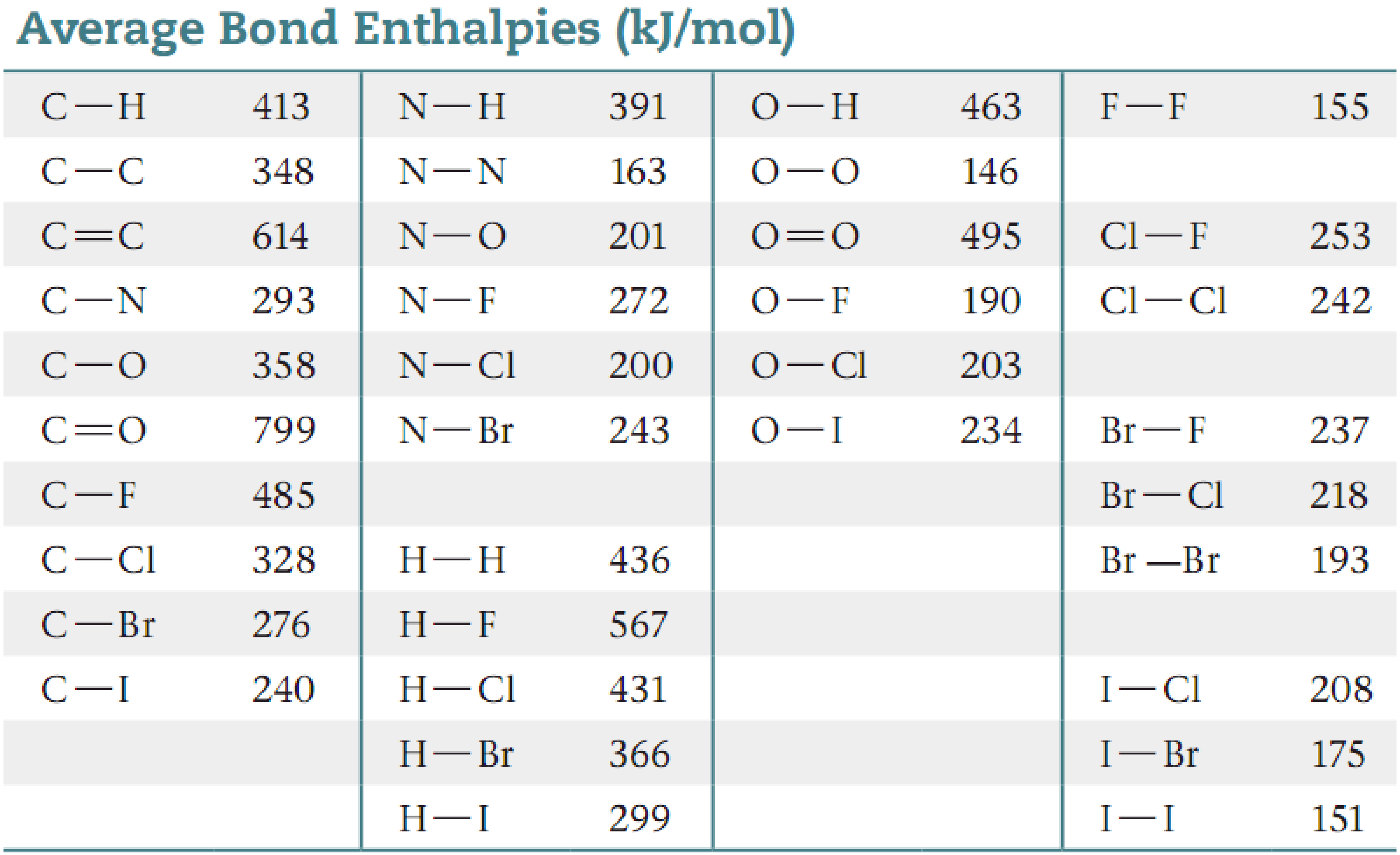
There are four equivalent C—H bonds in methane, the enthalpy of this reaction is four times the enthalpy needed to break a single C—H bond.

➔The average C—H bond enthalpy in CH_4 is

$$D(C\text{-}H) = (1660/4)\text{ kJ/mol} = 415\text{ kJ/mol}.$$

*The **bond enthalpy is always a positive quantity** because energy is required to break chemical bonds. Conversely, energy is always released when a bond forms between two gaseous atoms or molecular fragments.*

The greater the bond enthalpy, the stronger the bond.



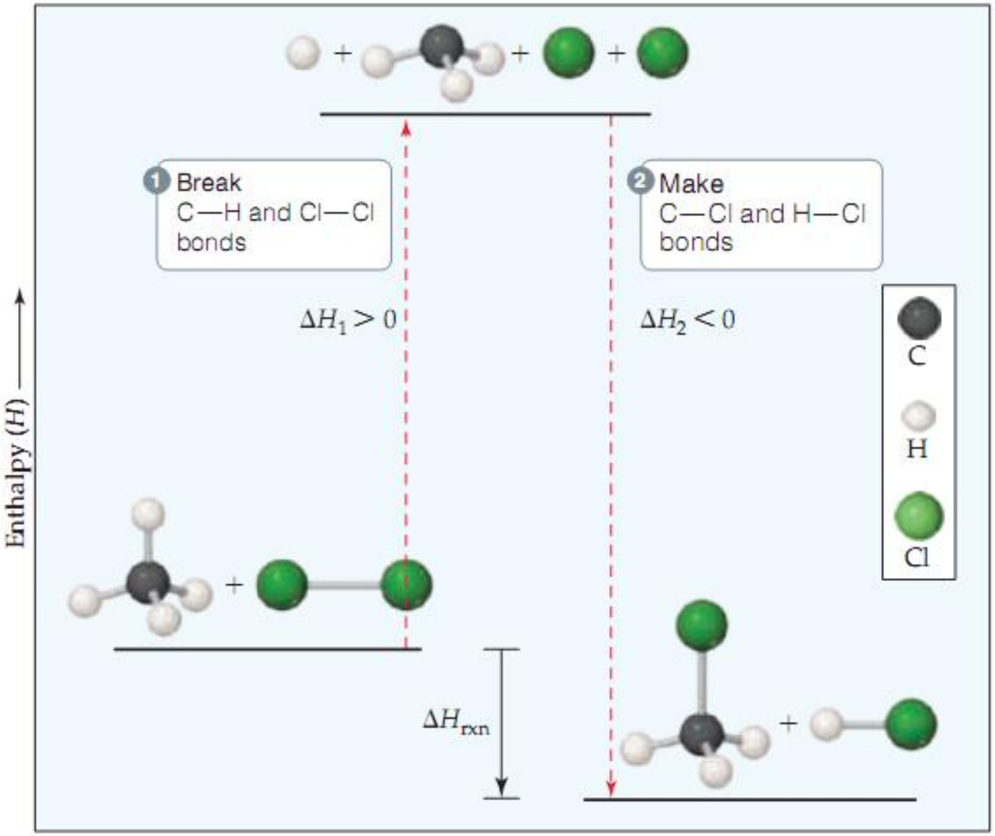
Average Bond Enthalpies (kJ/mol)

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

Bond Enthalpies and the Enthalpies of Reactions

$$\Delta H_{rxn} = \sum \begin{pmatrix}\text{bond enthalpies}\\ \text{of bonds broken}\end{pmatrix} - \sum \begin{pmatrix}\text{bond enthalpies}\\ \text{of bonds formed}\end{pmatrix}$$

$$H{-}CH_3(g) + Cl{-}Cl(g) \longrightarrow Cl{-}CH_3(g) + H{-}Cl(g) \qquad \Delta H_{rxn} = ?$$

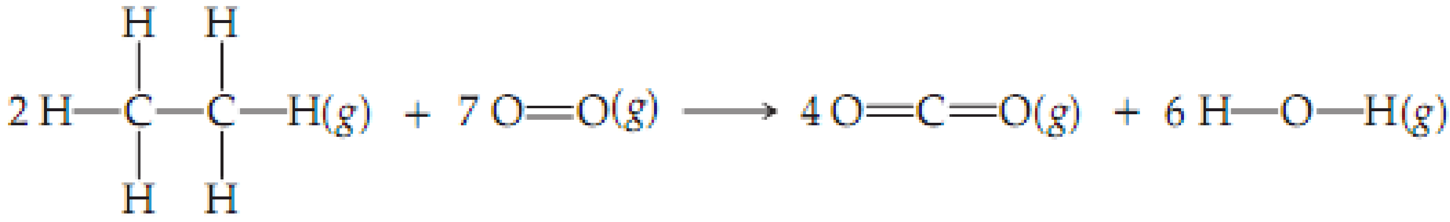


$$\Delta H_{rxn} = [D(C{-}H) + D(Cl{-}Cl)] - [D(C{-}Cl) + D(H{-}Cl)]$$

$$\Delta H_{rxn} = (413\text{ kJ} + 242\text{ kJ}) - (328\text{ kJ} + 431\text{ kJ}) = -104\text{ kJ}$$

EXAMPLE

Estimate ΔH for the following combustion reaction



$$2\,\mathrm{H_3C{-}CH_3}(g) + 7\,\mathrm{O{=}O}(g) \longrightarrow 4\,\mathrm{O{=}C{=}O}(g) + 6\,\mathrm{H{-}O{-}H}(g)$$

C—H	413
C—C	348
C—O	358
C═O	799
O—H	463
O—O	146
O═O	495

$$\Delta H = [12D(\mathrm{C{-}H}) + 2D(\mathrm{C{-}C}) + 7D(\mathrm{O{=}O})] \quad - [8D(\mathrm{C{=}O}) + 12D(\mathrm{O{-}H})]$$

$$= [12(413\text{ kJ}) + 2(348\text{ kJ}) + 7(495\text{ kJ})] \quad - [8(799\text{ kJ}) + 12(463\text{ kJ})]$$

$$= -2831\text{ kJ}$$

PRACTICE

1. Use the average bond enthalpies in Table 5.4 to estimate ΔH for the "water splitting reaction": $H_2O(g) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$.

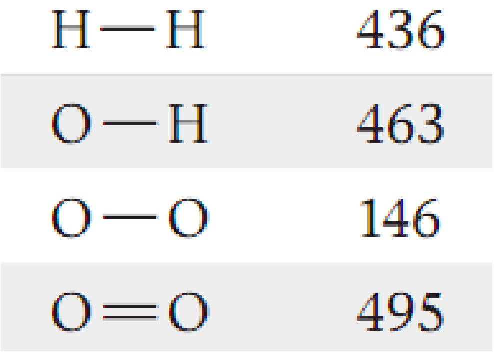
(a) 242 kJ

(b) 417 kJ

(c) 5 kJ

(d) -5 kJ

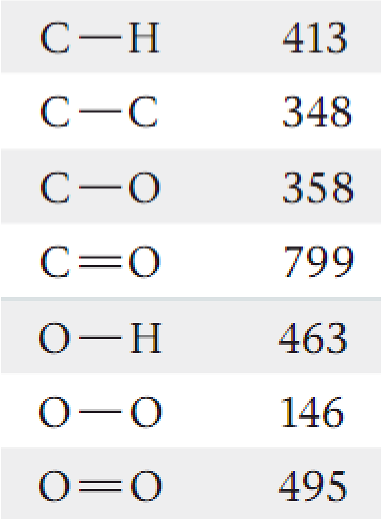
(e) -468 kJ



H—H	436
O—H	463
O—O	146
O═O	495

PRACTICE

2. Use the average bond enthalpies in Table 5.4 to estimate ΔH for the combustion of ethanol.



C—H	413
C—C	348
C—O	358
C=O	799
O—H	463
O—O	146
O=O	495

C_2H_5OH + 3 O_2 -> 2 CO_2 + 3 H_2O

1 C-C 3 O=O 4 C=O 6 H-O

5 C-H

1 C-O

1 O-H

5-9 Foods and Fuels

(This is a self-reading section)

Glucose is soluble in blood, and in the human body it is known as blood sugar. It is transported by the blood to cells where it reacts with O_2 in a series of steps, eventually producing $CO_2(g)$, $H_2O(l)$, and energy:

$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l) \quad \Delta H° = -2803\ \text{kJ}$$

Tristearin, $C_{57}H_{110}O_6$, a typical fat produce CO_2 and H_2O when metabolized:

$$2\ C_{57}H_{110}O_6\ (s) + 163\ O_2 \rightarrow 114\ CO_2(g) + 110\ H_2O(l) \qquad \Delta H° = -71{,}609\ \text{kJ}$$

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[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

EXAMPLE

A 28-g serving of a popular breakfast cereal served with 120 mL of skim milk provides 8 g protein, 26 g carbohydrates, and 2 g fat.

(a) Using the average fuel values of these substances, estimate the fuel value (caloric content) of this serving.

(b) A person of average weight uses about 100 Cal/km when running or jogging. How many servings of this cereal provide the fuel value requirements to run 3 km?

$$(8\ \cancel{\text{g protein}})\left(\frac{17\ \text{kJ}}{1\ \cancel{\text{g protein}}}\right) + (26\ \cancel{\text{g carbohydrate}})\left(\frac{17\ \text{kJ}}{1\ \cancel{\text{g carbohydrate}}}\right)$$

$$+\ (2\ \cancel{\text{g fat}})\left(\frac{38\ \text{kJ}}{1\ \cancel{\text{g fat}}}\right) = 650\ \text{kJ (to two significant figures)}$$

This corresponds to 160 kcal:

$$(650\ \cancel{\text{kJ}})\left(\frac{1\ \text{kcal}}{4.18\ \cancel{\text{kJ}}}\right) = 160\ \text{kcal}$$

$$\text{Servings} = (3\ \cancel{\text{mi}})\left(\frac{100\ \cancel{\text{Cal}}}{1\ \cancel{\text{km}}}\right)\left(\frac{1\ \text{serving}}{160\ \cancel{\text{Cal}}}\right) = 2\ \text{servings}$$

PRACTICE

1. A stalk of celery has a caloric content (fuel value) of 9.0 kcal.

If 1.0 kcal is provided by fat and there is very little protein, estimate the number of grams of carbohydrate and fat in the celery.

(a) 2 g carbohydrate and 0.1 g fat

(b) 2 g carbohydrate and 1 g fat

(c) 1 g carbohydrate and 2 g fat

(d) 32 g carbohydrate

PRACTICE

2. Dry red beans contain 62% carbohydrate, 22% protein, and 1.5% fat. Estimate the fuel value of these beans.

PRACTICE

3. During a very light activity, such as reading or watching television, the average adult expends about 7 kJ/min. How many minutes of such activity can be sustained by the energy provided by a serving of chicken noodle soup containing 13 g protein, 15 g carbohydrate, and 5 g fat?

Fuels

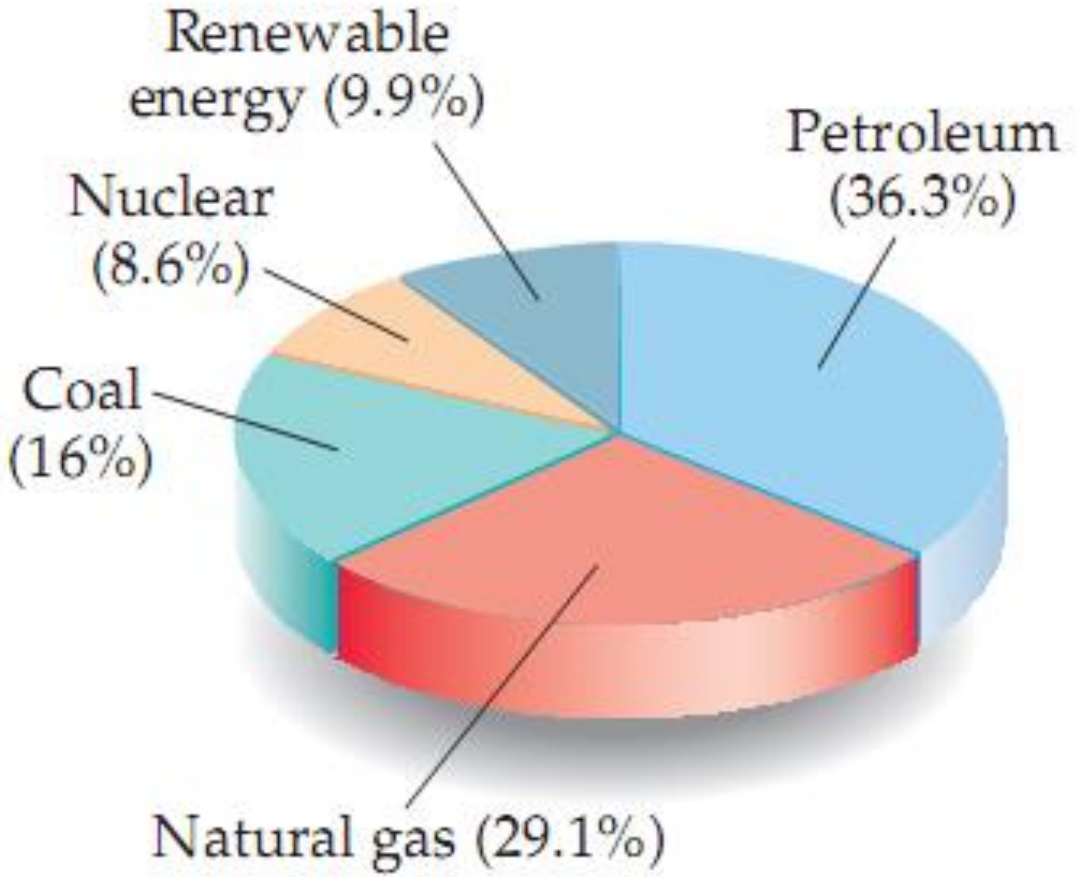

Renewable energy (9.9%)
Petroleum (36.3%)
Nuclear (8.6%)
Coal (16%)
Natural gas (29.1%)

TABLE 5.6 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

$$12\,CO_2(g) + 11\,H_2O(l) + \text{sunlight} \longrightarrow C_{12}H_{22}O_{11} + 12\,O_2(g)$$

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

$$C_6H_{12}O_6(s) \longrightarrow 2\,C_2H_5OH(l) + 2\,CO_2(g) \qquad \Delta H = 15.8\text{ kJ}$$

Homeworks

Excercises:

5.13

5.25

5.37

5.51

5.69

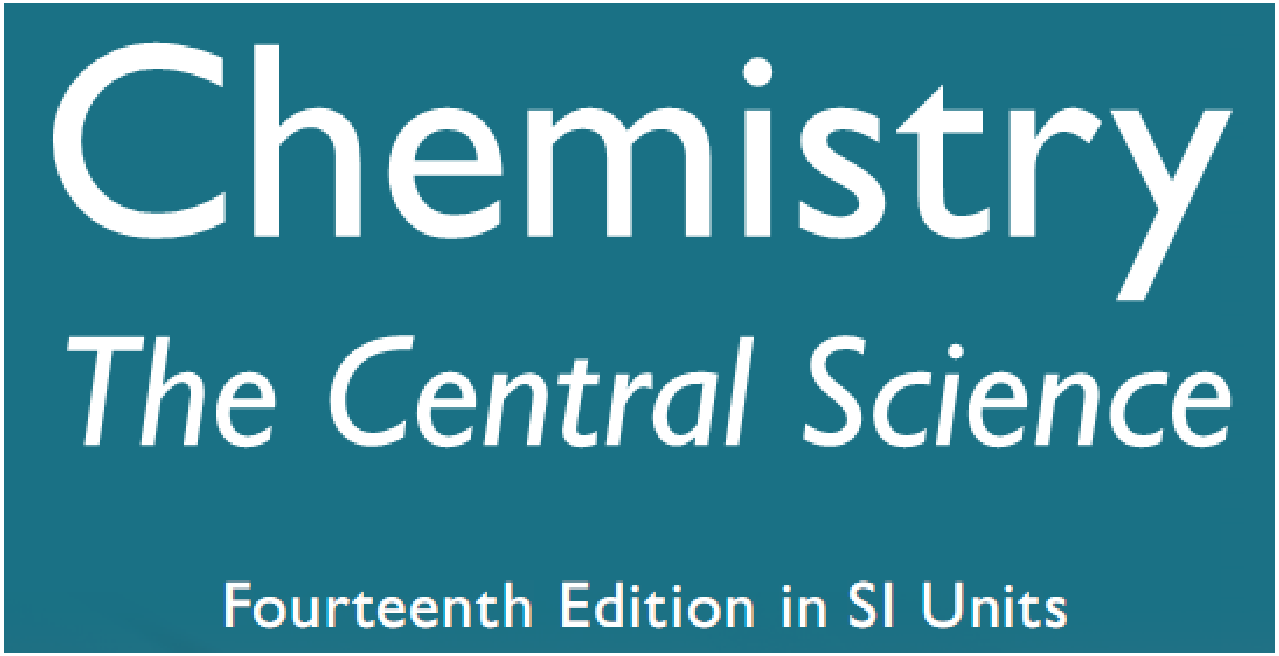
5.71

5.95

5.108

5.112

5.122



Chemistry

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Fourteenth Edition in SI Units

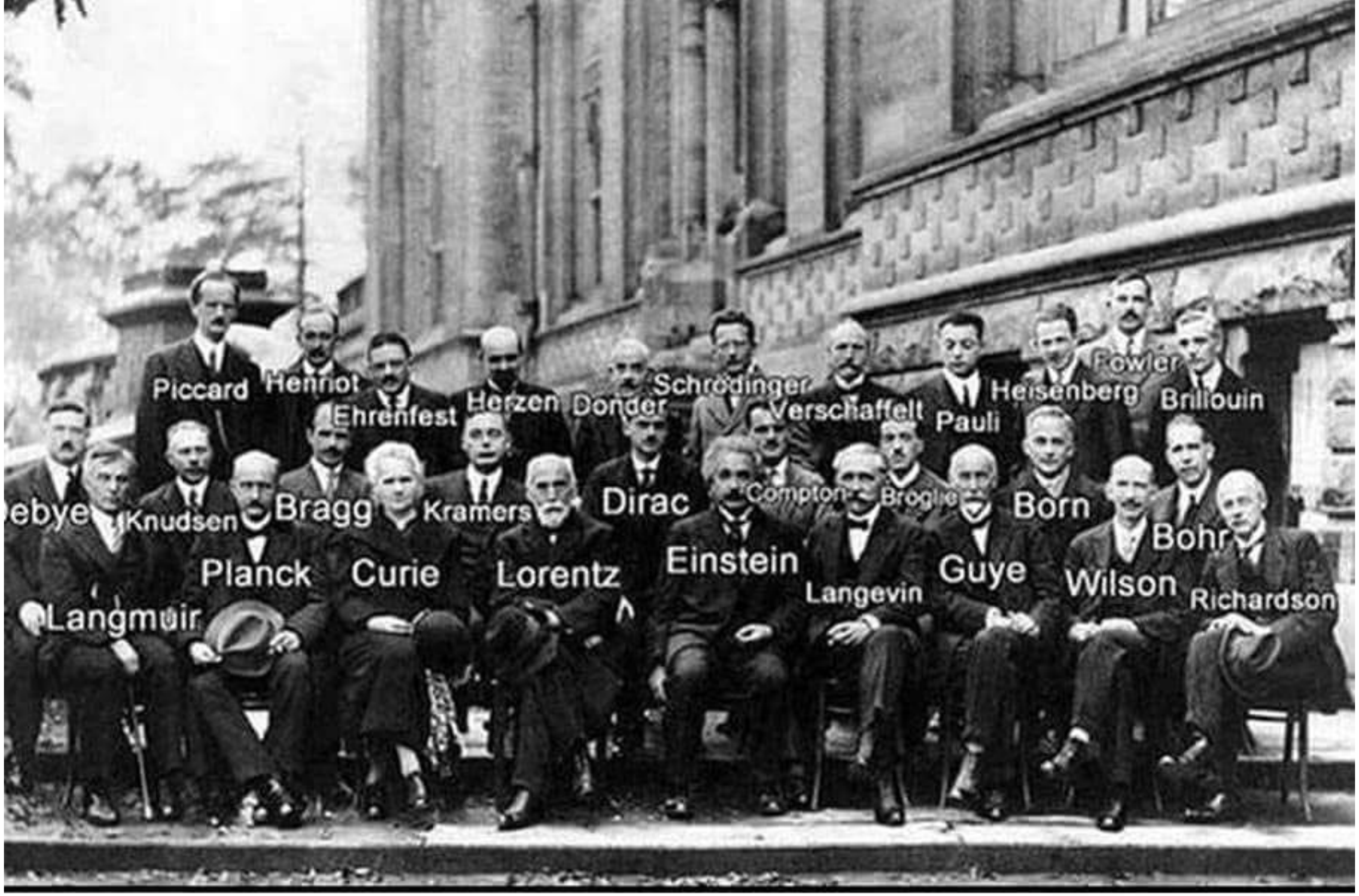
Due date: April 29th 2020

You will have a midterm exam next time

What are allowed?

- A pen
- A periodic table
- An A4-sized sheet of hand written notes
- A calculator

No other devices are allowed!



Here Are All The People Who Made Me Fail In Exams.