Chapter 5
Thermochemistry

The *energy* of chemical reactions

How do you keep track of it?
Where does it come from?

What is Energy?

- **The ability to:**
  - ➤ do work
  - ➤ Transfer heat

- **Work:**
  - ➤ Energy that causes an object that has mass to move.

- **Heat:**
  - ➤ Energy that causes the temperature of an object to rise.

Units of Energy

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

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

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

1 cal = 4.184 J

Energy has units of (mass)(velocity)^2

Remember kinetic energy was 1/2mv^2

Work

- Energy used to move an object over some distance.

- $w = F \cdot d,$

  w = work,

  F = force

  d = distance over which the force is exerted.

(a)

(b)

Note units:

F = ma, mass(distance/s^2)

W = F(d) = mass(distance^2/s^2)

= mv^2

Kinetic Energy

Energy an object possesses by virtue of its motion.

$$KE = \frac{1}{2}\,mv^2$$

Heat

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

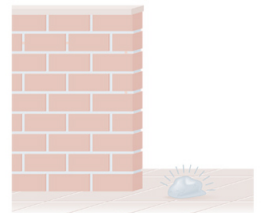# Potential Energy

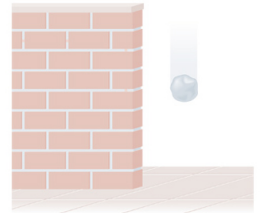Energy an object possesses by virtue of its position or chemical composition.
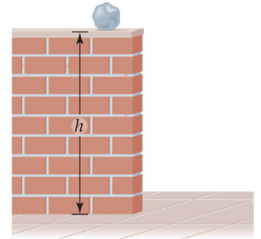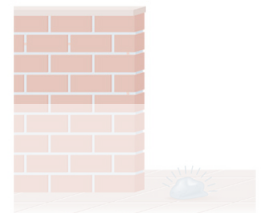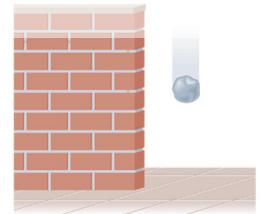
More potential E

Less P.E. as bike goes down.

Transfer of Energy

a) Add P.E. to a ball by lifting it to the top of the wall

Transferal of Energy

a) Add P.E. to a ball by lifting it to the top of the wall
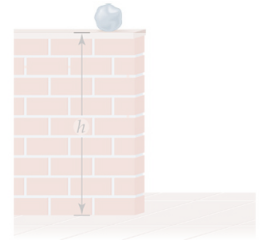
b) As the ball falls,

P.E ------> K. E. ($1/2mv^2$)

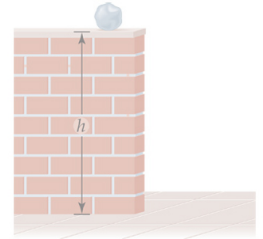# Transfer of Energy

a) Add P.E. to a ball by lifting it to the top of the wall

b) As the ball falls,

P.E ------> K. E. $(1/2mv^2)$
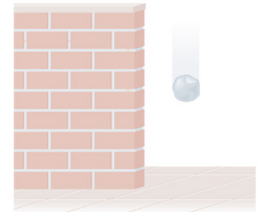
Ball hits ground, K.E. =0, but E has to go somewhere. So

1. Ball gets squashed
2. Heat comes out.
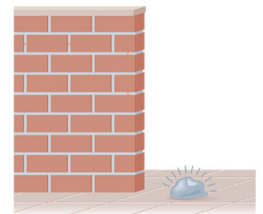
Energy accounting

- We must identify where different types of energy go.

- Therefore, we must identify the *places.*

System and Surroundings

- The **system** includes the stuff we want to study (here, the hydrogen and oxygen molecules).

- The **surroundings** are everything else (here, the cylinder, piston and everything else).

Internal Energy

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

$E_{internal,total} = E_{KE} + E_{PE} + E_{electrons} + E_{nuclei} + \ldots\ldots$

Almost impossible to calculate total internal energy

Instead we always look at the ***change*** in energy (ΔE).

Internal Energy

By definition, the change in internal energy, ΔE, is the final energy of the system minus the initial energy of the system:

$$\Delta E = E_{final} - E_{initial}$$
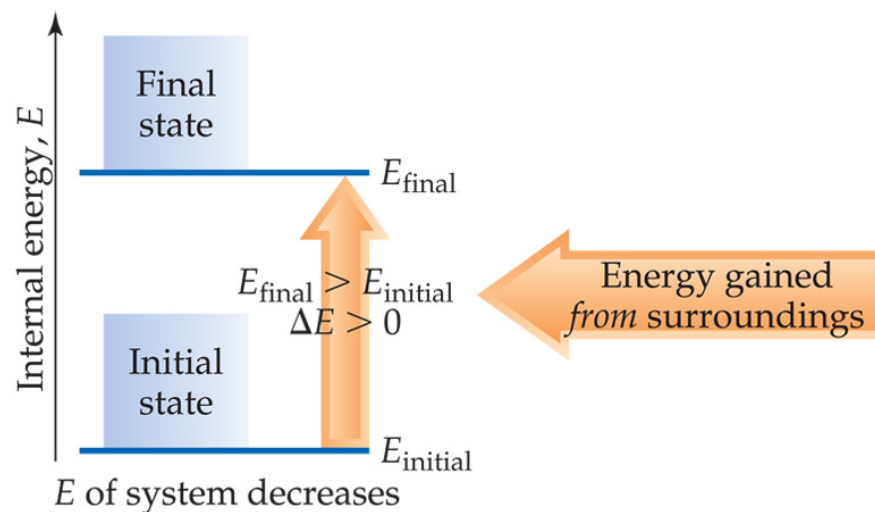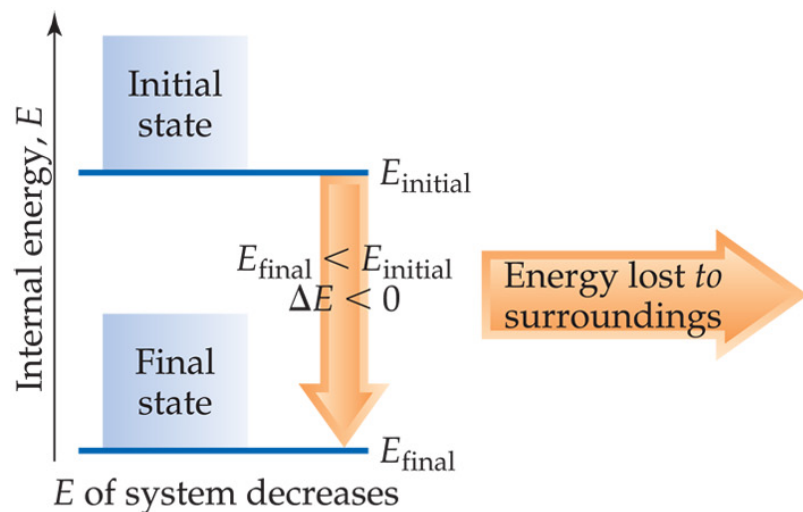
Heat review...
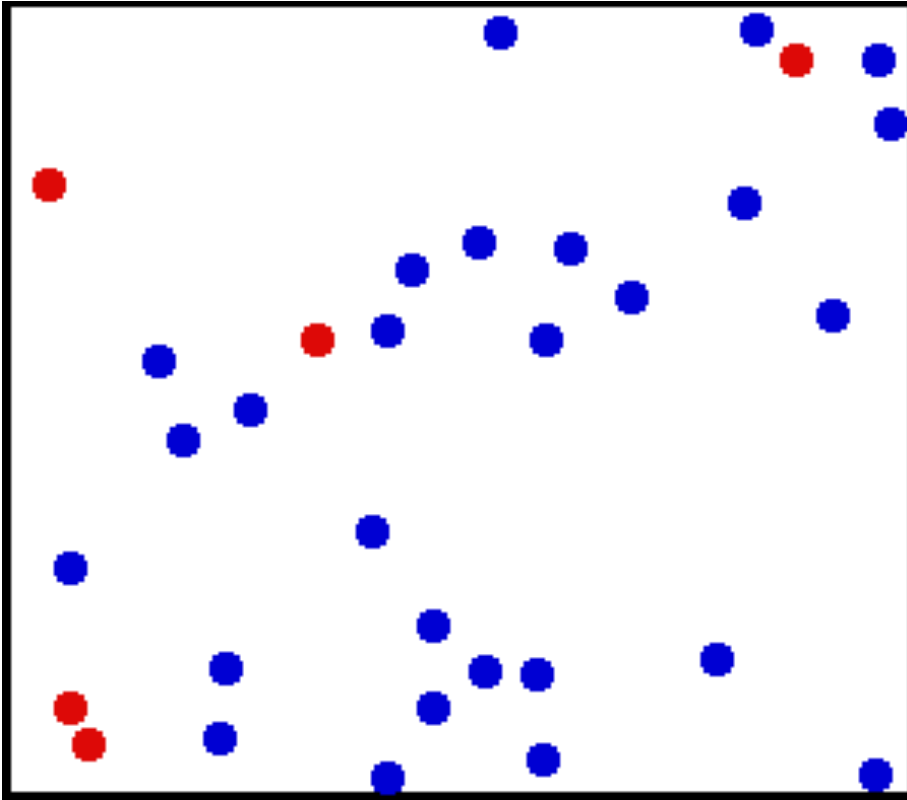
- Heat is transfer of *random* kinetic energy from:
- Stuff with lower K.E. to stuff with higher K.E.
- When faster atoms/molecules hit slower ones:
- The faster ones get slower and the slower get faster.

Heat.   work
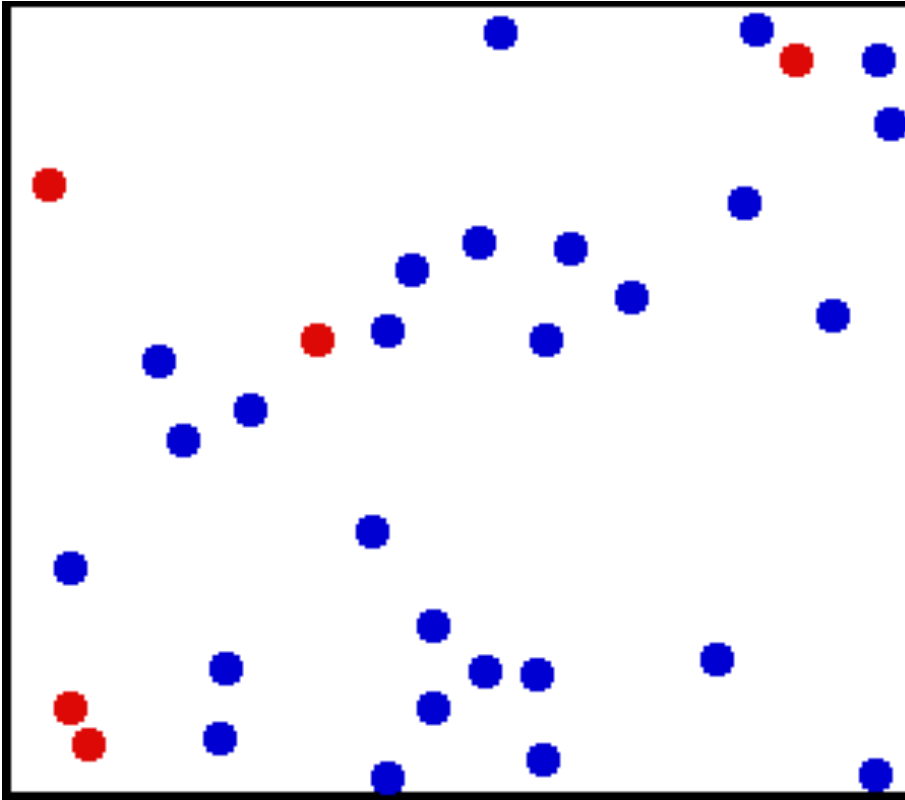
- Transfer of *random* atomic/molecular motion

- Transfer of *organized* atomic/molecular motion.

First Law of Thermodynamics

- Energy is conserved.

- In other words, the total energy of the universe is a constant; $\Delta E_{System} = -\Lambda E_{surroundings}$
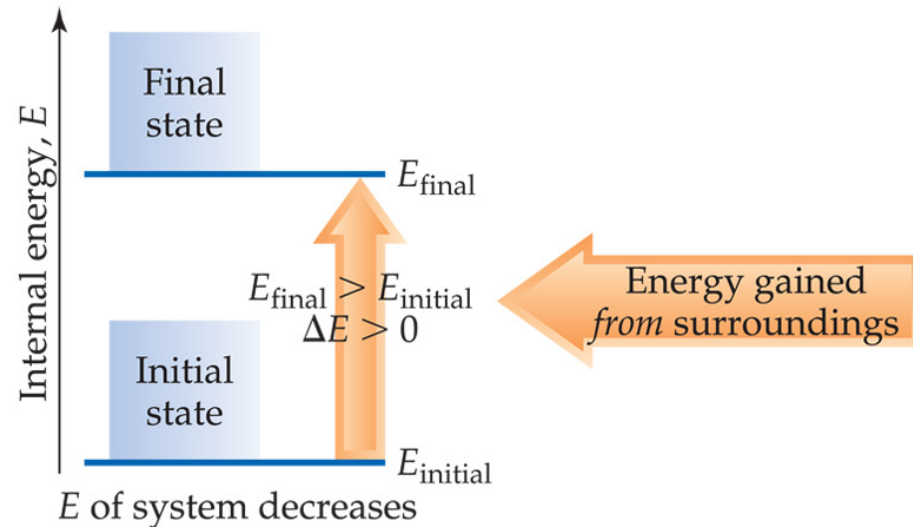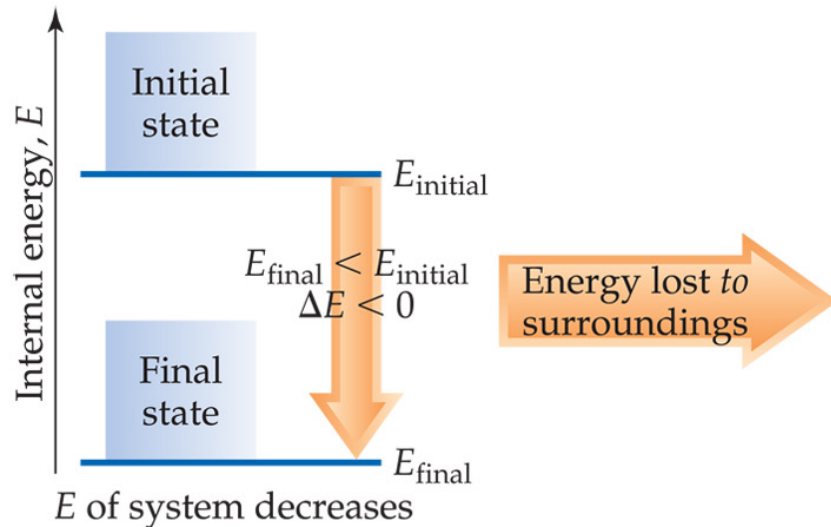
Changes in Internal Energy

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

- If $\Delta E < 0$, $E_{\text{final}} < E_{\text{initial}}$
  - ➤ Therefore, the system *released* energy to the surroundings.
  - ➤ This energy change is called **exergonic.**
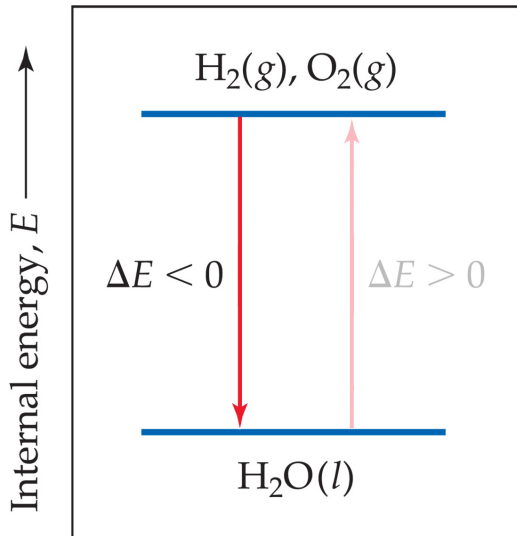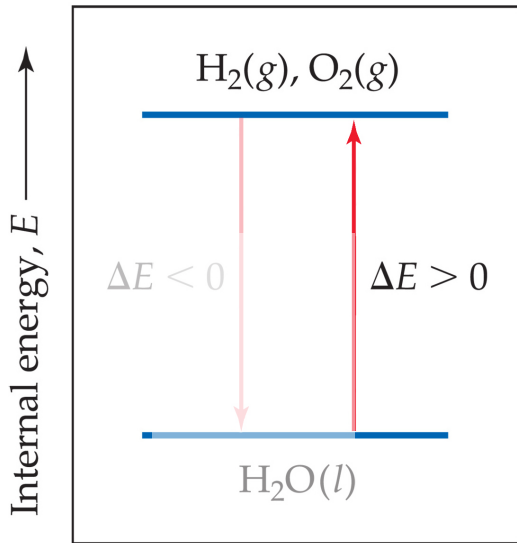
Changes in Internal Energy
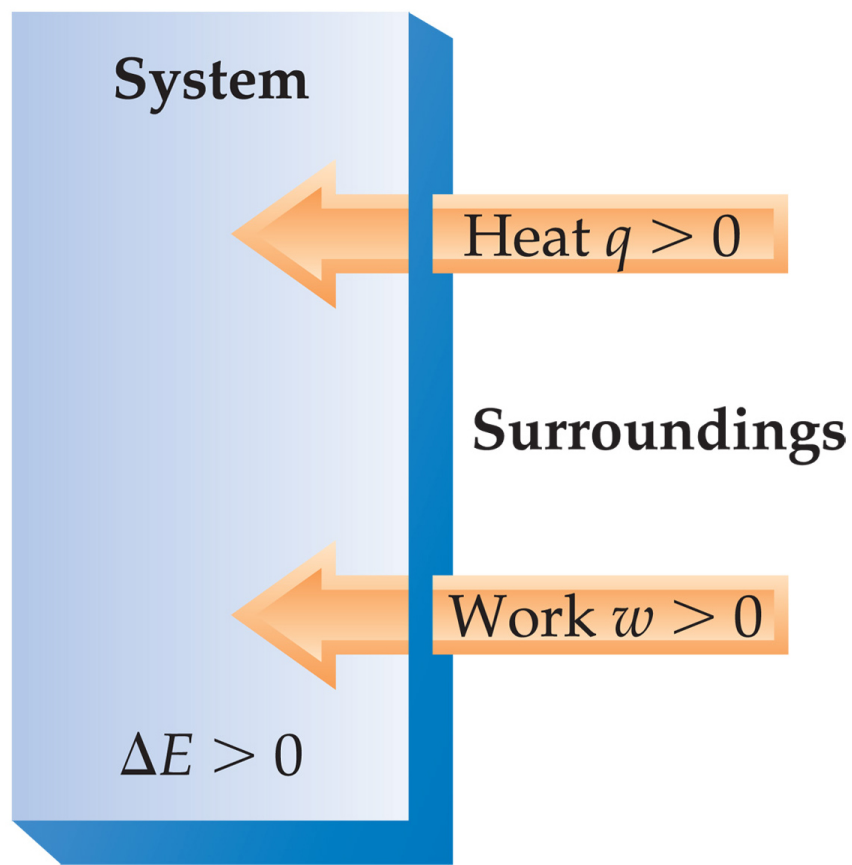
- When energy is exchanged between the system and the surroundings, it is exchanged as either heat (q) or work (w).

- That is,

- $\Delta E = q + w.$

ΔE, q, w, and Their Signs

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

50 g
H_2O (l)
100°C

-q

Cooling →

50 g
H_2O (l)
25°C

+q

← Heating

50 g
H_2O (s)
0°C

Surroundings suck heat out of water.

hot plate adds heat to water
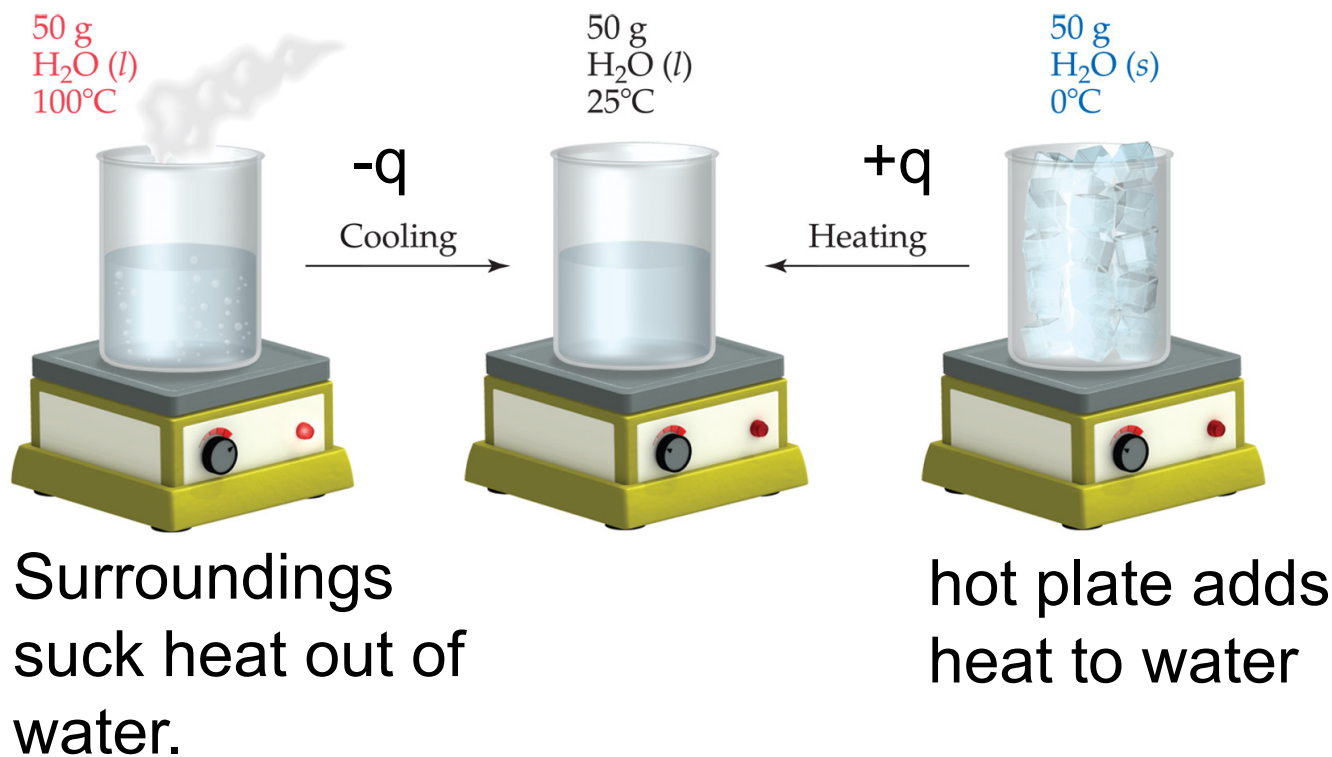
Sign of work

block pushes truck down
does work on truck

$w_{block}-$

$w_{truck}+$

Truck pushes block up.
Does work on block

$w_{truck}-$

$w_{block}+$
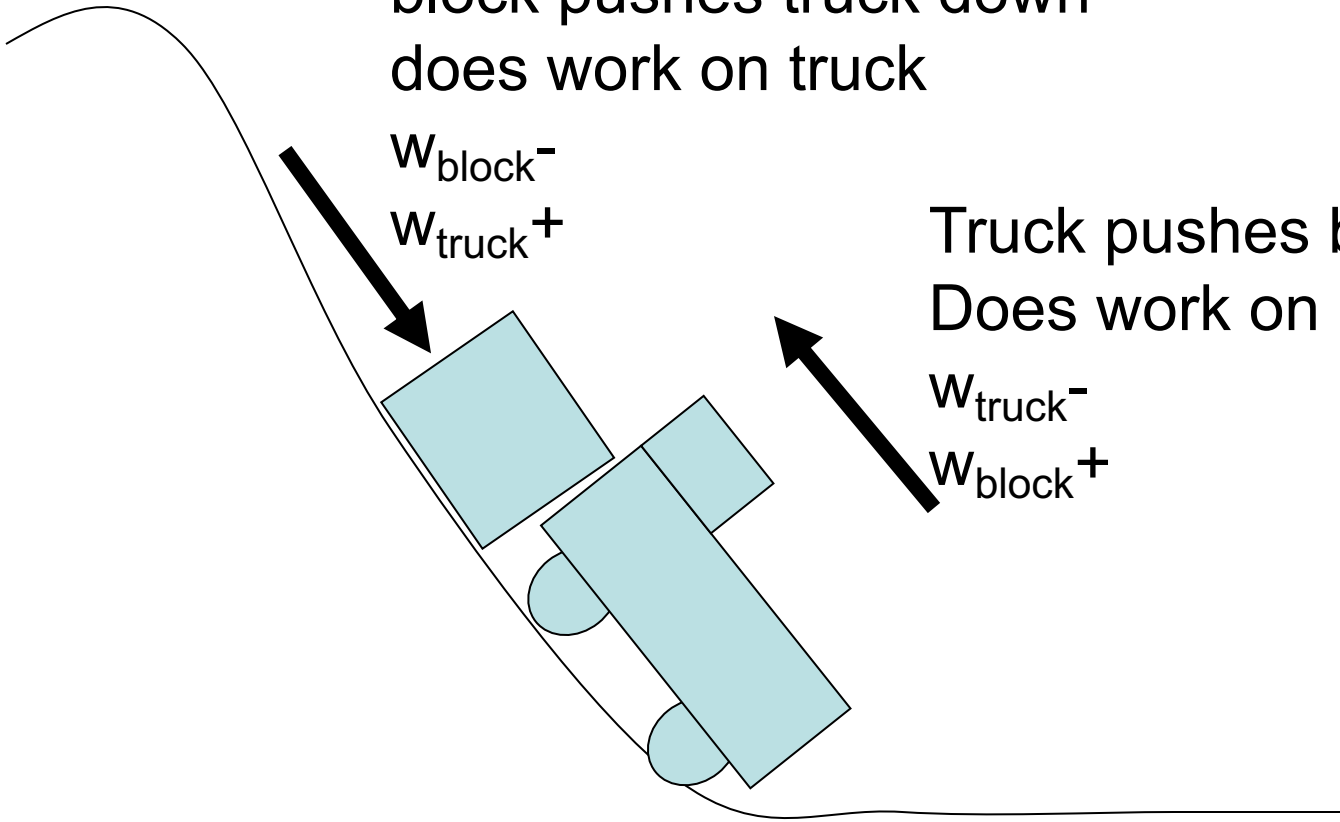
Exchange of Heat between System and Surroundings

Surroundings
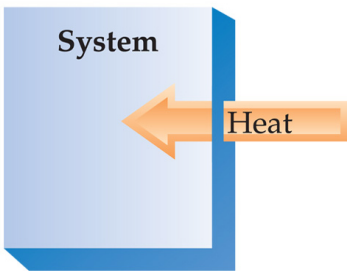
System

Heat →

$\Delta H > 0$
(Endothermic)

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

Surroundings
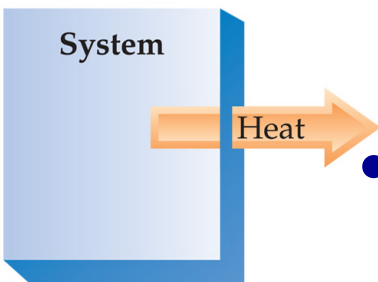
System

Heat →

$\Delta H < 0$
(Exothermic)

- Heat absorbed by system from surroundings, is ***endothermic***.
- Heat released by system to surroundings, is ***exothermic***.

Exchange of Heat between System and Surroundings

- Heat absorbed by system from surroundings, is **endothermic**.

- Heat released by system to surroundings, is **exothermic**.

Surroundings
System
Heat
$\Delta H < 0$
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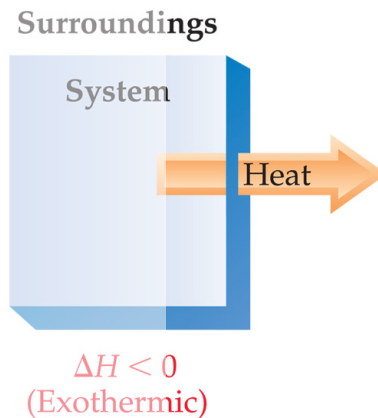
State Functions

Total internal energy of a system:

K.E. + $E_{electrons}$ + $E_{nucleus}$ + $P.E._{total}$

virtually impossible to measure/calculate
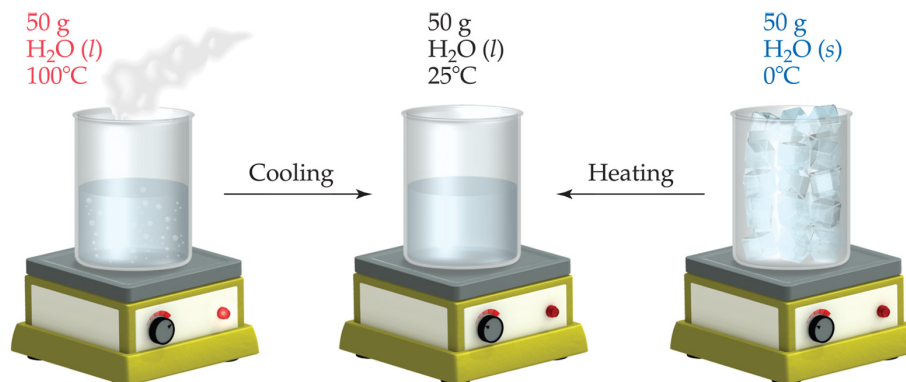
50 g H_2O (l) 100°C — Cooling → 50 g H_2O (l) 25°C ← Heating — 50 g H_2O (s) 0°C

State Functions

- However, the internal energy of a system is independent of the *path* by which the system achieved that state.

  ➢ In the system below, the water could have reached room temperature from either direction.

50 g
H_2O (*l*)
100°C

50 g
H_2O (*l*)
25°C

50 g
H_2O (*s*)
0°C

Cooling

Heating
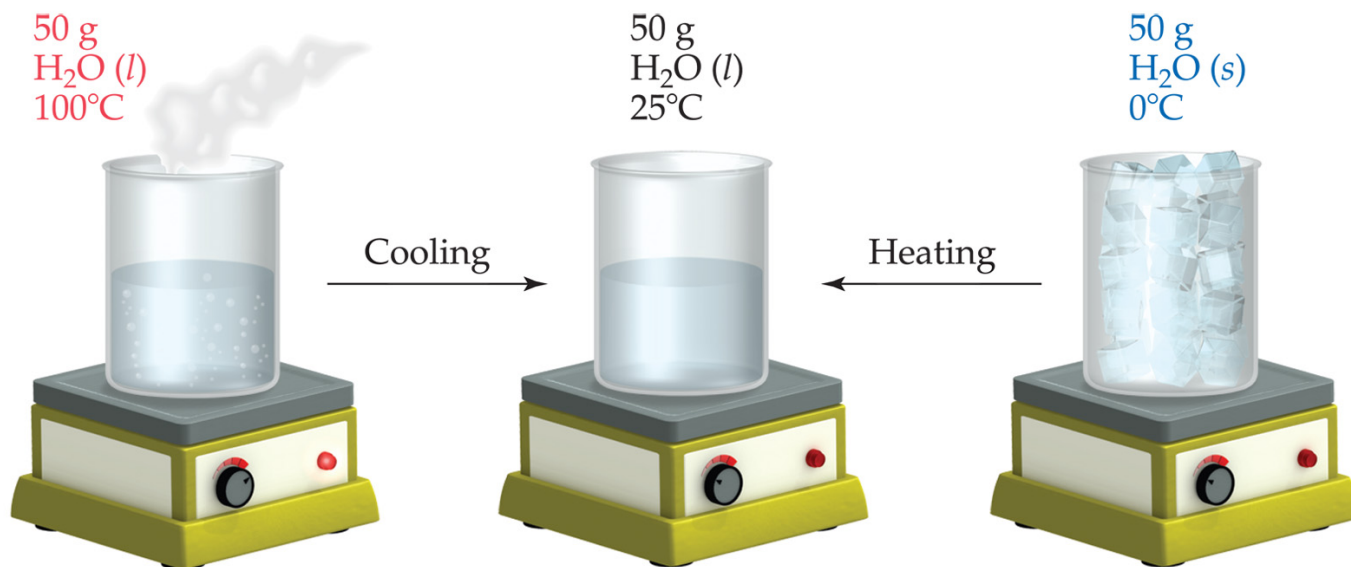
State Functions

- Therefore, internal energy is a state function.

- because its **PATH INDEPENDENT**

- And so, ΔE depends only on $E_{initial}$ and E_{final}.

50 g
H_2O (l)
100°C

Cooling →

50 g
H_2O (l)
25°C

← Heating

50 g
H_2O (s)
0°C
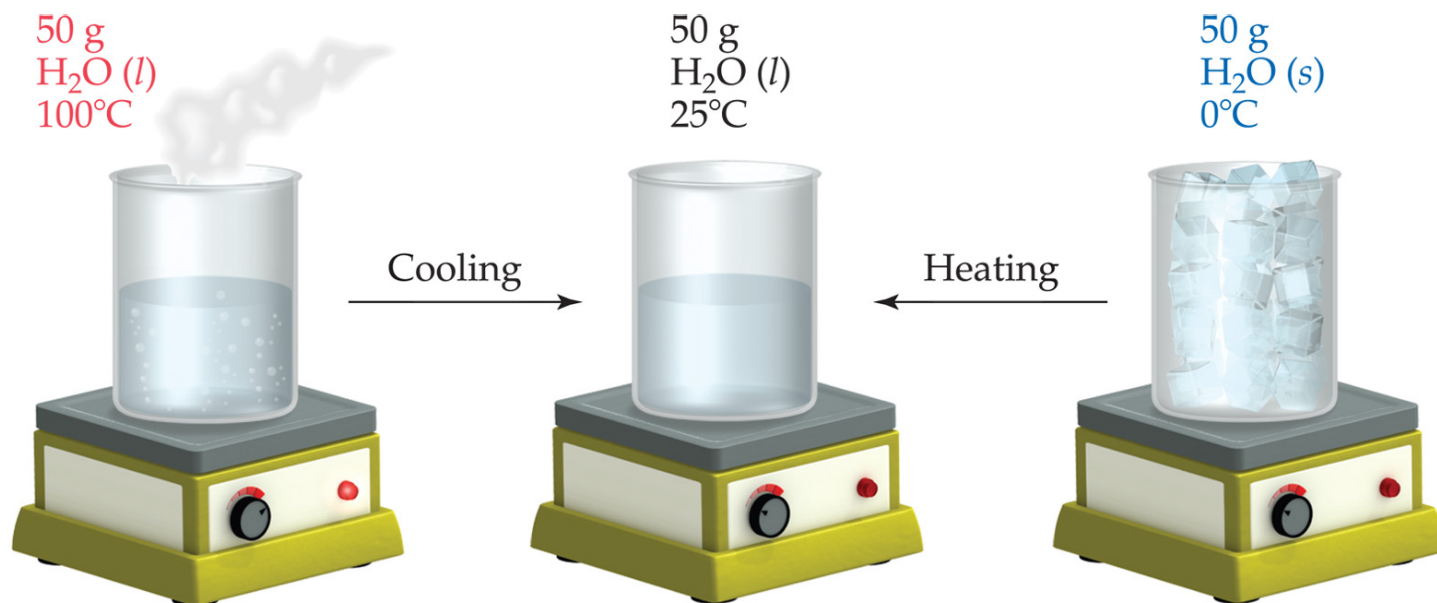
State Functions

All heat.　　　Work and heat

(a)

(b)

Charged battery

Heat

Heat

Work

ΔE　Energy lost by battery

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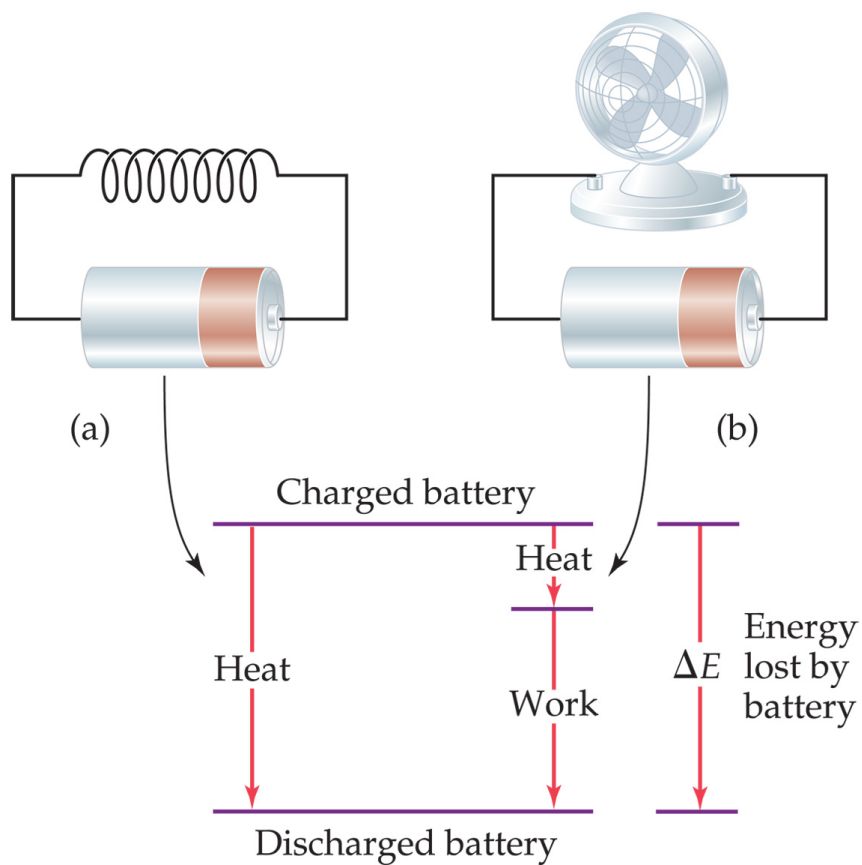
- However, *q* and *w* are **not** state functions.
- Whether the battery is shorted out or is discharged by running the fan, its ΔE is the same.
  - ➢ But *q* and *w* are different in the two cases.

Work
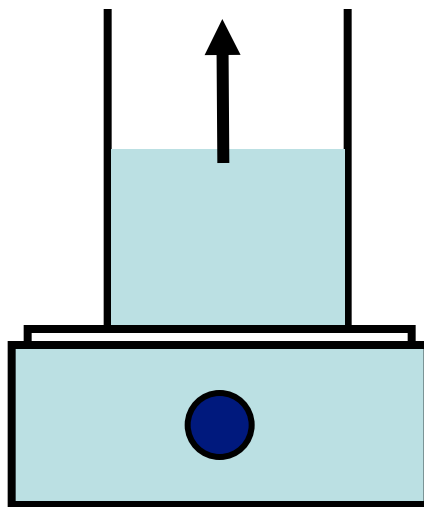
process in an open container (chemical reaction in a beaker)
w? (can there be any work)?

 Yes, evolving gases could push on the surroundings.

Catch the work, do the same process in a cylinder

$P = F/A$

$P = F/A$

h_i

h_f

Δh

ΔV

Volume change

Cross-sectional area $= A$

Initial state

Final state
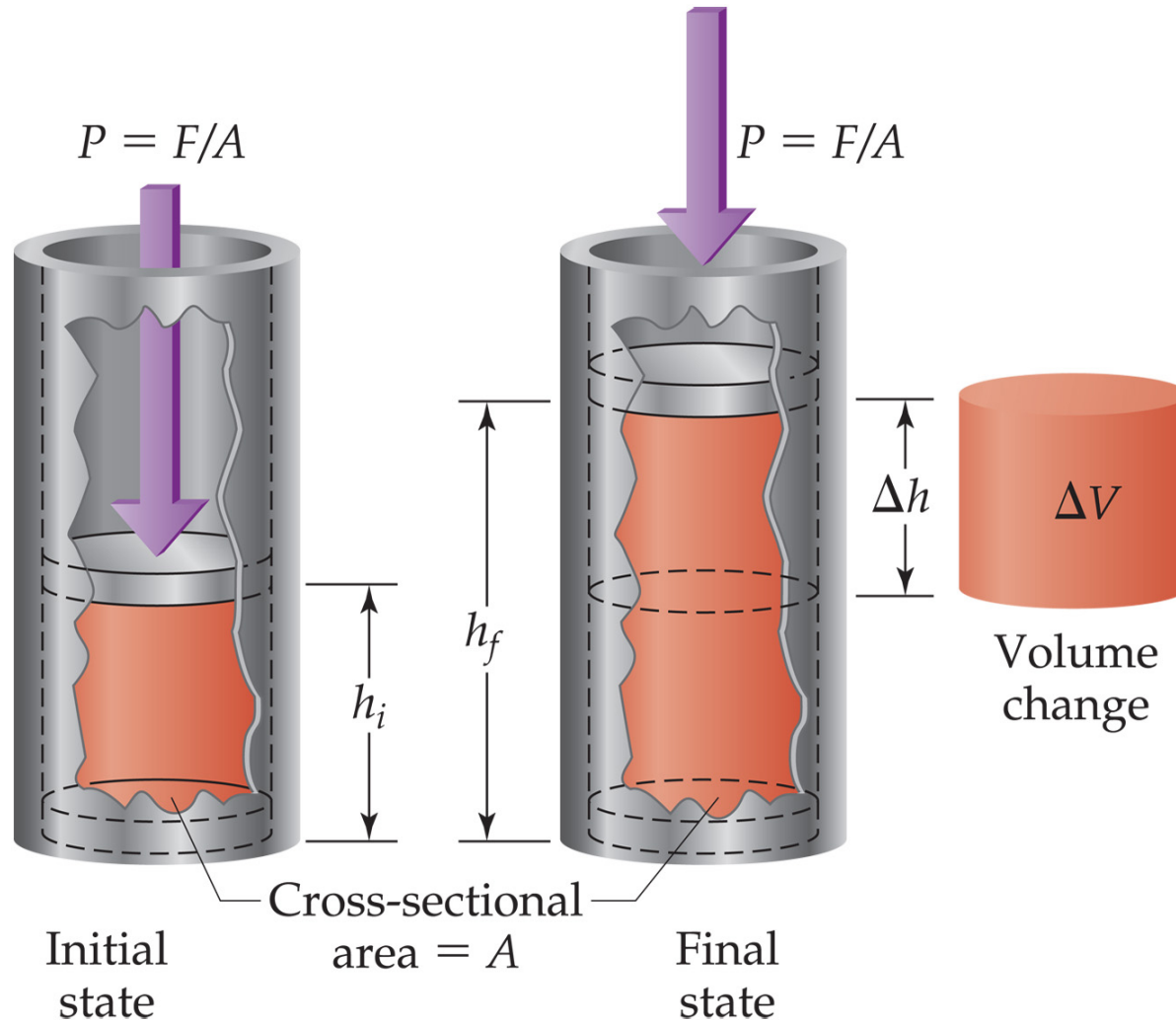
Process evolves gas, pushes on piston, work done on piston.

The internal combustion engine

Catch the work, do the same process in a cylinder

$w = F*d, \quad F = P*A, \quad d = \Delta h$

$w = -P*A\Delta h = -P\Delta V$

Negative because an **increase** in Volume means that the system is doing work **on** the surroundings.

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

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

$P = F/A$

$P = F/A$

h_i

h_f

Δh

ΔV

Volume change

Initial state

Cross-sectional area $= A$

Final state
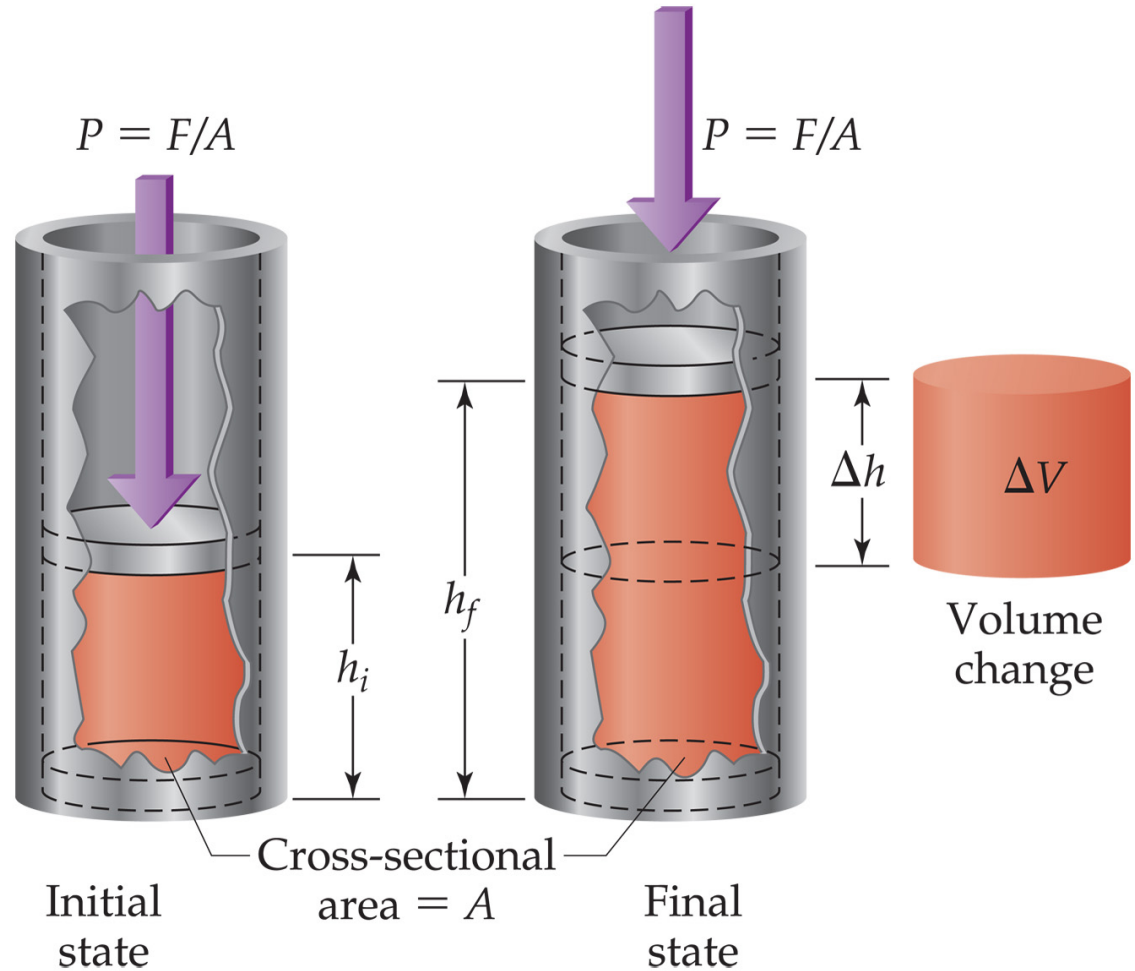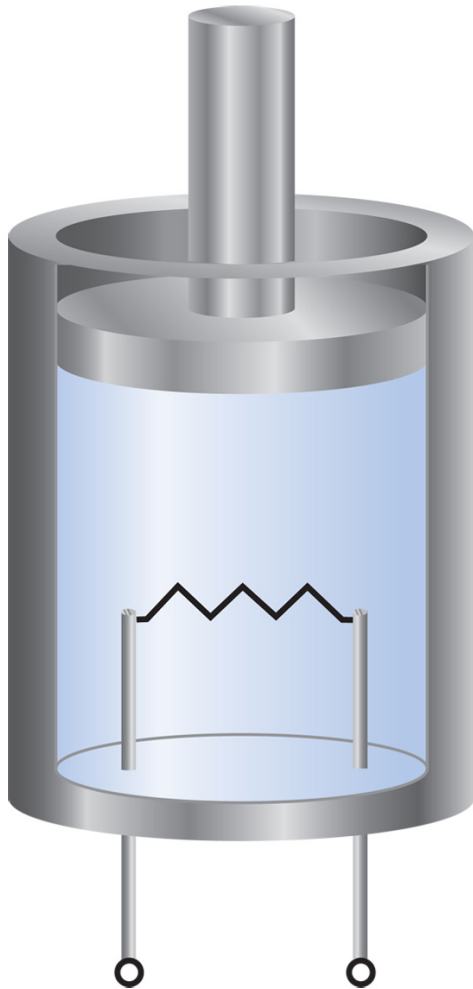
Example

- Gas inside cylinder with electric heater.
- Add 100 j heat with heater.
- 1. Piston can go up and down
- 2. Piston stuck.
- a. What happens to T in each case?
- b. What about q and w for each case?
- c. What about ΔE in each case?

Example

- Gas inside cyclinder with electric heater.
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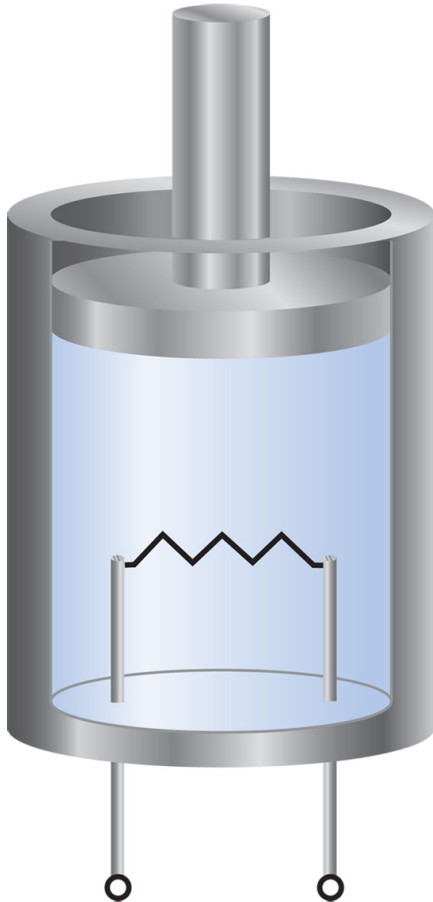
a.1. Piston goes up, some E goes to expand gas, do work. T goes up less

a.2 T goes up more, all E goes to q.

b.1. both q and w positive

b.2. w 0, q larger

c. ΔE the same & + in each case

Work

Now we can measure the work:

$$w = -P\Delta V$$
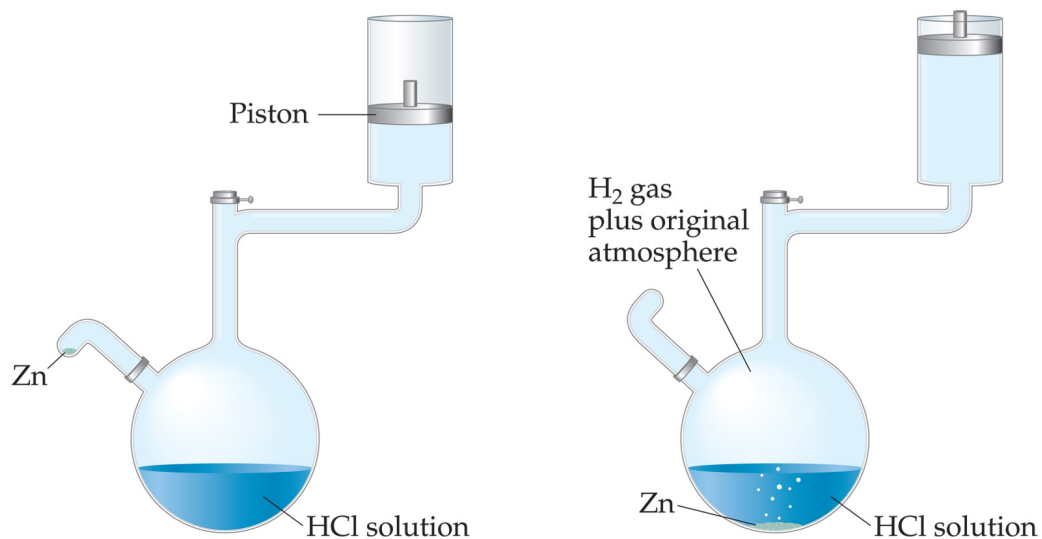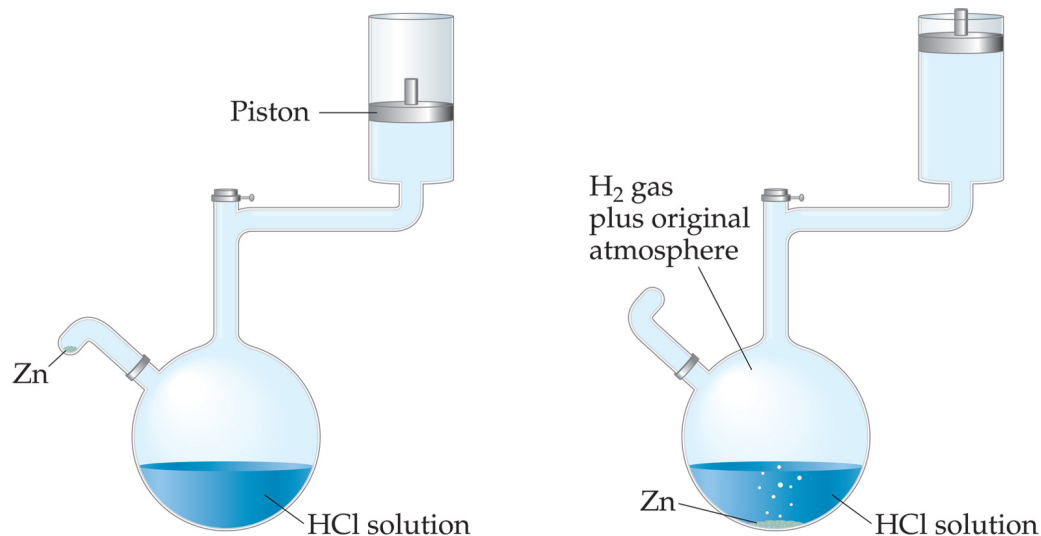
Zn + 2HCl --------> H$_{2(g)}$ + ZnCl$_2$

Work

Zn + 2HCl ---------> $H_{2(g)}$ + $ZnCl_2$

I mole of Zn reacts. How much work is done (P = 1 atm, density of H_2 = 0.0823 g/L)?
1 mole of H_2 is produced.

Work

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1 mole of H_2 is produced.

$Zn + 2HCl \ \text{---------}> \ H_{2(g)} + ZnCl_2$
1mol   1 mol
                        2. 014 g/mol
                        2.014 g
                        d=m/V
                        V=m/d
                        V = 2.014g/0.0823g/L = 24.47 L
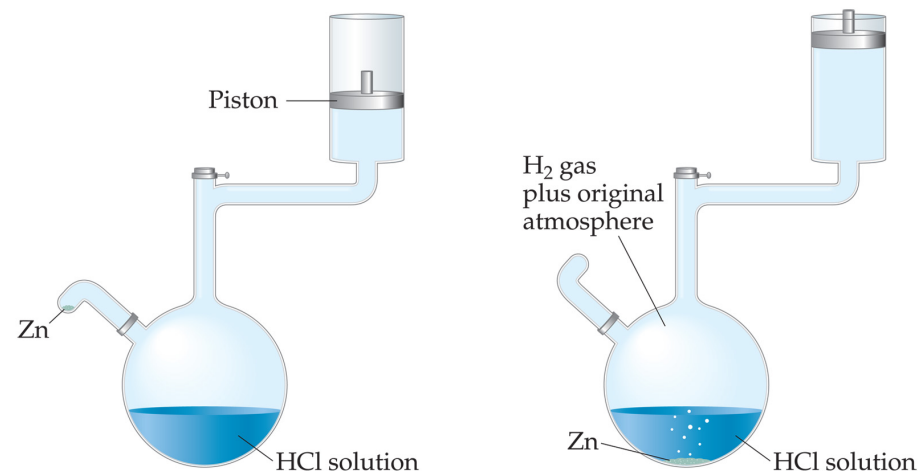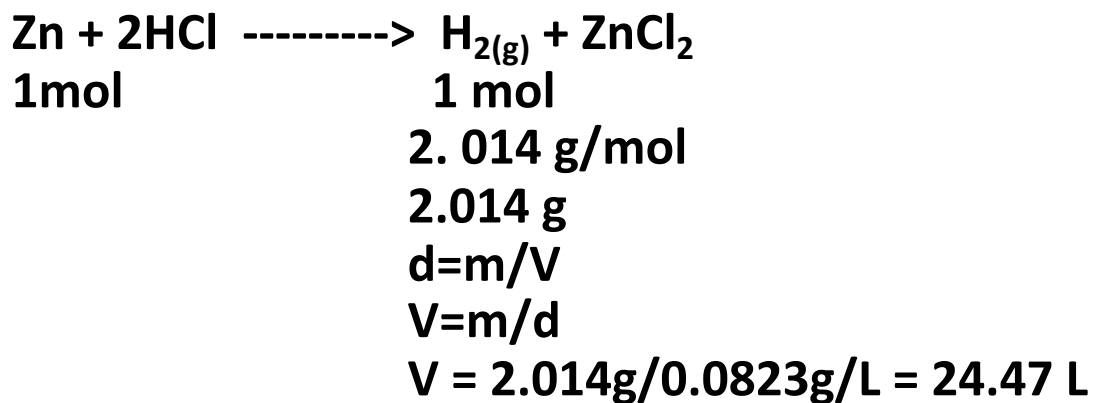
$W = -P\Delta V = 1atm(24.47L) = -24.47 \ L(atm)$

Enthalpy(H)

$$H = E + PV$$

This is the definition of Enthalpy for *any* process Buy why do we care?

Enthalpy

$$H = E + PV$$

- at constant pressure, ΔH, is

(Δ = change in thermodynamics)

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

- If P constant:

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

Enthalpy

- Since $\Delta E = q + w$ and $w_P = -P\Delta V$ *(P const.)* substitute these into the enthalpy expression:

$$\Delta H_P = \Delta E_P + P\Delta V$$

$$\Delta H_P = (q_P + w_P) - w_P$$

$$\Delta H_P = q_P$$

- **Note: true at constant pressure**
- *q is a state function* **at const P & only PV work.**

H = E + PV

- **Because:**
- If pressure is constant (like open to atmosphere, i.e. most things) and

w = -$\triangle$PV.

heat flow (q) = H (enthalpy) of system.

And: H is a state function, so q is also.

but only in the right conditions

Endothermic vs. Exothermic
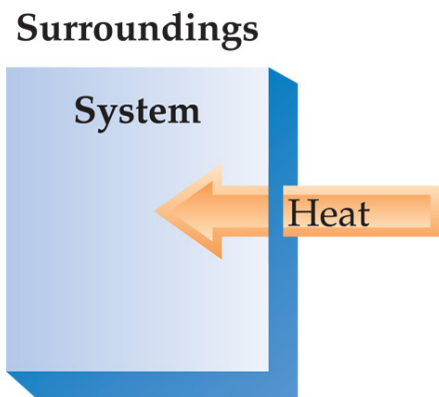
Surroundings

System

Heat

$\Delta H > 0$
(Endothermic)

Surroundings

System

Heat

$\Delta H < 0$
(Exothermic)

- A process is endothermic when ΔH is positive.
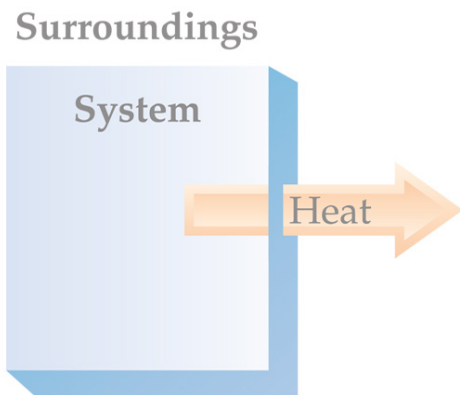
Endothermicity and Exothermicity

Surroundings

System

Heat

$\Delta H > 0$
(Endothermic)

Surroundings

System

Heat

$\Delta H < 0$
(Exothermic)
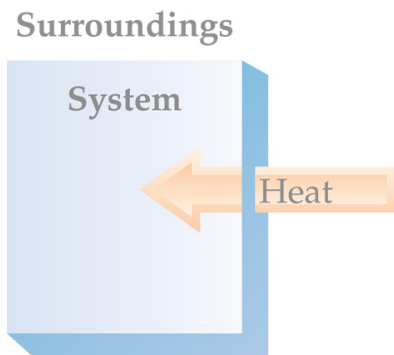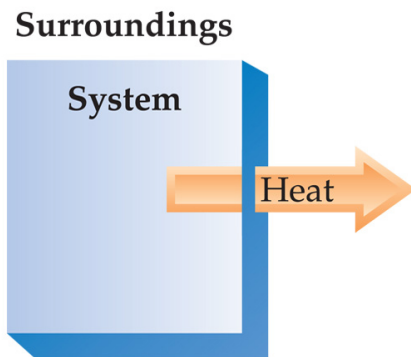
- A process is endothermic when ΔH is positive.

- A process is exothermic when ΔH is negative.

Enthalpies of Reaction

The *change* in enthalpy, ΔH, is the enthalpy of the products minus the enthalpy of the reactants:

$\Delta H = H_{products} - H_{reactants}$
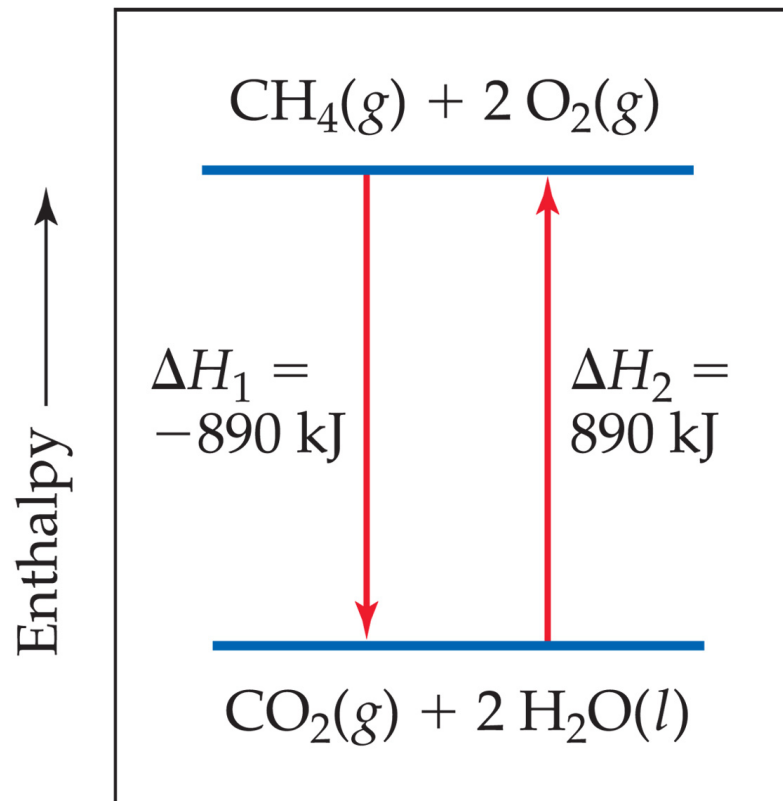
Enthalpies of Reaction

This quantity, ΔH, is called the enthalpy of reaction, or the heat of reaction.
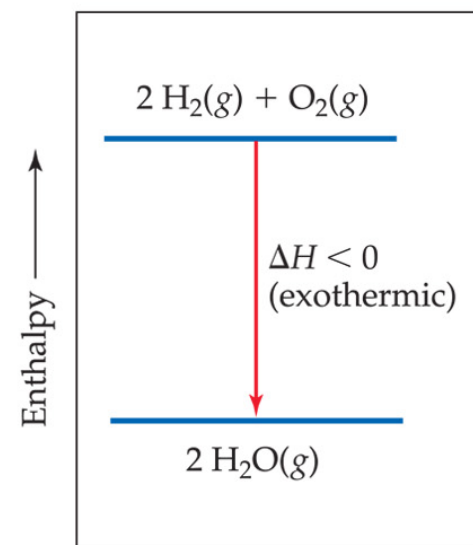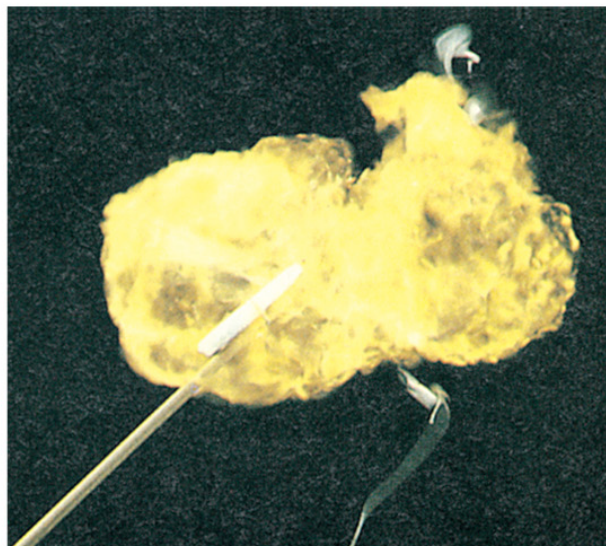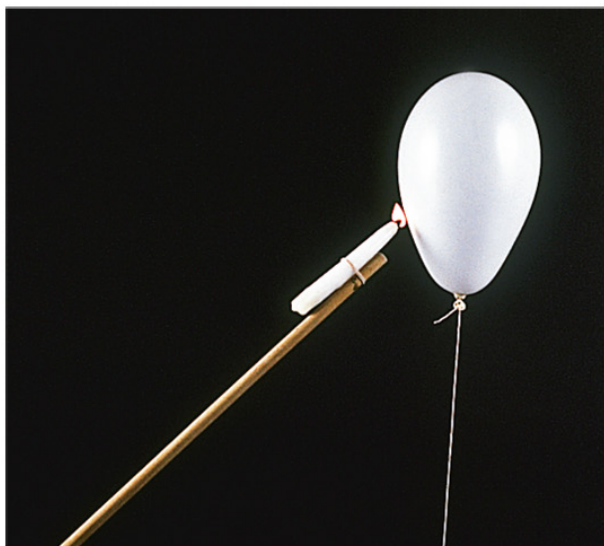
Reaction Enthalpy summary

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

Enthalpy of reaction example

Consider the reaction:

$2KClO_3$ -------> $2KCl + 3O_2$ $\Delta H = -89.4$ kJ/mol

a. What is the enthalpy change for formation of 0.855 moles of O_2?

Enthalpy of reaction example

Consider the reaction:

$2KClO_3$ -------> $2KCl + 3O_2$ $\Delta H = -89.4$ kJ/mol So If:

2 mol   2 mol   3 mol   -89.4 kJ of heat released.

What is the enthalpy change for formation of 0.855 moles of O_2?

$2KClO_3$ -------> $2KCl$ + $3O_2$ $\Delta H = -89.4$ kJ/mol
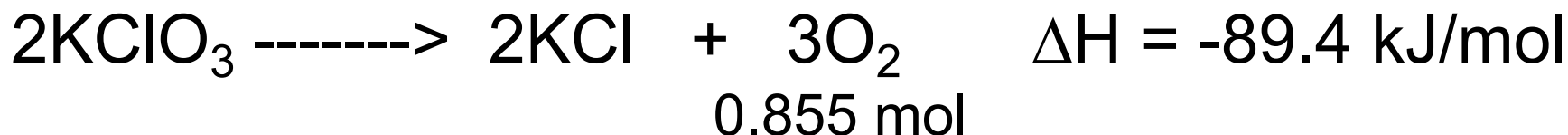
0.855 mol

$\Delta H = -89.4$ kJ/(3 mol O_2)(.855 mol O_2) = -25.5 kJ

Calorimetry

$$CH_4(g) + 2\,O_2(g)$$

$\Delta H_1 = -890\ kJ$

$\Delta H_2 = 890\ kJ$

Enthalpy

$$CO_2(g) + 2\,H_2O(l)$$

Motorized stirrer

Electrical leads for igniting sample

Thermometer

Insulated container

O_2 inlet

Bomb (reaction chamber)

Fine wire in contact with sample

Cup holding sample

Water
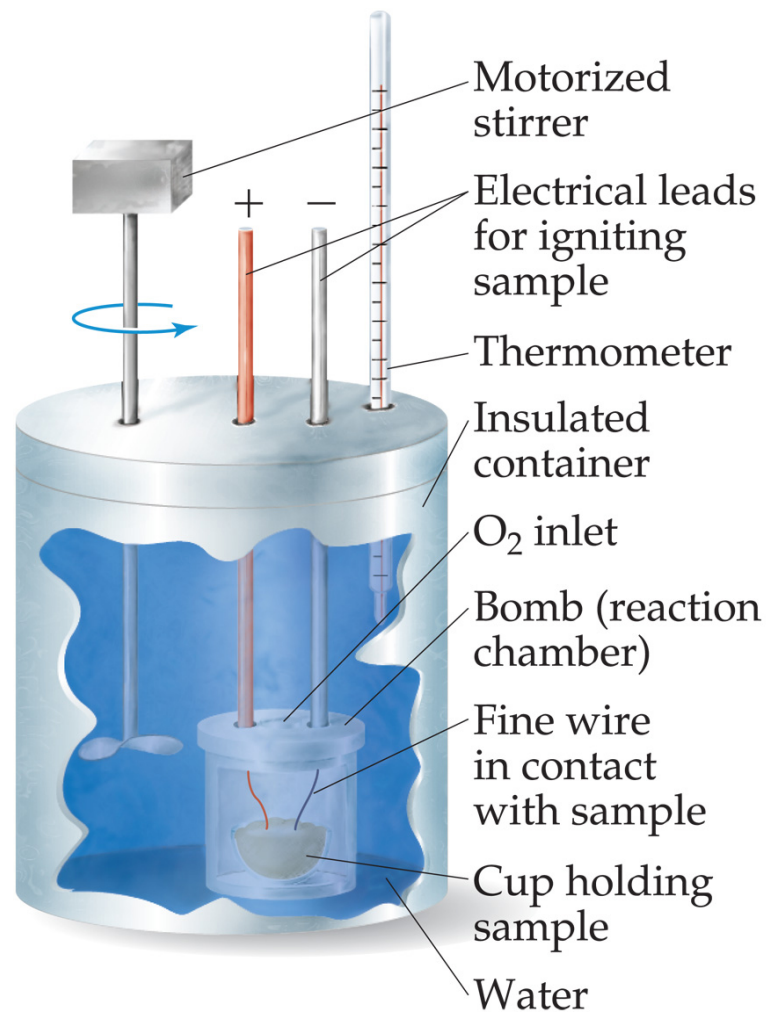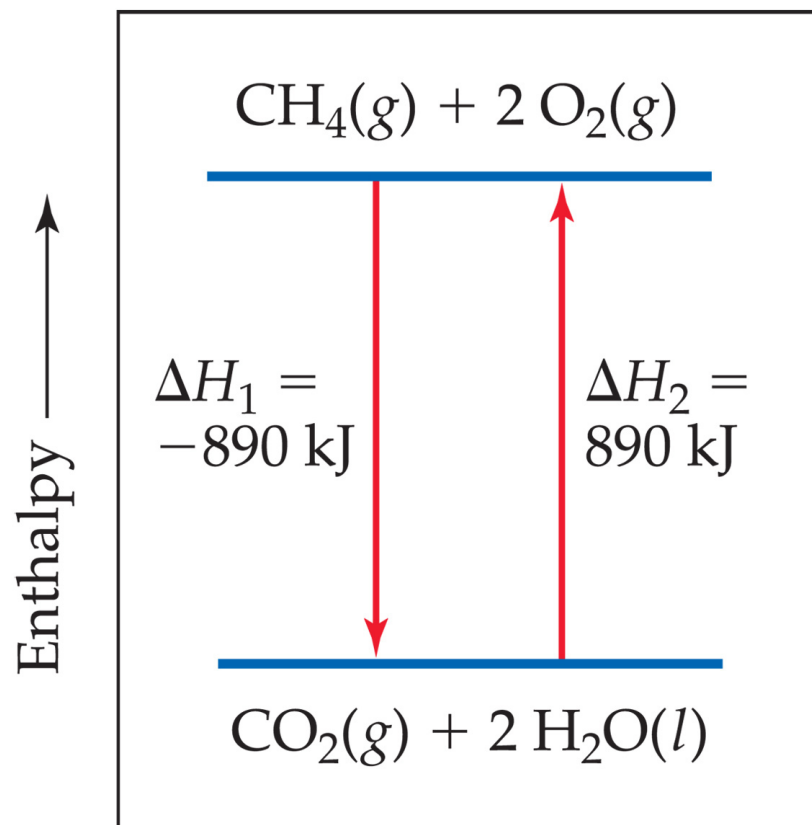
Since we cannot know the exact enthalpy of the reactants and products,

we measure ΔH through calorimetry, the measurement of heat flow.

Heat Capacity and Specific Heat

- **heat capacity:** amount of E required to raise the temperature of **an object, container, thing, etc.** by 1 K

- **specific heat:** amount of E required to raise the temperature of 1 g of a substance by 1 K.

Heat Capacity and Specific Heat

Specific heat is:

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

$$s = \frac{q}{m\,\Delta T}$$

$$sm\Delta T = q$$

Constant Pressure Calorimetry

Thermometer

Glass stirrer

Cork stopper

Two Styrofoam®
cups nested
together containing
reactants in solution
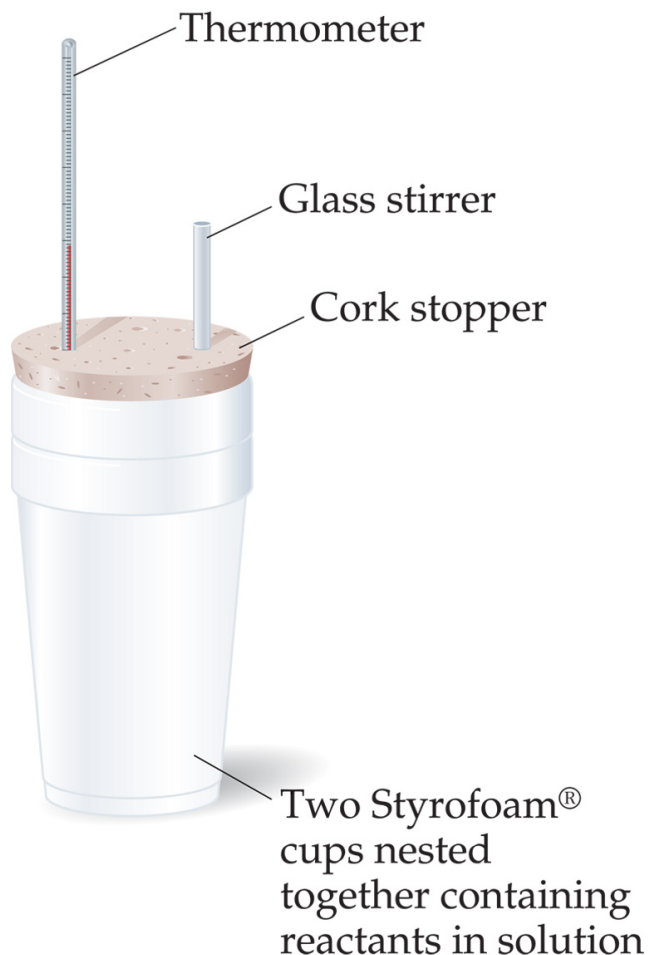
indirectly measure the heat change for the system by measuring the heat change for the water in the calorimeter.

Constant Pressure Calorimetry

Thermometer

Glass stirrer

Cork stopper

Two Styrofoam® cups nested together containing reactants in solution
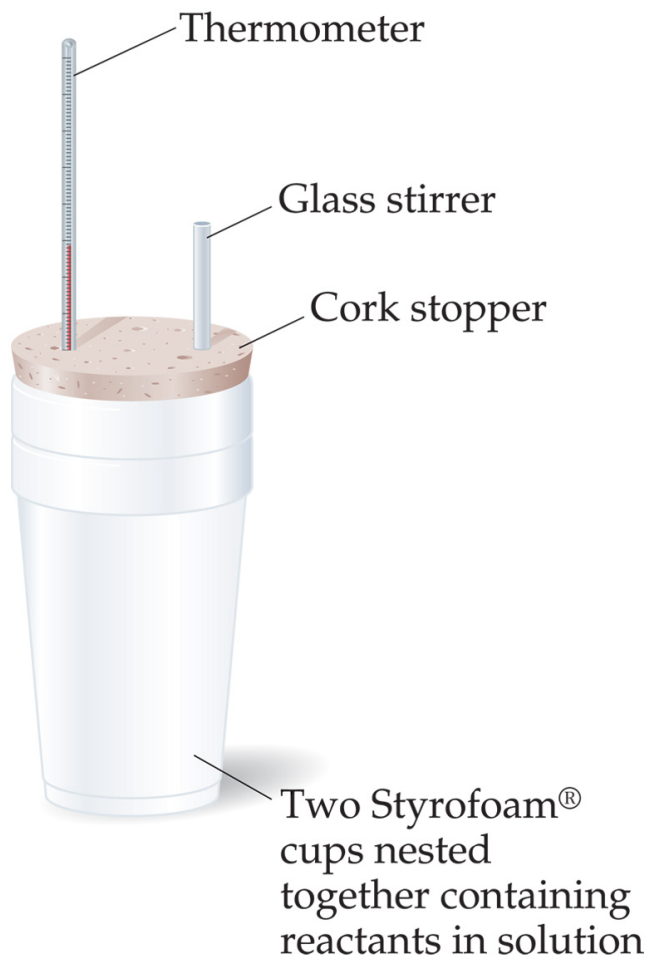
Because the specific heat for water is well known (4.184 J/g-K), we can measure ΔH for the reaction with this equation:

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

$m = mass$

$s = specific\ heat$

Example

Thermometer

Glass stirrer

Cork stopper

Two Styrofoam® cups nested together containing reactants in solution

When a 3.88 g sample of solid ammonium nitrate disolves in 60.0 g of water in a coffee cup calorimeter, the temperature drops from 23.0 ° C to 18.4 ° C. (a) Calculate ΔH (in kJ/mol ammonium nitrate) for the solution process. Assume that the specific heat is constant and = 4.184 J/° C g. (b) Is this process endothermic or exothermic?
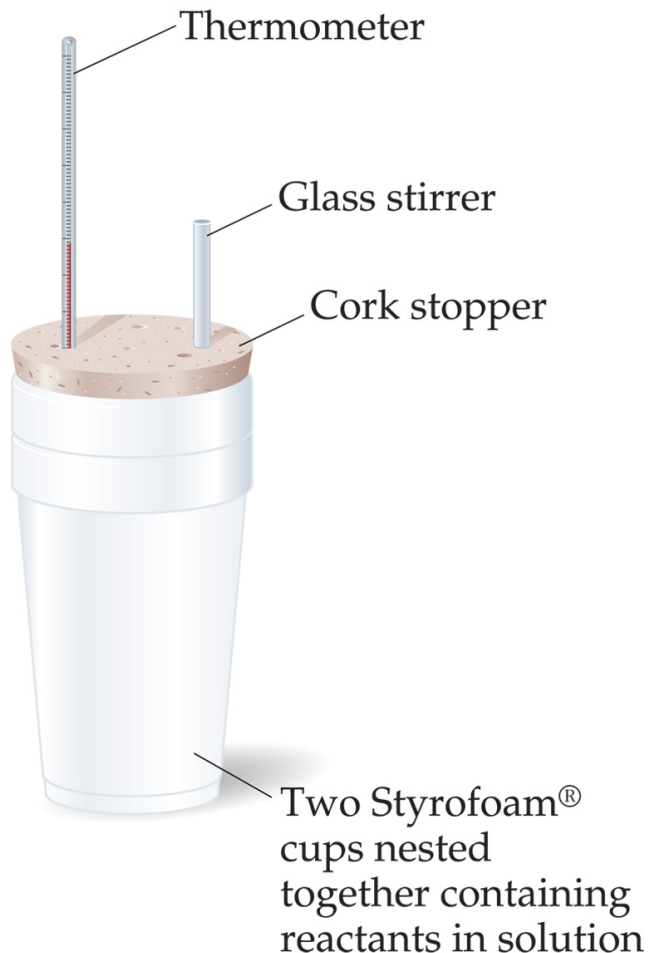
Example

When a 3.88 g sample of solid ammonium nitrate disolves in 60.0 g of water in a coffee cup calorimeter, the temperature drops from 23.0 water° C to 18.4 ° C. (a) Calculate ΔH (in kJ/mol ammonium nitrate) for the solution process. Assume that the specific heat is constant and = 4.184 J/g° C. (b) Is this process endothermic or exothermic?

Reaction:

$$NH_4NO_3(s) \quad ------> \quad NH_4^+(aq) + NO_3^-(aq)$$

gr   3.88 g

MW   80.04 g/mol

#Mol   3.88 g/80.04 g/mol = 0.0484 mol

Mass of solution = 3.88 g + 60 g = 63.88 g.

System: Solid AmNO$_3$

Surroundings: Solution (water AND NH$_4$NO$_3$)

Why? You are cooling BOTH the AND the dissolved **NH$_4$NO$_3$**

Example

When a 3.88 g sample of solid ammonium nitrate disolves in 60.0 g of water in a coffee cup calorimeter, the temperature drops from 23.0 ° C to 18.4 ° C. (a) Calculate ΔH (in kJ/mol ammonium nitrate) for the solution process. Assume that the specific heat is constant and = 4.184 J/g° C. (b) Is this process endothermic or exothermic?

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Mass of solution = 3.88 g + 60 g = 63.88 g.

System: Solid AmNO$_3$

Surroundings: Solution (water AND NH$_4$NO$_3$)

$q = sm\Delta T.$ (s= specific heat, m= mass ΔT=T change).

$q = s(J/g° C)m(grams)(T_{final} - T_{initial})$

$q_{solution}$ = 4.184(J/g ° C)(63.88 g)(18.4° C - 23.0° C) = -1229 J

q_{water}=-$q_{ammonium\ nitrate}$ = +1229 J

Example

When a 3.88 g sample of solid ammonium nitrate disolves in 60.0 g of water in a coffee cup calorimeter, the temperature drops from 23.0 $^\circ$ C to 18.4 $^\circ$ C. (a) Calculate ΔH (in kJ/mol ammonium nitrate) for the solution process. Assume that the specific heat is constant and = 4.184 J/g$^\circ$ C. (b) Is this process endothermic or exothermic?

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Surroundings: Solution (water AND NH$_4$NO$_3$)

q = s(specific heat)m(mass)ΔT

q = s(J/g$^\circ$ C)m(grams)(T_{final} - $T_{initial}$)

$q_{solution}$ = 4.184(J/g $^\circ$ C)(63.88 g)(18.4 $^\circ$ C - 23.0 $^\circ$ C) = -1229 J

q_{water}=-$q_{ammonium\ nitrate}$ = +1229 J

ΔH(per mol NH$_4$NO$_3$) = 1.229 kJ/.0484 mol = 25.39 kJ/mol

(b) Endothermic

Bomb Calorimetry

Reactions can be carried out separated from the water in a "bomb," such as this one,

And still measure the heat absorbed by the water.
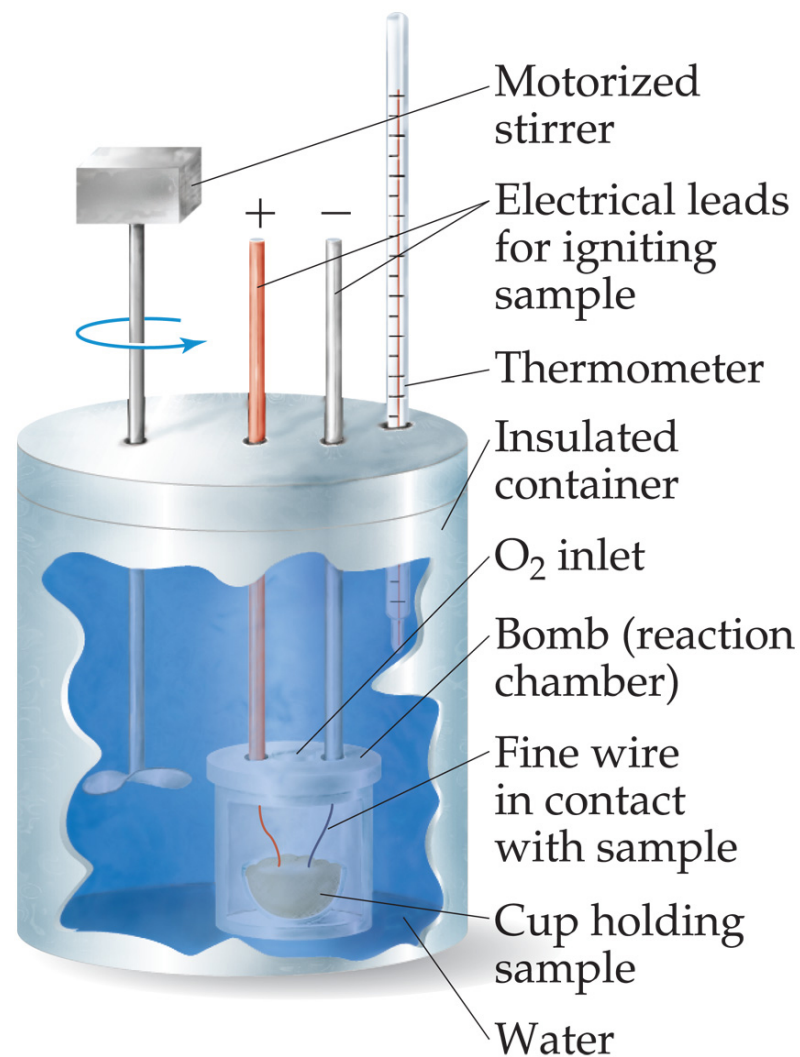
- Motorized stirrer
- Electrical leads for igniting sample
- Thermometer
- Insulated container
- O_2 inlet
- Bomb (reaction chamber)
- Fine wire in contact with sample
- Cup holding sample
- Water

Bomb Calorimetry

- Because the volume in the bomb calorimeter is constant, what is measured is really the ΔE, not ΔH.

- For most reactions,

- $\Delta E \approx \Delta H$

- *Why?*

Motorized stirrer

Electrical leads for igniting sample

Thermometer

Insulated container

O_2 inlet

Bomb (reaction chamber)

Fine wire in contact with sample

Cup holding sample

Water
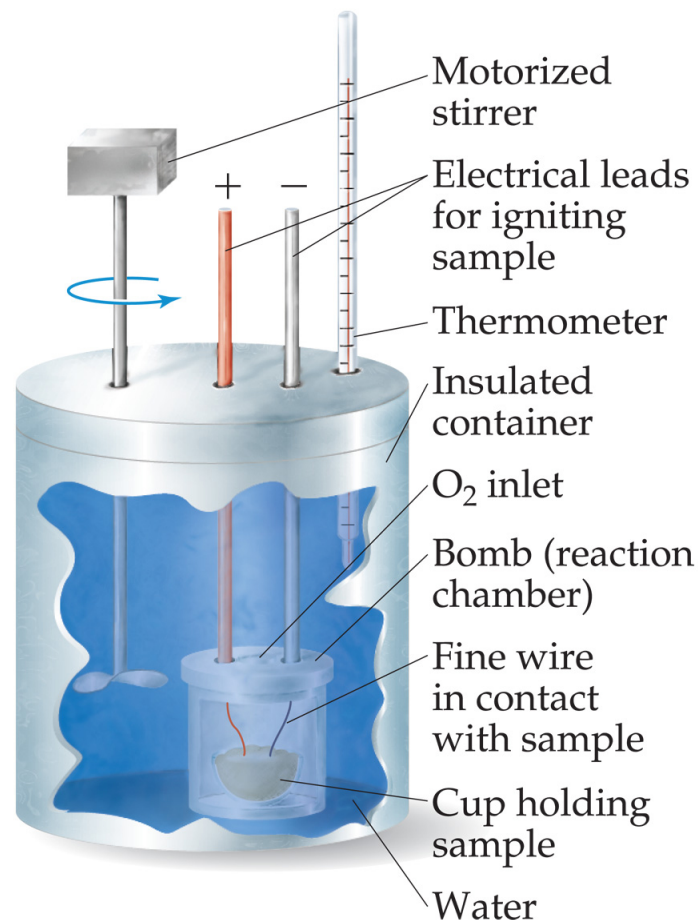
Bomb Calorimetry

- Because the volume in the bomb calorimeter is constant, what is measured is really the ΔE, not ΔH.

- For most reactions,

- $\Delta E \approx \Delta H$

- *Why?*

- *No work, no Volume change.*

- $\Delta E = q + w \approx \Delta H = \Delta E + \Delta PV$

Both 0, no V or P change.

Motorized stirrer

Electrical leads for igniting sample

Thermometer

Insulated container

O_2 inlet

Bomb (reaction chamber)

Fine wire in contact with sample

Cup holding sample

Water
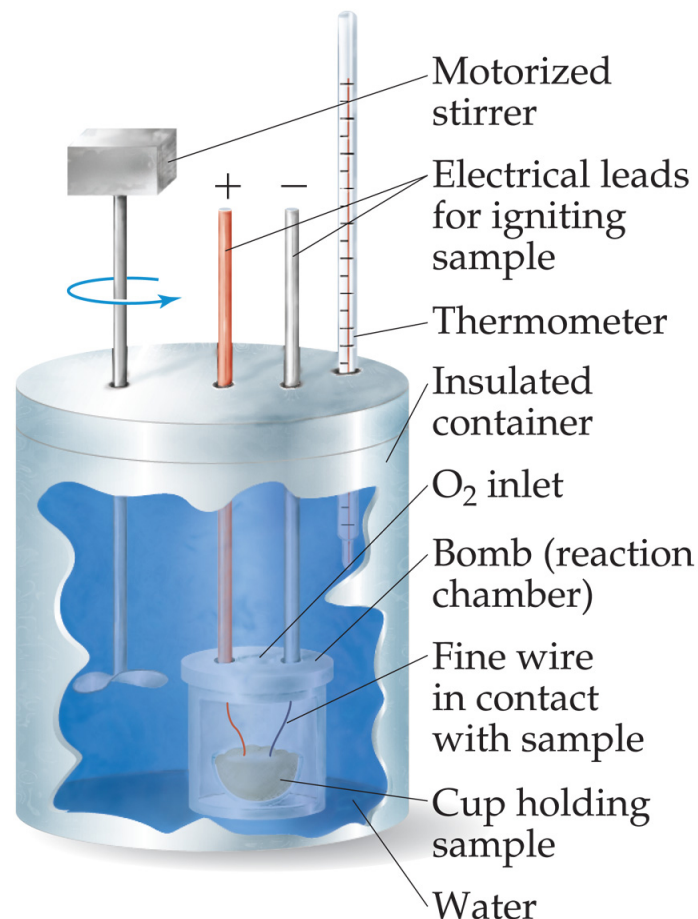
Bomb Calorimetry

$H = E + PV$

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

In a bomb calorimeter, $\Delta V = 0$
For a process that doesn't evolve gas:
$\Delta P \approx 0$ as well.

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

Example

- A 50 g sample of gasoline was burned by combustion (with excess oxygen) in a calorimeter with a heat capacity of 10 kJ/°C. The temperature increased by 100°C. Calculate the change in E per g of gasoline.

- $q_{surroundings} = C\Delta T = 10$ kJ/°C(100°C) = 1000 kJ

- $q_{surroundings} = -q_{system}$

- $\quad\quad q_{system} = -1000$

- -1000 kJ/50g = -20 kJ/g

- **Does** $\Delta E = \Delta H$ in this case?

Example

- A 50 g sample of gasoline was burned by combustion (with excess oxygen) in a calorimeter with a heat capacity of 10 kJ/°C. The temperature increased 100°C. Calculate the change in E per g of gasoline.

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- $q_{system} = -1000$

- -1000 kJ/50g = -20 kJ/g

- **Does** $\Delta E = \Delta H$ in this case?

- **NO! Pressure can't stay constant in this case.**

Hess's Law

- $\Delta H = \Delta E + \Delta PV = q_P$
- ΔH is known for many reactions.
- measuring ΔH can be a pain
- Can we estimate ΔH using ΔH values for other reactions?

Hess's Law

CH$_4$(g) + 2 O$_2$(g)

$\Delta H_2 = -607$ kJ

$\Delta H_1 = -890$ kJ

CO(g) + 2 H$_2$O(l) + $\frac{1}{2}$O$_2$(g)

$\Delta H_3 = -283$ kJ

CO$_2$(g) + 2 H$_2$O(l)
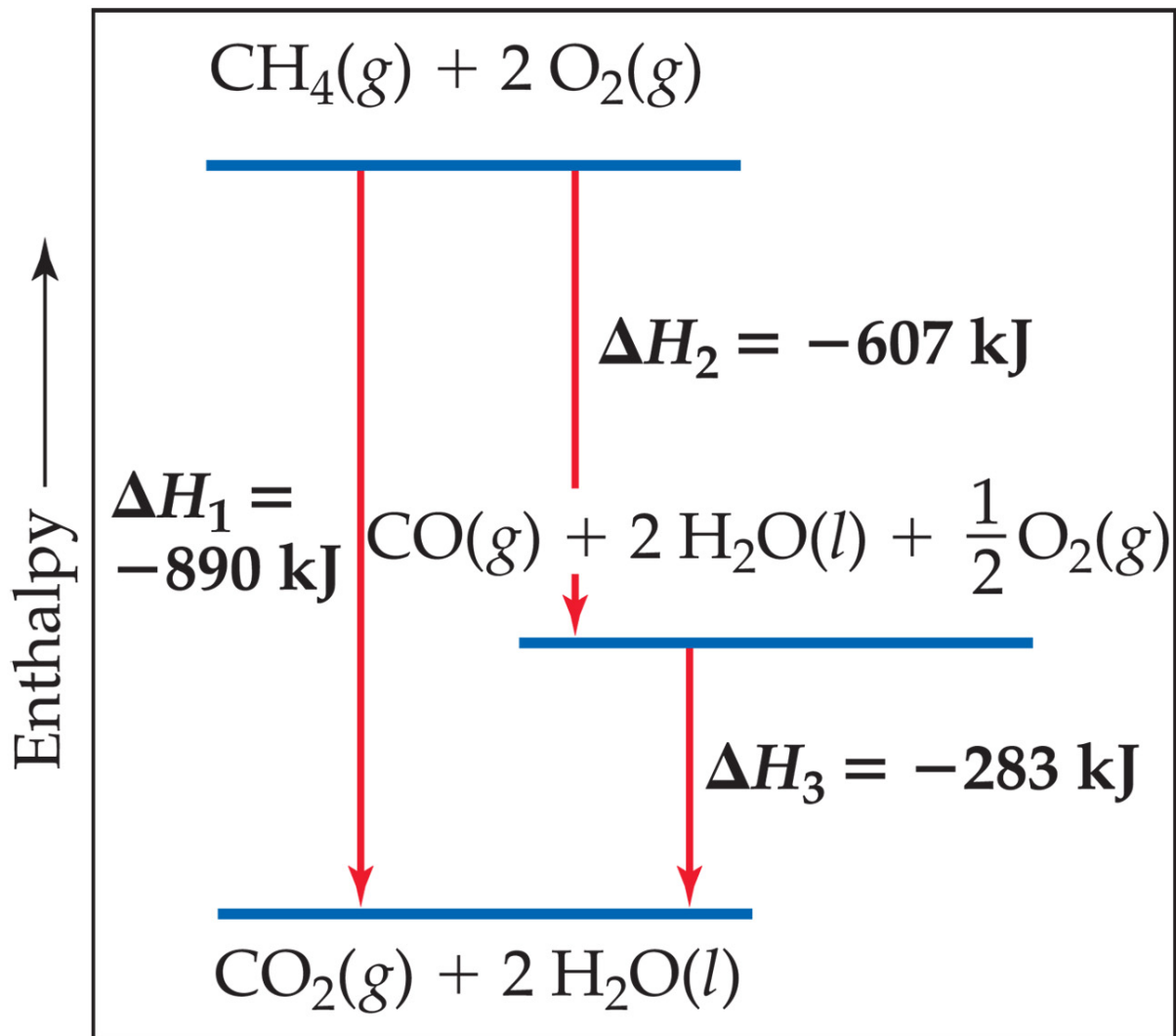
Enthalpy

Yes!

Hess's law: states that:

ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps.

Hess's Law

Why?

Because ΔH is a state function, and is pathway independent.

Only depends on initial state of the reactants and the final state of the products.
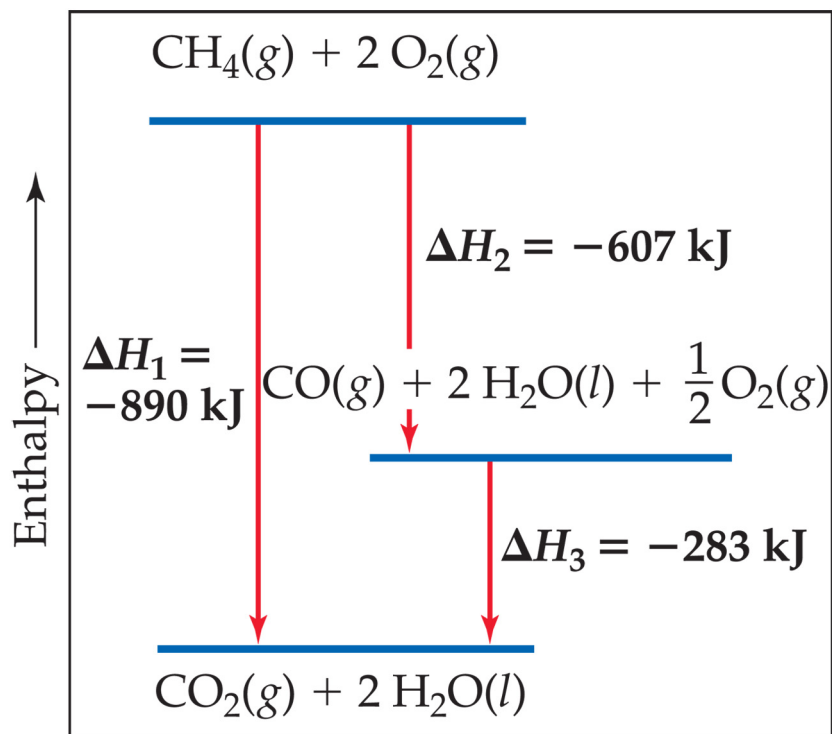
A series of chemical reactions is a **path.**

start with the same reactants

end up with the same products, ΔH is the same.

because it's a state function.

CH$_4(g)$ + 2 O$_2(g)$

$\Delta H_2 = -607$ kJ

$\Delta H_1 = -890$ kJ

CO(g) + 2 H$_2$O(l) + $\frac{1}{2}$O$_2(g)$

$\Delta H_3 = -283$ kJ

CO$_2(g)$ + 2 H$_2$O(l)

Enthalpy

Hess's law, example:

- Given:
- $N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta H = 180.7$ kJ
- $2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H = -113.1$ kJ
- $2N_2O(g) \longrightarrow 2N_2(g) + O_2(g) \quad \Delta H = -163.2$ kJ
- use Hess's law to calculate ΔH for the reaction:
- $N_2O(g) + NO_2(g) \longrightarrow 3NO(g)$

- How do you think through this?
- What do I need on left side of the arrow? $N_2O(g)$ and $NO_2(g)$
- What do I need on the right side of the arrow? $3NO(g)$

Hess's law, example:
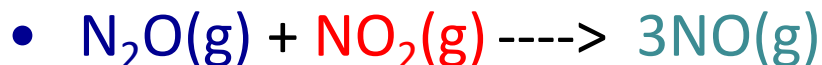
- Given:

- $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\Delta H = \quad 180.7 \text{ kJ}$

- $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\Delta H = \quad -113.1 \text{ kJ}$

- $2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$ $\Delta H = \quad -163.2 \text{ kJ}$

- use Hess's law to calculate ΔH for the reaction:

- $N_2O(g) + NO_2(g) \longrightarrow 3NO(g)$

- $N_2O(g) \longrightarrow \cancel{N_2(g)} + \cancel{1/2O_2(g)}$ $\Delta H = -163.2/2 = -81.6 \text{kJ}$
- $NO_2(g) \longrightarrow NO(g) + \cancel{1/2O_2(g)}$ $\Delta H = 113.1 \text{ kJ}/2 = 56.6 \text{kJ}$
- $\cancel{N_2(g)} + \cancel{O_2(g)} \longrightarrow 2NO(g)$ $\Delta H = \quad\quad 180.7$

- $N_2O(g) + NO_2(g) \longrightarrow 3NO(g)$ $\Delta H = \quad\quad 155.7 \text{ kJ}$

Enthalpies of Formation

An enthalpy of formation, ΔH_f, is defined as the ΔH for the reaction in which a compound is made from its constituent elements in their ***most stable*** elemental forms.

- $2Al_{(s)} + Fe_2O_{3(s)} \text{-------> } Al_2O_{3(s)} + 2Fe_{(s)}$

- What is the heat of reaction given:
- $2Fe_{(s)} + 3/2O_{2(g)} \text{-----> } Fe_2O_{3(s)} \quad \Delta H = -825.5 \text{ KJ (heat of formation } Fe_2O_{3(s)})$
- $2Al_{(s)} + 3/2O_{2(g)} \text{-----> } Al_2O_{3(s)} \quad \Delta H = -1675.7 \text{ KJ (heat of formation } Al_2O_{3(s)})$

Enthalpies of Formation

An enthalpy (heat) of formation, ΔH_f, is defined as the ΔH for the reaction in which a compound is made from its constituent elements in their *most stable* elemental forms.

- $2Al_{(s)} + Fe_2O_{3(s)} \text{-------}> Al_2O_{3(s)} + 2Fe_{(s)}$

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- $2Fe_{(s)} + 3/2O_{2(g)} \text{----->} Fe_2O_{3(s)} \quad \Delta H = -825.5$ KJ (heat of formation)
- $2Al_{(s)} + 3/2O_{2(g)} \text{----->} Al_2O_{3(s)} \quad \Delta H = -1675.7$ KJ (heat of formation)

- $2Al_{(s)} + 3/2O_{2(g)} \text{----->} Al_2O_{3(s)} \quad \Delta H = -1675.7$ KJ (heat of formation)
- $Fe_2O_{3(g)} \text{----->} 2Fe_{(s)(} + 3/2O_{2(s)} \quad \Delta H = 825.5$ kJ

- $2Al_{(s)} + Fe_2O_{3(s)} \text{------->} Al_2O_{3(s)} + 2Fe_{(s).} \quad \Delta H = -850.2$ kJ
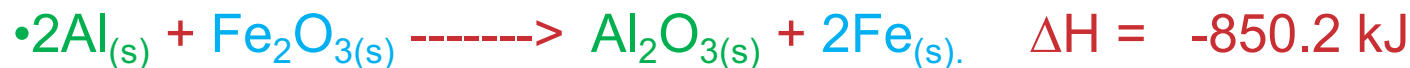
Enthalpies of Formation

An enthalpy of formation, ΔH_f, is defined as the ΔH for the reaction in which a compound is made from its constituent elements in their ***most stable*** elemental forms.

In other words, a reaction like these:

$$H_{2(g)} + 1/2 O_{2(g)} \text{ --}\rightarrow H_2O_{(g)}$$

$$2C_s + O_2(g) + 2H_2(g) \text{ ---} \rightarrow C_2H_4O_{2(l)}$$
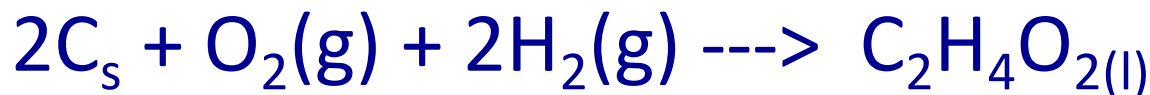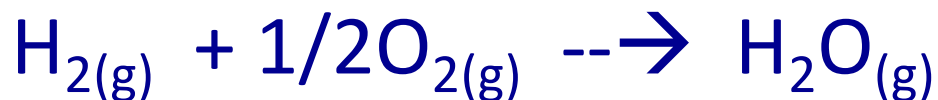
Elements in their most stable forms:

- $H_{2(g)}$, $N_{2(g)}$, $O_{2(g)}$, $F_{2(g)}$, $Cl_{2(g)}$
- $Br_{2(l)}$, $I_{2(s)}$
- All metals (except Hg): M(s)
- Hg(l)
- All other nonmetals: N(s) example: S(s), Si(s)

Calculation of ΔH
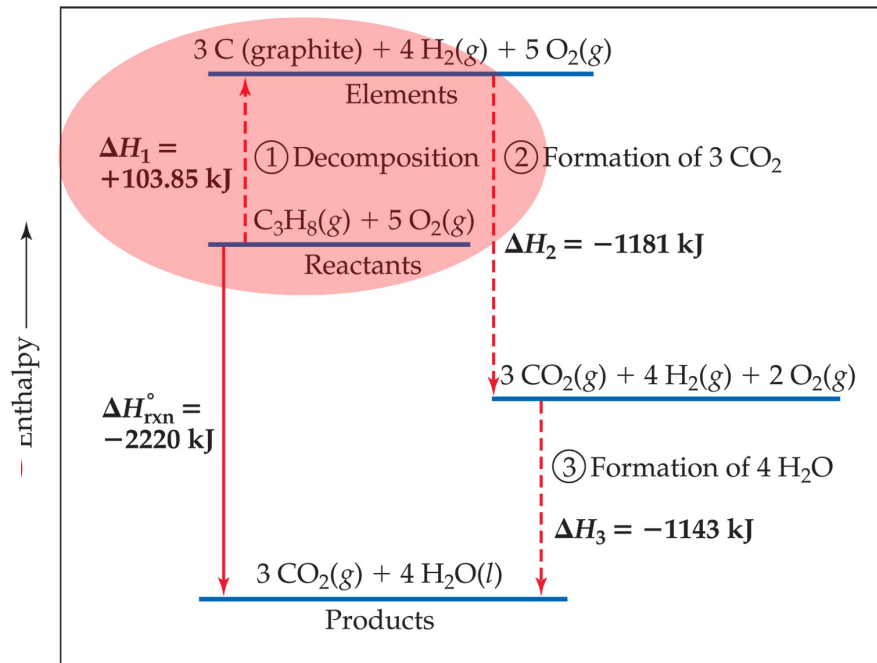
$$C_3H_8 \ (g) + 5 \ O_2 \ (g) \longrightarrow 3 \ CO_2 \ (g) + 4 \ H_2O \ (l)$$

- Imagine this as occurring in 3 steps:

$$C_3H_8 \ (g) \longrightarrow 3 \ C_{(graphite)} + 4 \ H_2 \ (g)$$

Enthalpy diagram:

3 C (graphite) + 4 H$_2$(g) + 5 O$_2$(g) — Elements

$\Delta H_1 = +103.85$ kJ

① Decomposition   ② Formation of 3 CO$_2$

C$_3$H$_8$(g) + 5 O$_2$(g) — Reactants

$\Delta H_2 = -1181$ kJ

3 CO$_2$(g) + 4 H$_2$(g) + 2 O$_2$(g)

③ Formation of 4 H$_2$O

$\Delta H_3 = -1143$ kJ

$\Delta H^{\circ}_{rxn} = -2220$ kJ

3 CO$_2$(g) + 4 H$_2$O(l) — Products

Calculation of ΔH

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

- Imagine this as occurring in 3 steps:

$$C_3H_8\,(g) \longrightarrow 3\,C_{(graphite)} + 4\,H_2\,(g)$$

$$3\,C_{(graphite)} + 3\,O_2\,(g) \longrightarrow 3\,CO_2\,(g)$$

Calculation of ΔH

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

- Imagine this as occurring in 3 steps:

$$C_3H_8\,(g) \longrightarrow 3\,C_{(graphite)} + 4\,H_2\,(g)$$

$$3\,C_{(graphite)} + 3\,O_2\,(g) \longrightarrow 3\,CO_2\,(g)$$

$$4\,H_2\,(g) + 2\,O_2\,(g) \longrightarrow 4\,H_2O\,(l)$$

Calculation of ΔH

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$
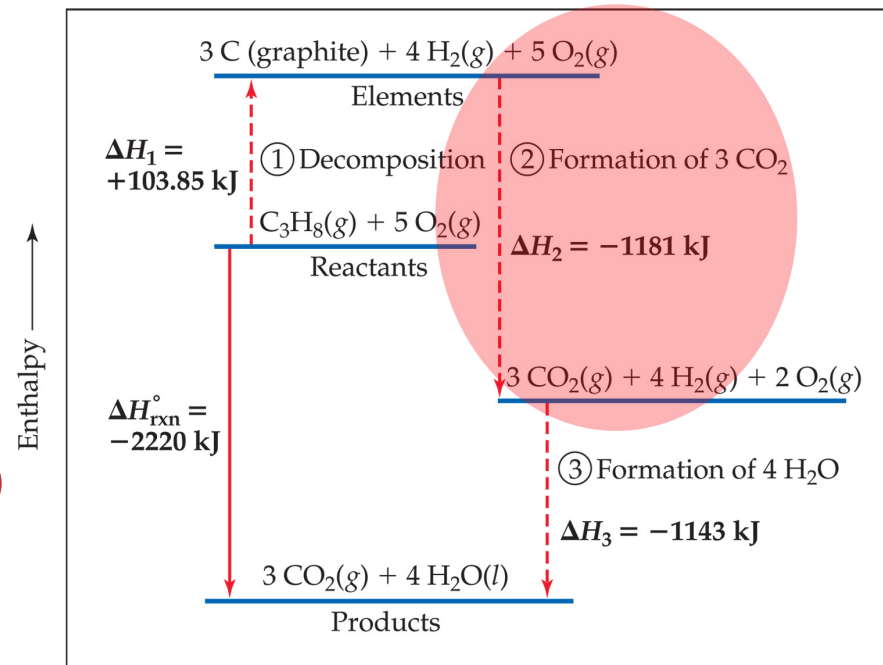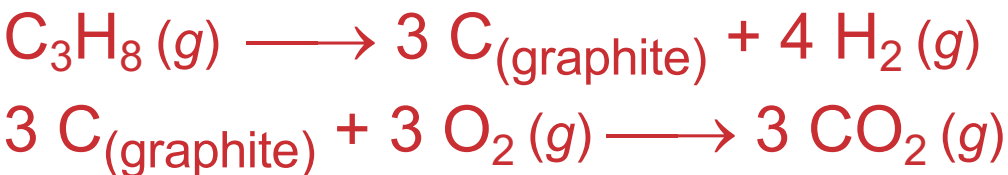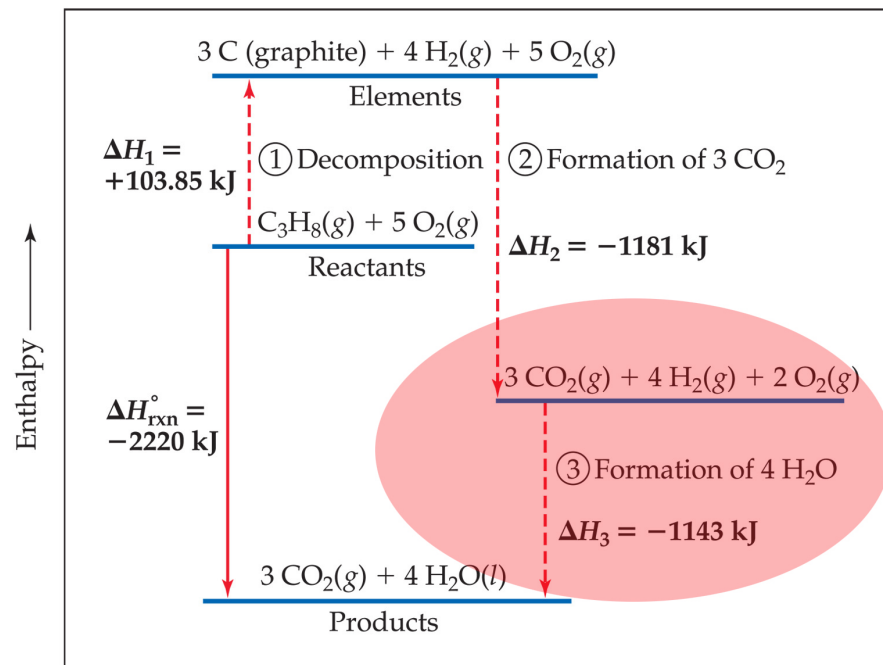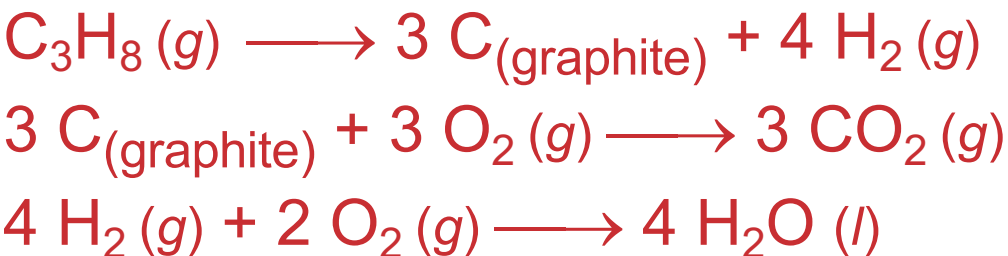
- The sum of these equations is:

$C_3H_8\,(g) \longrightarrow 3\,C_{(graphite)} + 4\,H_2\,(g)$

$3\,C_{(graphite)} + 3\,O_2\,(g) \longrightarrow 3\,CO_2\,(g)$

$4\,H_2\,(g) + 2\,O_2\,(g) \longrightarrow 4\,H_2O\,(l)$

$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$
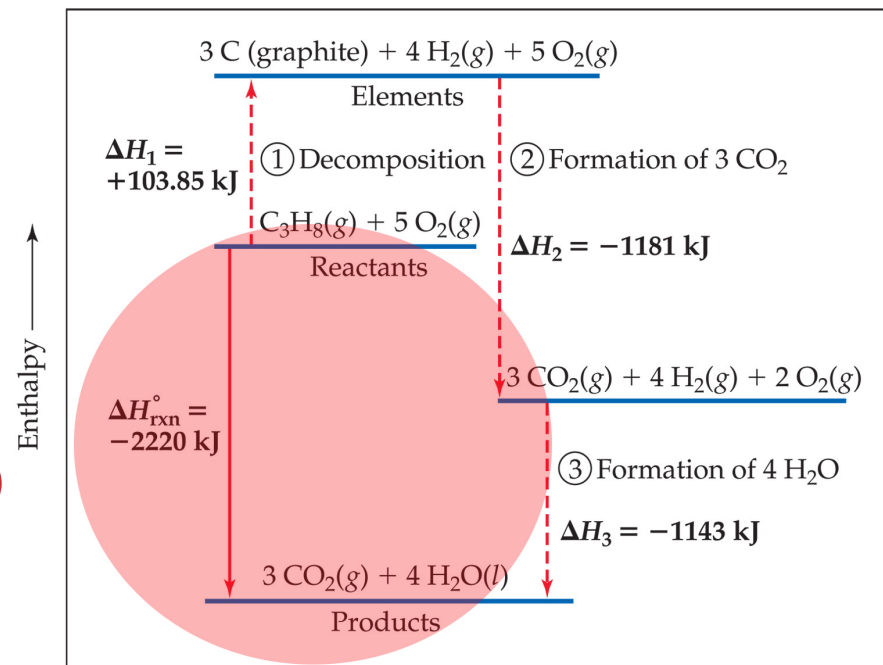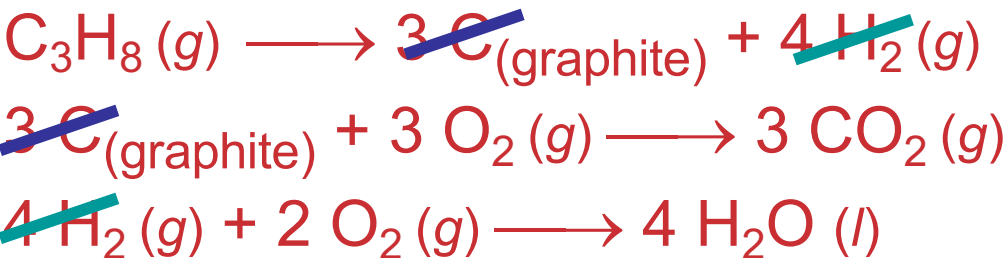
Make each reactant or product from its elements
This is called the heat of formation of a compound

Calculation of ΔH

We can use Hess's law in this way:

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

where n and m are the stoichiometric coefficients.

Standard Enthalpies of Formation

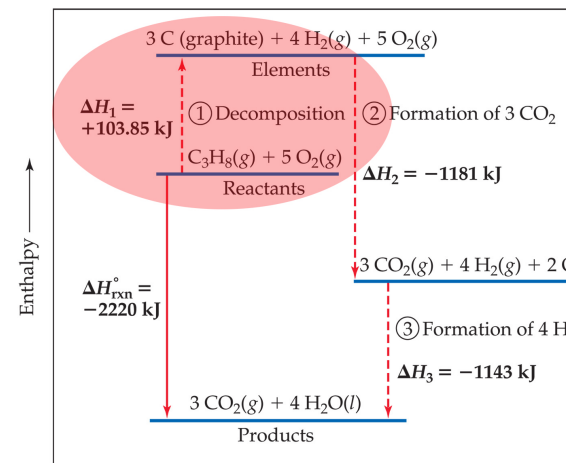Standard enthalpies of formation, ΔH_f°, are measured under standard conditions (25° C and 1.00 atm pressure).

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	$Na_2CO_3(s)$ 1	− 130.9
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

Calculation of ΔH

- Calculate ΔH using the table:
- $C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O(l)$

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Calculation of ΔH

- $C_3H_{8(g)} + 5\ O_{2(g)} \ \text{-----}> 3CO_{2(g)} + 4H_2O_{(l)}$

$\Delta H = [3(\Delta H_f CO_{2(g)}) + 4(\Delta H_f H_2O_{(l)})] - [(\Delta H_f\ C_3H_{8(g)}) + (5\Delta H_f\ O_{2(g)})]$

$= [3(-393.5\ \text{kJ}) + 4(-285.8\ \text{kJ})] - [(-103.85\ \text{kJ}) + 5(0)]$

$= [-1180.5\ \text{kJ} + (-1143.2\ \text{kJ})] - [(-103.85\ \text{kJ}) + 0\ \text{kJ}]$

$= [-2323.7\ \text{kJ}] - [-103.85\ \text{kJ})]$

$= -2219.9\ \text{kJ}$
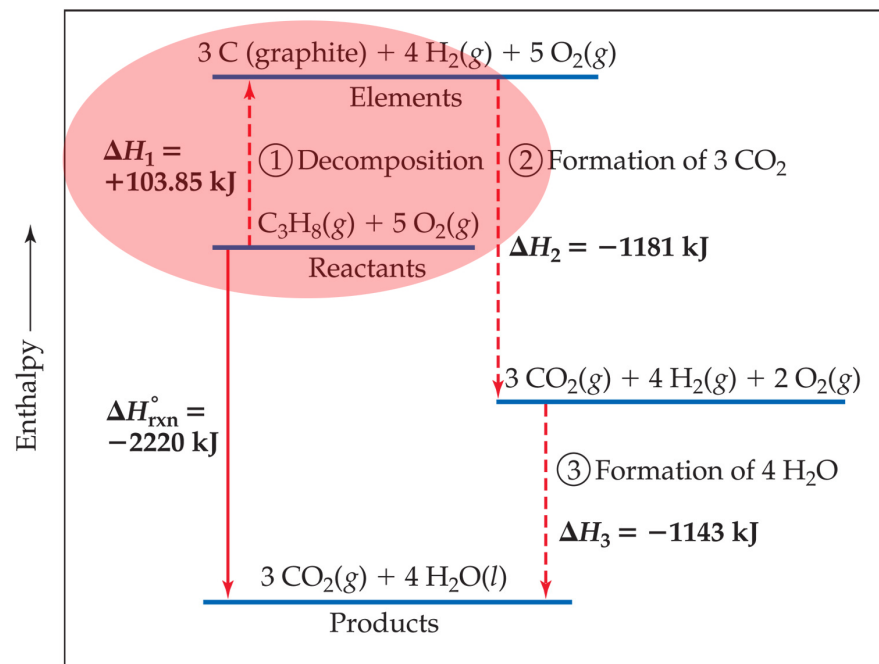
The Nobel Prize in Chemistry 2020
Jennifer Doudna,
Emmanuelle Charpentier

CRISPR

What is CRISPR?

The Nobel Prize in Chemistry 2020
Jenifer Doudna,
Emmanuelle Charpentier

CRISPR

What is CRISPR?

- CRISPR:
  - **C**lustered, **R**egularly **I**nterspaced **P**alindromic **R**epeats.
  - Originally observed as a weird DNA sequence in bacteria. Who cares? So what?
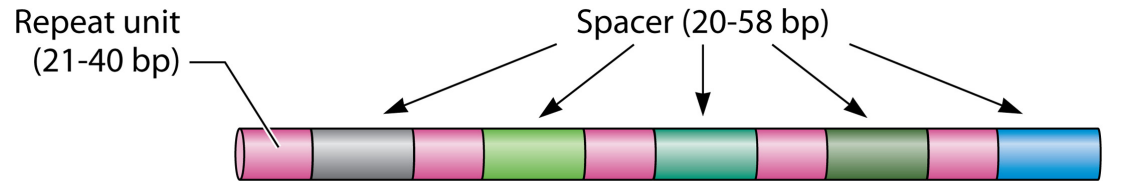
1.Ishino Y, Shinagawa H, Makino K, Amemura M, Nakata A. 1987. Nucleotide sequence of the *iap* gene, responsible for alkaline phosphatase isozyme conversion in *Escherichia coli*, and identification of the gene product. J Bacteriol 169:5429 –5433.

Observation 1 1987

Repeat unit
(21-40 bp)

Spacer (20-58 bp)

E. coli (1987)

→   ←

CGGTTTATCCCCGCTGCGCGGGGAACTC

H. mediterranei (1993)

→   ←

GTTACAGACGAACCCTAGTTGGGTTGAAGC

```
        G
      T   C
      C•G
      G•C
      C•G
      C•G
      C•G
      C•G
      T•A
GCCTTT  A   A CTC
```

```
        G
      A•T
      T   T
      C•G
      C•G
      C•G
      A•T
      A•T
GTTACAGACG   A   GAAGC
```

- ## CRISPR:

  ➢ **C**lustered,**R**egularly **I**nterspaced **P**alindromic **R**epeats. Data, just DNA sequence.

1.Ishino Y, Shinagawa H, Makino K, Amemura M, Nakata A. 1987. Nucleotide sequence of the *iap* gene, responsible for alkaline phosphatase isozyme conversion in *Escherichia coli*, and identification of the gene product. J Bacteriol 169:5429 –5433.

Observation 2 2005

Repeat unit
(21-40 bp)

Spacer (20-58 bp)

E. coli (1987)

CGGTTTATCCCCGCTGCGCGGGGAACTC

H. mediterranei (1993)

GTTACAGACGAACCCTAGTTGGGTTGAAGC

```
       G
      T C
      C•G
      G•C
      C•G
      C•G
      C•G
      C•G
      T•A
GCCTTT A  A CTC
```
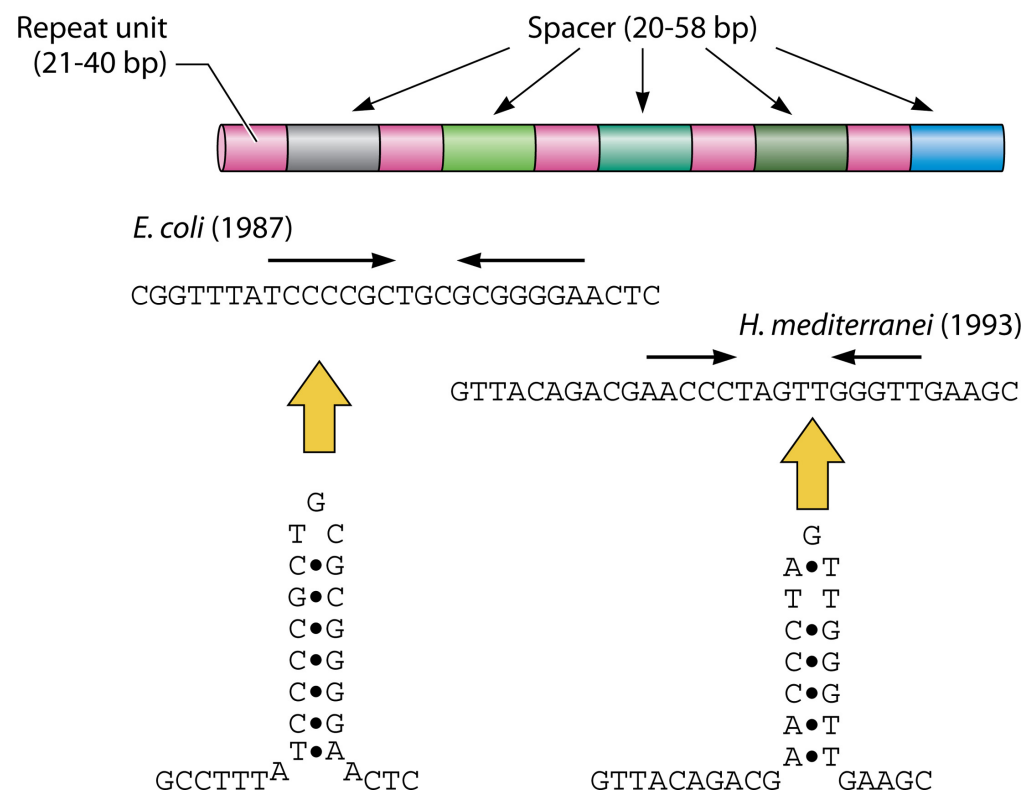
```
       G
      A•T
      T T
      C•G
      C•G
      C•G
      A•T
      A•T
GTTACAGACG  GAAGC
```

- Spacer regions found to match sequences of viruses and plasmids.

that infect bacteria

- **Bacteria that harbor a certain bacteriophage DNA are resistant to that bacteriophage!!!**
- **A bacterial immune system.**

1.Mojica FJM, Díez-Villaseñor C, García-Martínez J, Soria E. 2005. Intervening sequences of regularly spaced prokaryotic repeats derive from for- eign genetic elements. J Mol Evol 60:174–182.

The mechanism of adaptive immunity

CAS1 and 2.
Invading DNA recognized by Cas proteins
Chopped up and stuck into spacer regions
Now stored in genome passed on

1 Repeat and spacer DNA transcribed
(RNA made from DNA)
2. Chopped up into units of
1 repeat, one spacer (CrRNA)

3. Cas9 binds CrRNA. Chops DNA
That matches that sequence.
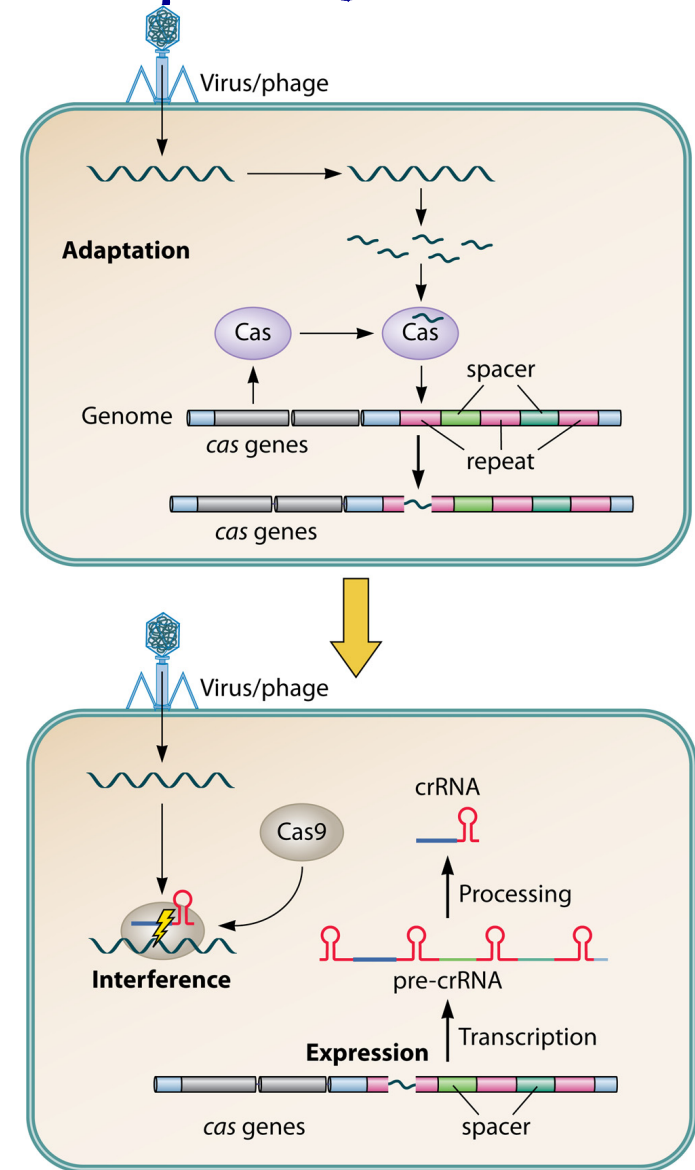Kill invading viruses DNA.

FIG 4 Process of CRISPR-Cas acquired immune system. (Top) Adaptation. The invading DNA is recognized by Cas proteins, fragmented and incorporated into the spacer region of CRISPR, and stored in the genome. Expression (bottom). Pre-crRNA is generated by transcription of the CRISPR region and is processed into smaller units of RNA, named crRNA. (Bottom) Interference. By taking advantage of the homology of the spacer sequence present in crRNA, foreign DNA is captured, and a complex with Cas protein having nuclease activity cleaves DNA.

Gene Editing

If you can specifically cut a genome
in a living cell….
You can edit it anyway you want.
If you do it to the germ line (egg, sperm)
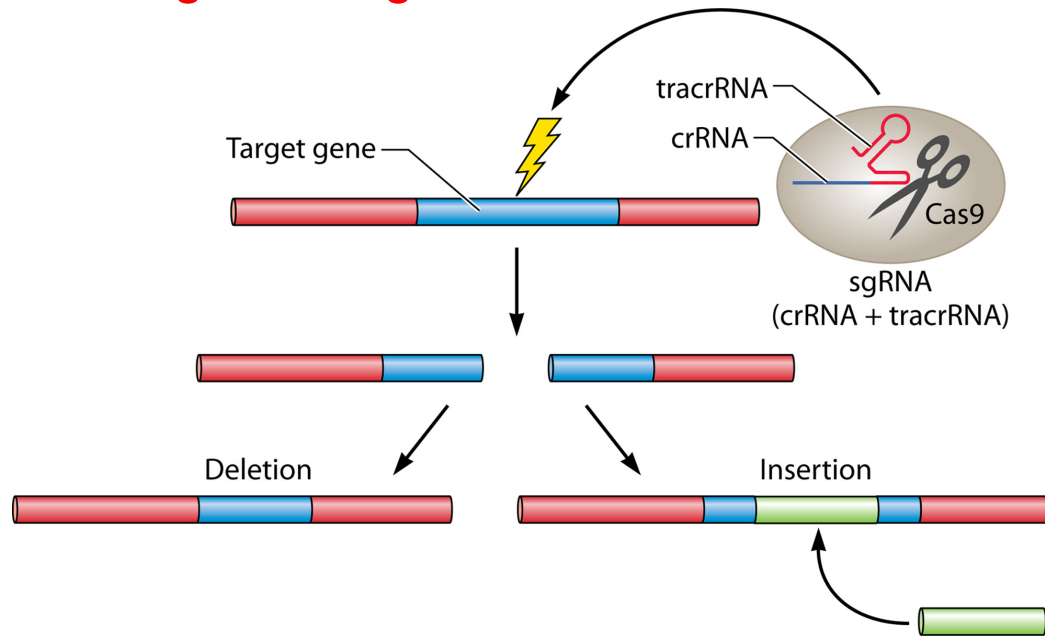You change the organism forever.

FIG 5 Genome editing by CRISPR-Cas9. The principle of genome editing is the cleavage of double-stranded DNA at a targeted position on the genome. The type II is the simplest as a targeted nuclease among the CRISPR-Cas systems. The CRISPR RNA (crRNA), having a sequence homologous to the target site, and *trans*-activating CRISPR RNA (tracrRNA) are enough to bring the Cas9 nuclease to the target site. The artificial linkage of crRNA and tracrRNA into one RNA chain (single-guide RNA [sgRNA]) has no effect on function. Once the Cas9-sgRNA complex cleaves the target gene, it is easy to disrupt the function of the gene by a deletion or insertion mutation. This overwhelmingly simple method is now rapidly spreading as a practical genomic editing technique.

Phase Changes
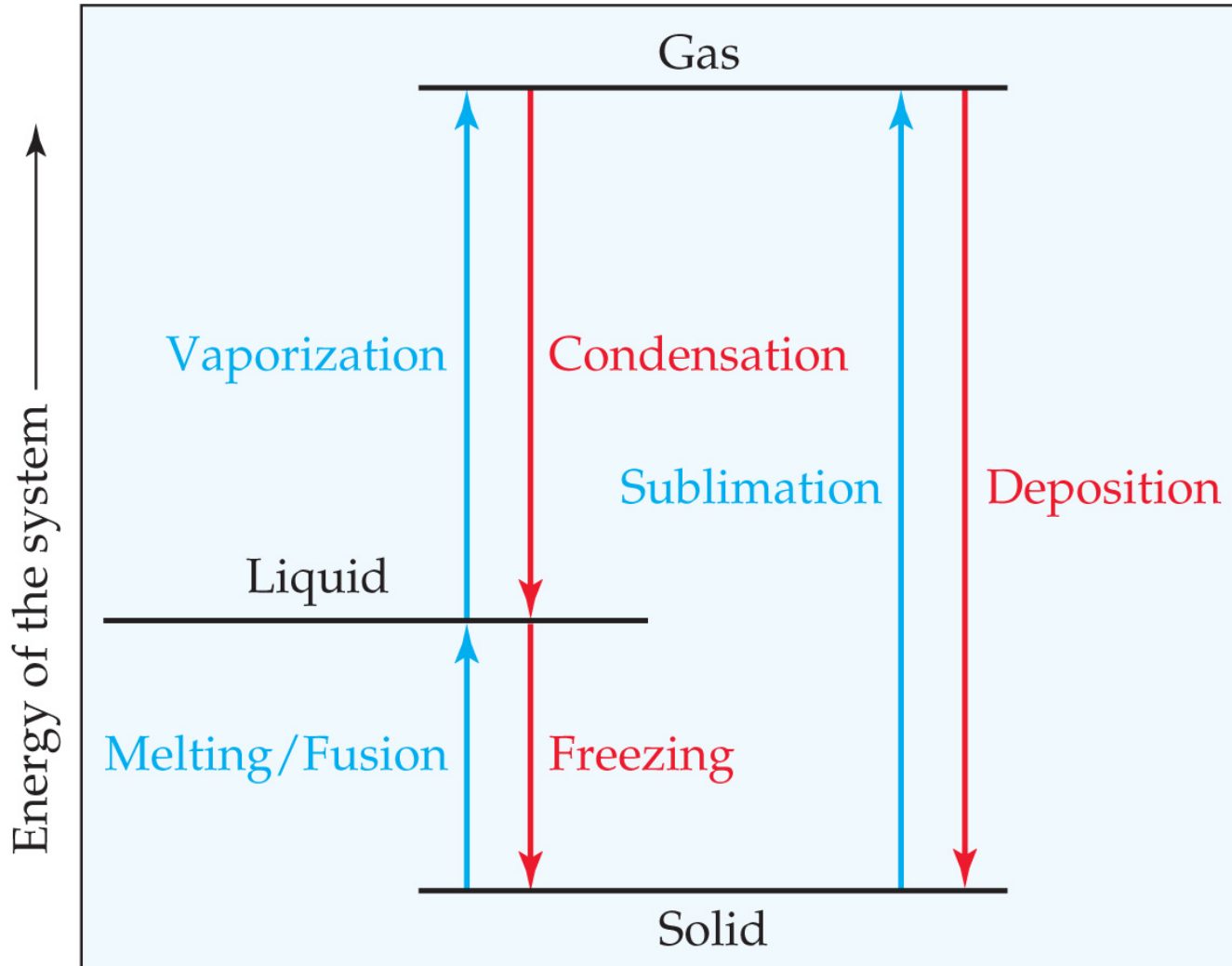
Conversion from one state of matter to another is a **phase change**.

Energy is either added or released in a phase change.

Why is E (Q,H) transferred in phase change?

- Atoms/molecules
  - ➤ **stick** to each other in liquid/solid always stick more in solid.
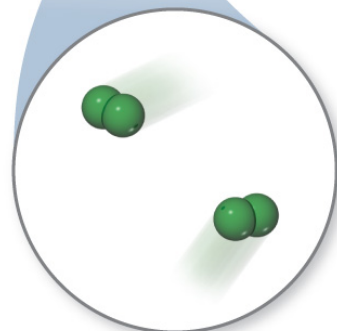 - ➤ Atoms/molecules **don't touch** in **gas**.
- Solid to liquid
  - ➤ Heat added to unstick.
- Liquid to gas,
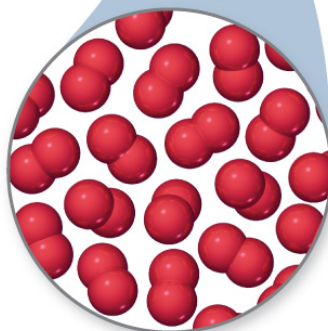 - ➤ E is needed to pull the atoms/molecules from each other.

Strength of intermolecular attractions increasing →

Gas

Liquid

Crystalline solid

Chlorine, Cl_2

Bromine, Br_2

Iodine, I_2

Particles far apart; possess complete freedom of motion
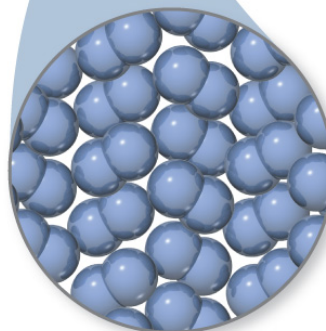
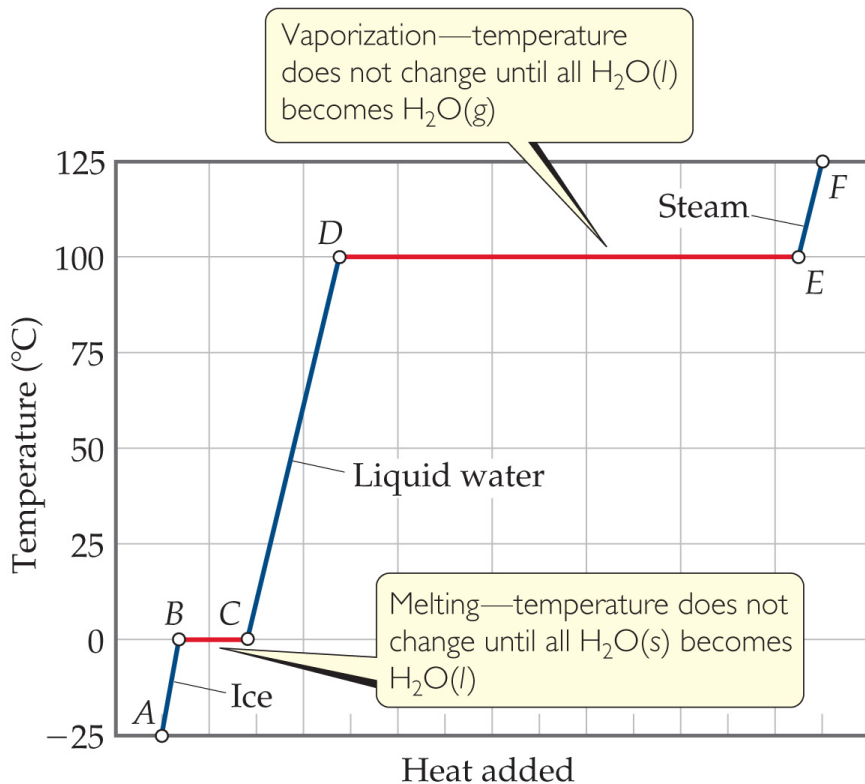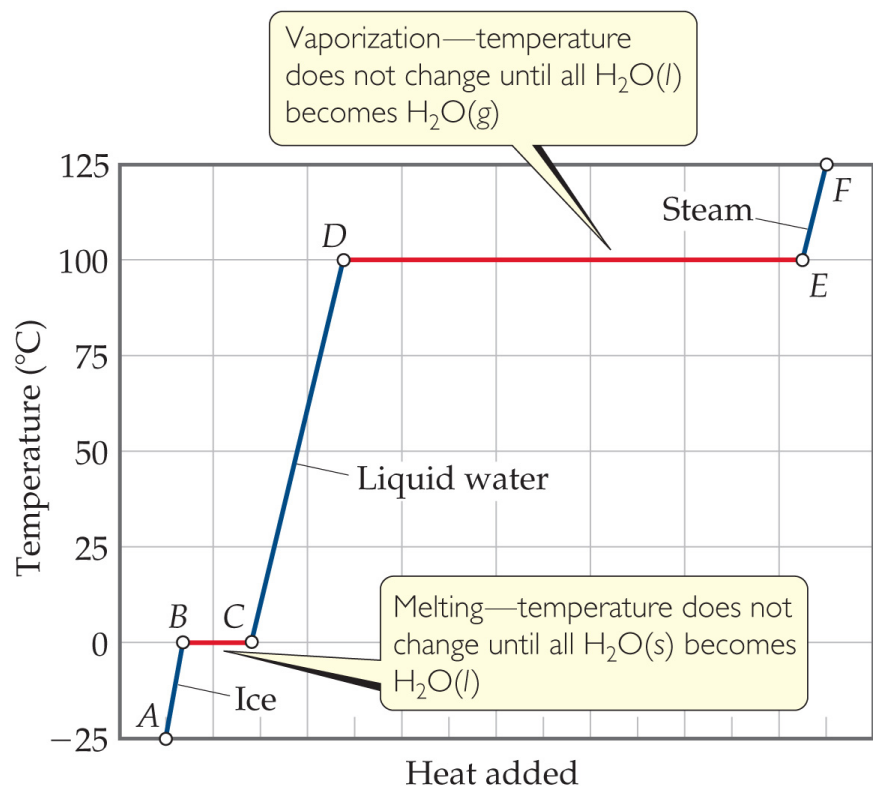Particles are closely packed but randomly oriented; retain freedom of motion; rapidly change neighbors

Particles are closely packed in an ordered array; positions are essentially fixed

Heating Curves

- A plot of T vs. q
- Within a phase:
- q= ms
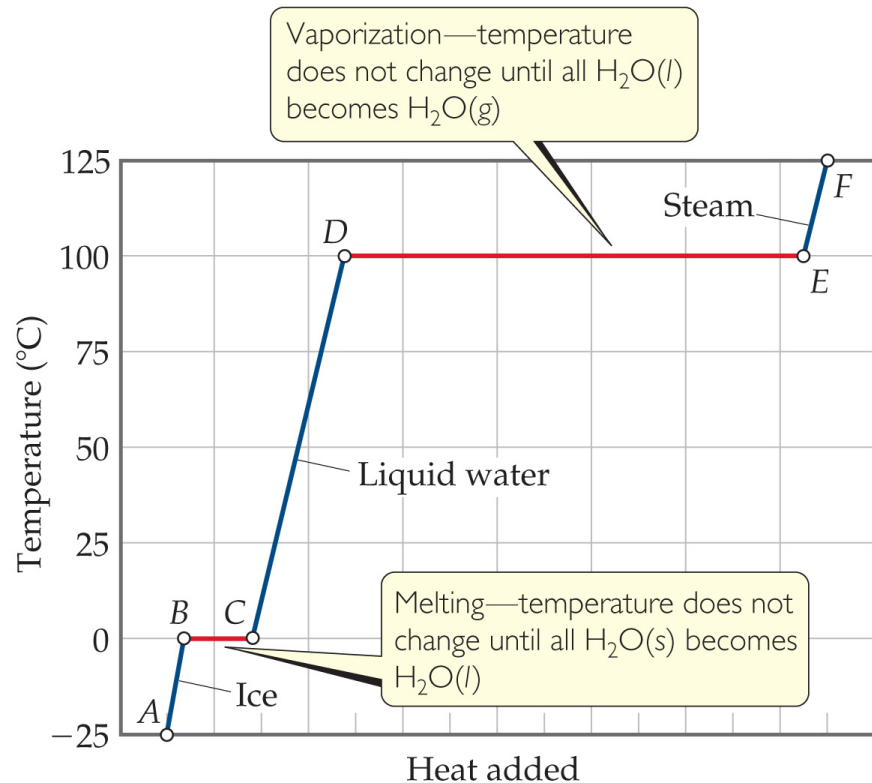- The temperature of the substance does not rise during a phase change.

Heating Curves
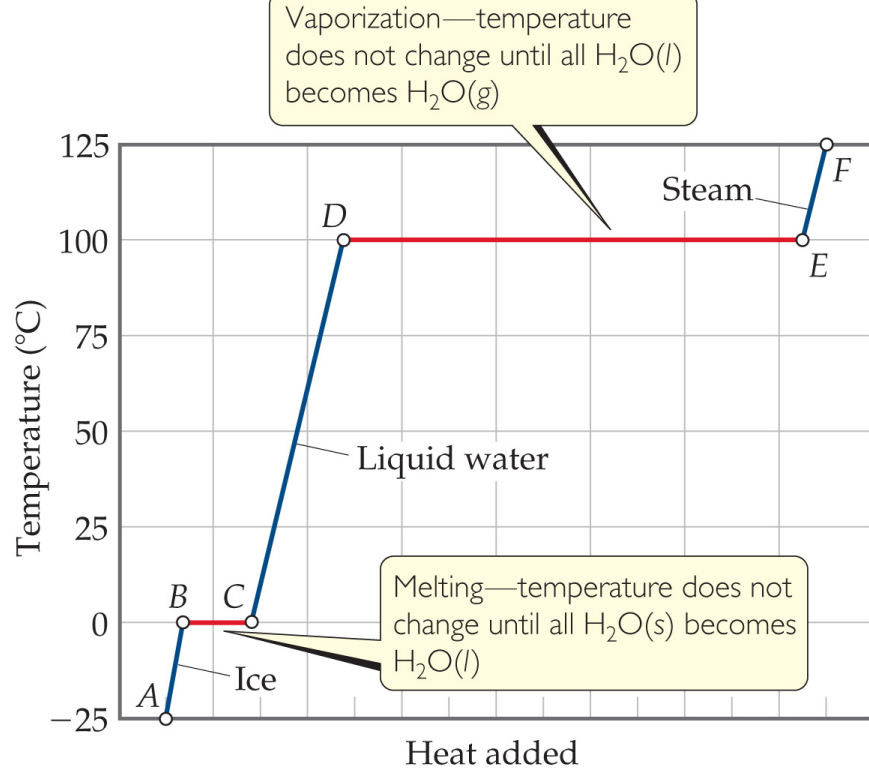

- A plot of T vs. q
- Within a phase:
- $q = ms\Delta T$
- During melting:
- $q = \Delta H_{Fus}m$
- During boiling:
- $q = \Delta H_{vap}m$

- For the phase changes, the product of mass and the heat of fusion or vaporization is heat.

Example:

Vaporization—temperature does not change until all $H_2O(l)$ becomes $H_2O(g)$

Melting—temperature does not change until all $H_2O(s)$ becomes $H_2O(l)$

- Calculate q for taking 10g ice from A to F:

Example:

ΔH_{Fus} water: 334 J/g
Δh_{vap} water: 2444 J/g
s water: 4.184 J/g° K
s ice: 2.05 J/gK
s vapor: 2.00 J/gK

Vaporization—temperature does not change until all $H_2O(l)$ becomes $H_2O(g)$

Steam

Melting—temperature does not change until all $H_2O(s)$ becomes $H_2O(l)$

Liquid water

Ice

Temperature (°C)

Heat added

Example:
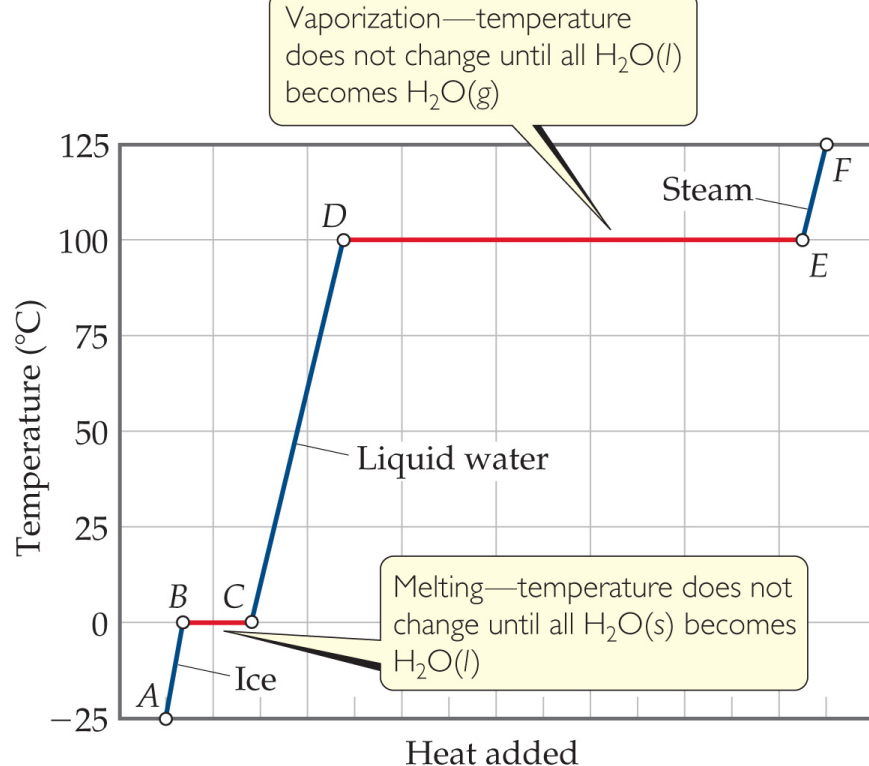
ΔH_{Fus} water: 334 J/g
Δh_{vap} water: 2444 J/g
s water: 4.184 J/g° K
s ice: 2.05 J/gK
s vapor: 2.00 J/gK

- Calculate q for taking 10g ice from A to F:
- A-> B: (10g)2.05J/gK(25 ° C)   =   512.5 J
- B-> C: 10g(334 J/g)   = 3340   J
- C -> D: 10g(4.184 J/gK)(100 K)   = 4184   J
- D -> E: 10g(2444 J/g)   = 24440   J
- E -> F: 10g(2.00 J/gK)(25 K)   =   500   J
- TOTAL   = 32977 J

Energy in Foods

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

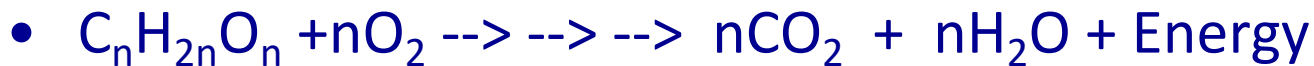| TABLE 5.4 Compositions and Fuel Values of Some Common Foods					
	Approximate Composition (% by mass)			Fuel Value	
	Carbohydrate	Fat	Protein	kJ/g	kcal/g (Cal/g)
Carbohydrate	100	–	–	17	4
Fat	–	100	–	38	9
Protein	–	–	100	17	4
Apples	13	0.5	0.4	2.5	0.59
Beer[*]	1.2	–	0.3	1.8	0.42
Bread	52	3	9	12	2.8
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

[*]Beers typically contain 3.5% ethanol, which has fuel value.

What's the deal with fat?
Note: Your life is one, long slow combustion reaction

- Carbohydrates:
- $C_nH_{2n}O_n + nO_2 \longrightarrow \longrightarrow \longrightarrow nCO_2 + nH_2O + $ Energy

- Fats:

more steps

- $C_nH_{2n}O_2 + mO_2 \longrightarrow \longrightarrow \longrightarrow \longrightarrow \longrightarrow \longrightarrow nCO_2 + nH_2O$
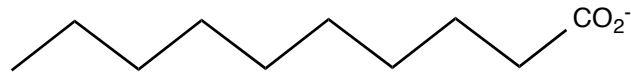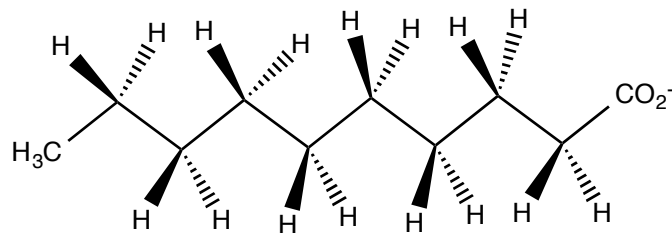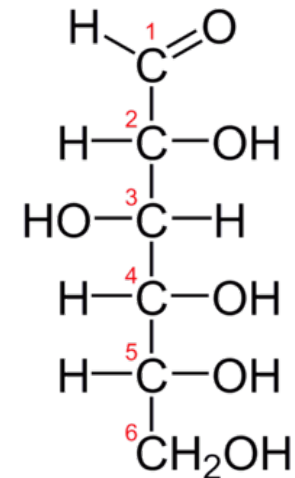
Fat storage.

It also clogs your arteries.

Energy and oxidation states
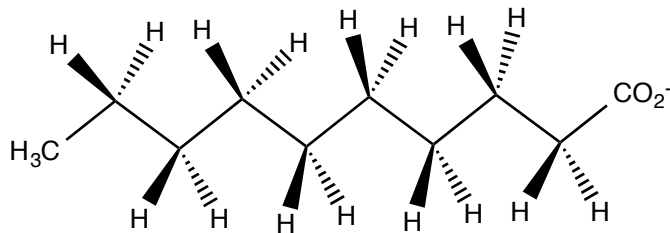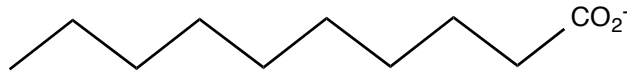
- Oxidation state of C in a fatty acid:

- Oxidation state of C in glucose:

- $C_6H_8O_6$

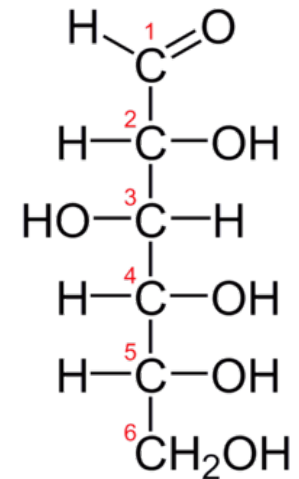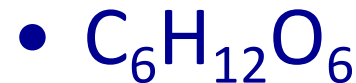# Energy and oxidation states

- Oxidation state of C in a fatty acid:

-3 -2 -2 -2 -2 -2 -2 -2 +3

- Oxidation state of C in glucose:

- $C_6H_{12}O_6$

- O

- Both go to CO_2 C: +4

Fuels

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

U.S. Energy Consumption by Energy Source, 2009
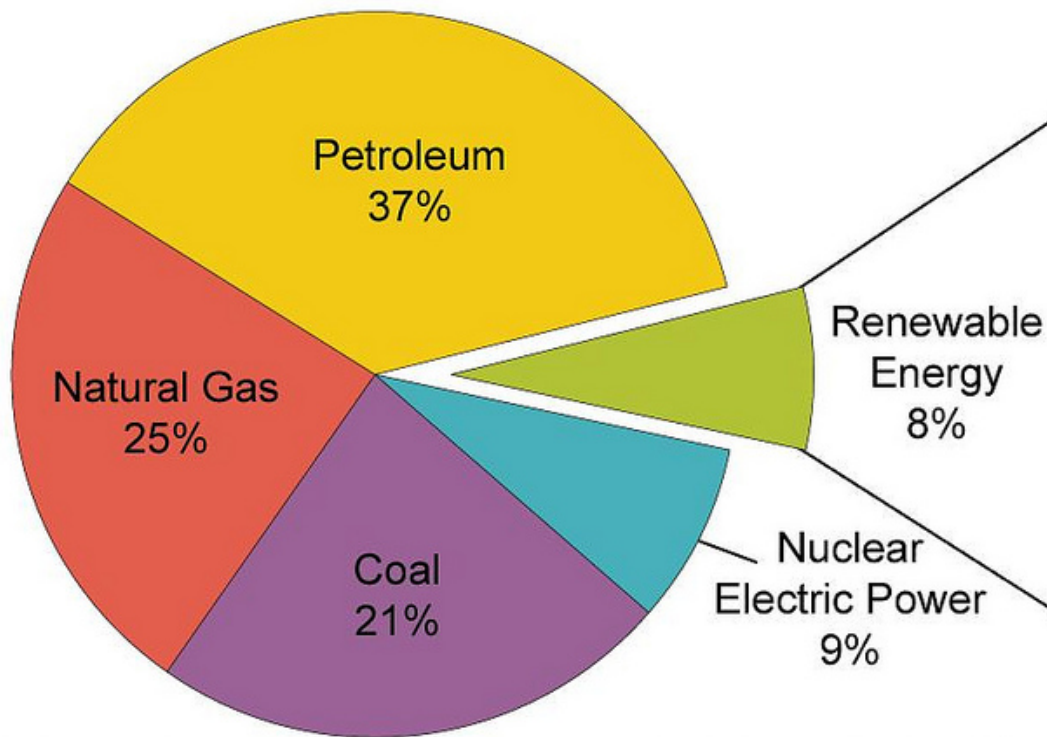
Total = 94.578 Quadrillion Btu

Total = 7.744 Quadrillion Btu

Petroleum 37%

Natural Gas 25%

Coal 21%

Nuclear Electric Power 9%

Renewable Energy 8%

Solar 1%
Geothermal 5%
Biomass waste 6%
Wind 9%
Biofuels 20%
Wood 24%
Hydropower 35%
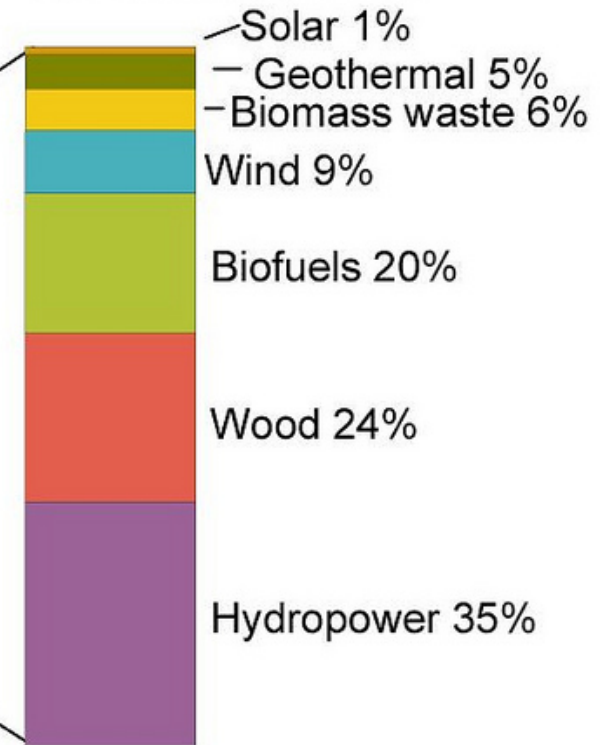
Note: Sum of components may not equal 100% due to independent rounding.
Source: U.S. Energy Information Administration, *Annual Energy Review 2009*, Table 1.3, Primary Energy Consumption by Energy Source, 1949-2009 (August 2010).

Major issues

- Portable fuel (liquid, relatively light), transportation
- Non-portable fuel (makes electricity).

U.S. Energy Consumption by Energy Source, 2009

Total = 94.578 Quadrillion Btu

Total = 7.744 Quadrillion Btu

transportation

Petroleum 37%

Natural Gas 25%

Coal 21%

Nuclear Electric Power 9%

Renewable Energy 8%

Solar 1%
Geothermal 5%
Biomass waste 6%
Wind 9%
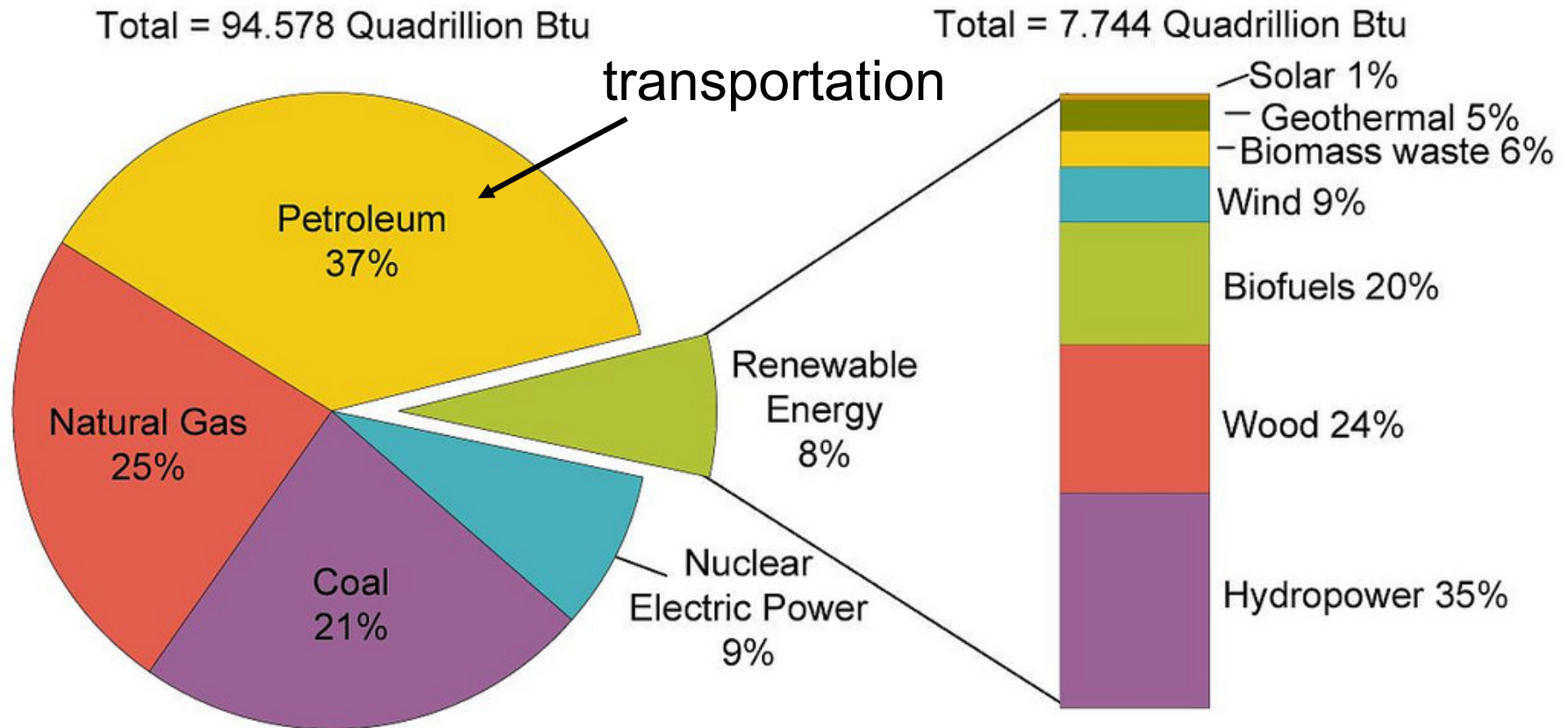Biofuels 20%
Wood 24%
Hydropower 35%

Note: Sum of components may not equal 100% due to independent rounding.
Source: U.S. Energy Information Administration, *Annual Energy Review 2009*, Table 1.3, Primary Energy Consumption by Energy Source, 1949-2009 (August 2010).

The Energy cycle:

- Us (and almost everything else alive on the earth):
- $C_6H_{12}O_6 + 6O_2$ ----> $6CO_2 + 6H_2O$

- Fossil fuel production:
- $CH_4 + 2O_2$ ----> $CO_2 + 2H_2O$ (for methane)

- Plants:
- $6CO_2 + 6H_2O + light$ ----> $C_6H_{12}O_6 + 6O_2$

Net CO_2 production could therefore be 0.

Energy research on Campus
ADREC
Anaerobic digestor

Energy research on Campus
ADREC
Anaerobic digestor

- Anaerobic Digestion:

  bacteria
- $C_6H_{12}O_6 \ ---> \ 3CO_2 + 3CH_4$

Basically:

Poop $---\rightarrow CO_2 + CH_4$

https://www.egr.msu.edu/bae/adrec/feature/south-campus-anaerobic-digester

The problem with oil

- Not "renewable" (will run out)
- Pollution (combustion not perfect).
- Global warming

    CO_2 absorbs heat.

    $C_nH_{2n+2} + (3n+1/2)O_2 \longrightarrow nCO_2 + (n+1)H_2O$

The end of fuel?

https://www.wired.com/story/general-motors-electric-cars-plan-gm/

The end of fuel?

80 — 1977 price $76.67/watt

70

The Swanson effect
Price of crystalline silicon
photovoltaic cells,
$/watt

60

50

40

30

20

10

2013 price $0.74/watt
FORECAST

0

1977 1979 1981 1983 1985 1987 1989 1991 1993 1995 1997 1999 2001 2003 2005 2007 2009 2011 2013

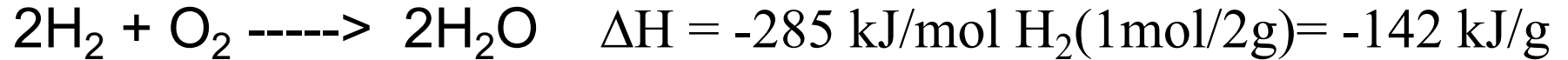Source: Bloomberg, New Energy Finance
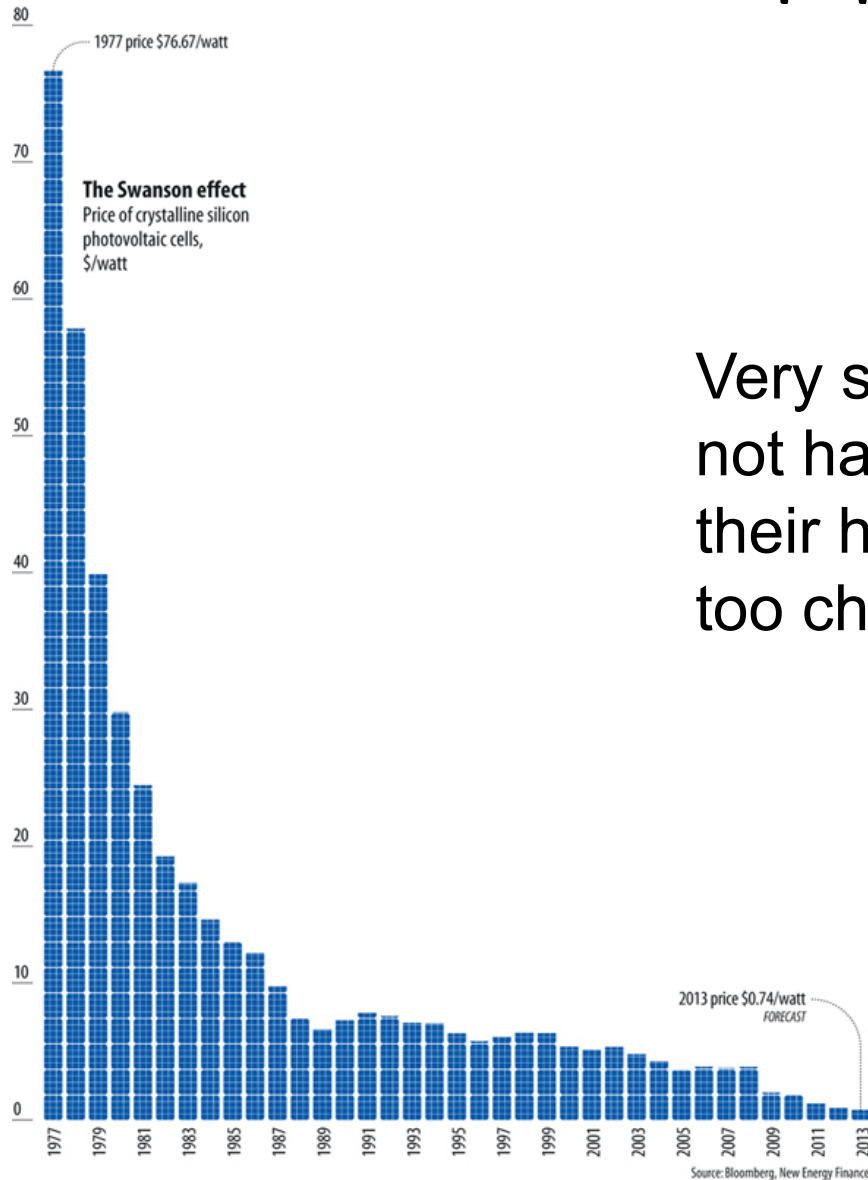
Very soon, only idiots will not have solar panels on their houses. It'll just be too cheap not to.

Battery prices are also plummeting

- https://electrek.co/2017/01/30/electric-vehicle-battery-cost-dropped-80-6-years-227k

Hydrogen, the perfect fuel?

$2H_2 + O_2 \longrightarrow 2H_2O$ $\Delta H = -285$ kJ/mol H_2(1mol/2g)= -142 kJ/g

This is literally what fuel cells do. You get nothing but water!

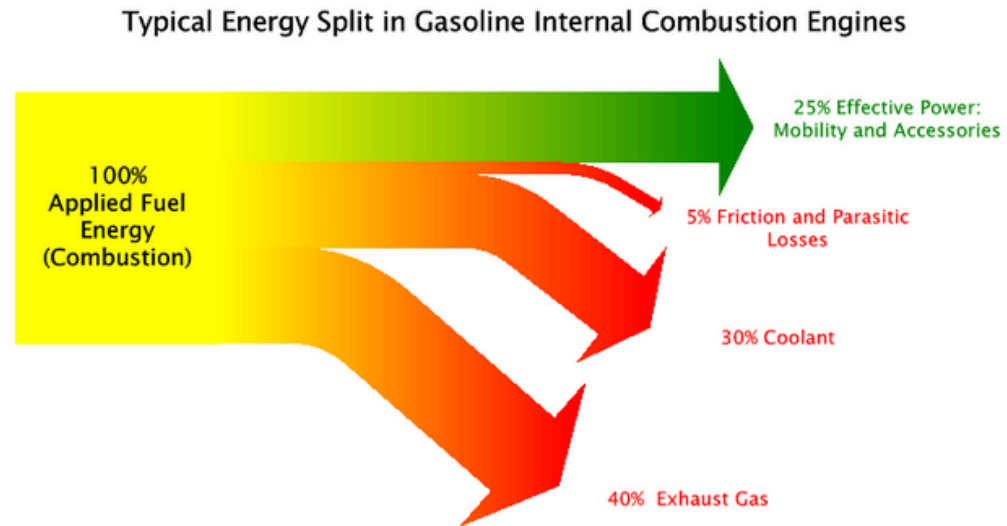# Efficiency/conservation

- U.S. could decrease energy needs by 20-50% by being less wasteful.

- High mileage cars

- more energy efficient building/homes.

Hybrid car

- Gas engine plus electric motor

- Why?

- All the energy is still coming from burning gasoline.

Hybrids

- Electric motors are way more efficient than gas engines. (94%)
- Note, your engine is very hot,
- It must be cooled
- Flush all that E down drain. No work, only heat.

Typical Energy Split in Gasoline Internal Combustion Engines

100% Applied Fuel Energy (Combustion)

25% Effective Power: Mobility and Accessories

5% Friction and Parasitic Losses

30% Coolant

40% Exhaust Gas

gas engines are 24-30% efficient

Problem: batteries suck!
Heavy, expensive, limited recharging cycles,
limited current etc.

Li ion battery

$$x \ e^- + xLi^+ + Li_{1-x}Co(IV)O_2 \ -----> \ LiCo(III)O_2$$

$$Li_xC_6 \ ------> \ xLi^+ + xe^- + C_6$$
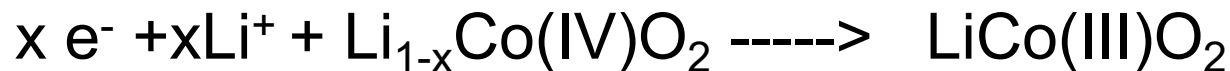
Lithium is really light.
Dissolves in organic solvents which are also light.
Li is at the top of the activity series. Means a higher
potential (more voltage per battery cell)

Hybrids

- Electric motors work at low speeds
- gas engine shuts off when not needed
- at low speeds, stop lights, etc.
- (infinite torque, really go from 0-15)
- Gas engine charges battery and is used at higher speeds
- Hybrids get BETTER gas milage in town versus highway

Other sources
How much bang for your buck?

|	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

The problem with Hydrogen

Storage

gas, less dense, hard to get enough in the car and have trunk space

Kaboom (Hindenburg)

Where do you get the hydrogen?

The problem with Hydrogen

Where do you get the hydrogen? (*petroleum*)

$CH_4(g) + H_2O(g)$ ---$\rightarrow$ $CO(g) + H_2(g)$

$CO(g) + H_2O(g)$ -$\rightarrow$ $CO_2(g) + H_2(g)$
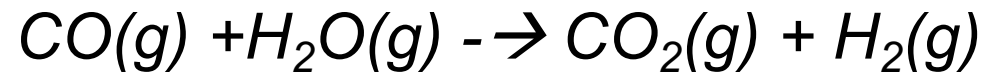
Ethanol, where does it come from

- Alcoholic fermentation:
- $C_6H_{12}O_6$ ----> $2CO_2 + 2C_2H_5OH$ (ethanol) $\Delta H = -76$ kJ/mol
- -1270   2(-393)   2(-280)
- (anaerobic, bacteria & yeast can do this, we can't)

Exactly the same place it comes from in your beer.

Ethanol

- Alcoholic fermentation:
- $C_6H_{12}O_6$ ----> $2CO_2$ + $2C_2H_6O$ (ethanol) $\Delta H = -76$ kJ/mol

  bug

- -1270   2(-393)   2(-280)
- (anaerobic, yeast can do this, we can't) only to 10%.
- Distillation (requires energy) to purify.

Alcohol combustion:

$C_2H_6O + O_2$ ---> $2CO_2 + 3H_2O$ $\Delta H = -1367$ kJ/mol(1mol/46g)=-29.7kJ/g

But why would this be better for global warming?

Ethanol, problems

- Lots of land to grow (yield 2-4 tons/acre)
- All present agricultural land in U.S. would not be enough for all transportation needs.
- requires fertilizer, tractors,etc. for growing (energy)
- Distillation requires energy
- For every 1.4 kJ need 1.0 kJ, much more than oil
- Brazil, however, is approaching 50% ethanol for transportation
- Why? Sugar cane, largest starch or sugar yield/acre.
- But, you can't grow sugar cane on the great plains.

Ethanol

Two major types of carbohydrates in plants
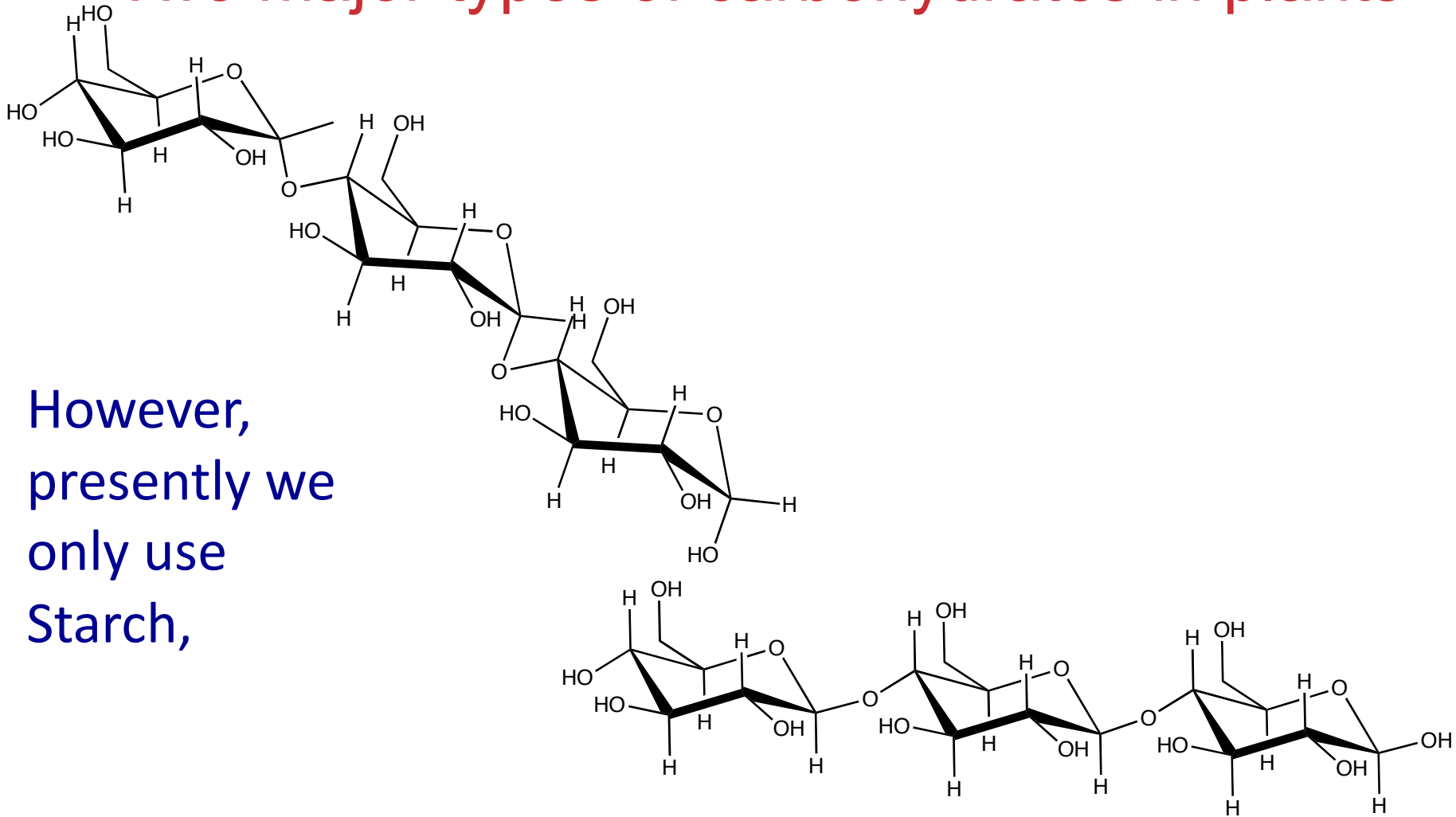
• However, presently we only use Starch,

not cellulose

Most stuff in plants is cellulose

Cellulosic ethanol

- 10+ tons/acre (as opposed to 2-4 tons/acre)
- Can use any crop, not just food crops with high starch ("switch grass").
- Problem: Breaking it down to small sugars that yeast can ferment.
- Need cellulase, the enzyme that breaks this up.
- This is a comparatively easy problem to solve
- (compared to hydrogen.)

Ethanol can work.

Things to consider

- Energy yield (how much E out versus E in)?
- Break even price (how much/gallon of gas equivalents (present corn ethanol is 2.25/gallon just to make).
- Where is the technology NOW?
- Is storage required, & if so, how you gonna do it
- (solar when the sun doesn't shine)
- Remember, at present Batteries suck!

The Chemistry Nobel Prize

- Daniel Shechtman,

- Technion, Israel

- For:

- The discovery of "quasi-crystals" in 1984

The Chemistry Nobel Prize

- An Ho-Mg-Zn quasi-crystal
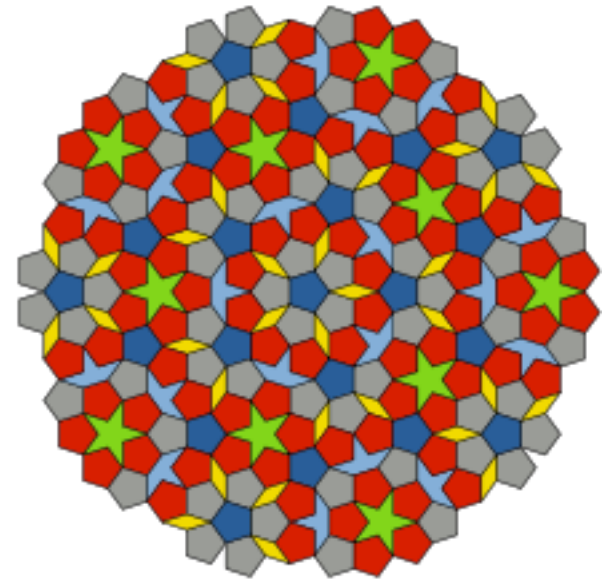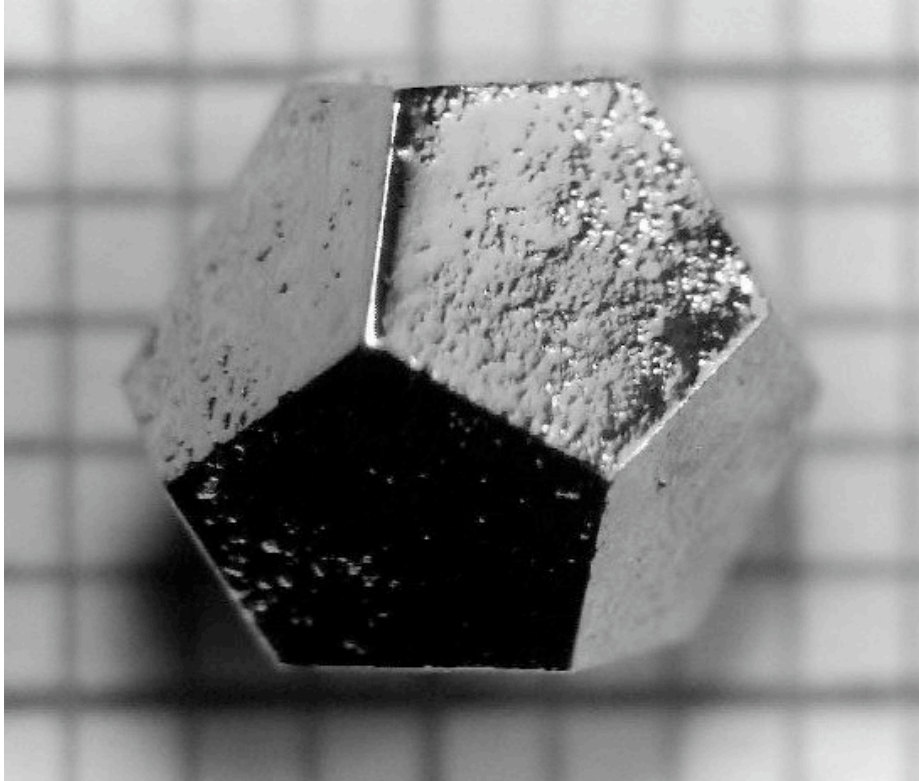
Note, the five-fold symmetry of the faces!
This was thought to be impossible!
Is this a solid?

The Thermite reaction

- $2Al + Fe_2O_3 \text{ -------> } Al_2O_3 + 2Fe$

- What kind of reaction is this?
- Why does it happen?
- Used for welding railroad tracks
- What is the heat of reaction given:

- $2Fe + 3/2 O_2 \text{ -----> } Fe_2O_3 \quad \Delta H = \text{ -825.5 KJ}$
- $2Al + 3/2 O_2 \text{ -----> } Al_2O_3 \quad \Delta H = \text{-1675.7 KJ}$

The Thermite Reaction

- $2Al + Fe_2O_3 \text{ -------> } Al_2O_3 + 2Fe$

- What is the heat of reaction given:

- $2Fe + 3/2O_2 \text{ -----> } Fe_2O_3 \qquad \Delta H = -825.5 \text{ KJ}$

- $2Al + 3/2O_2 \text{ -----> } Al_2O_3 \qquad \Delta H = -1675.7 \text{ KJ}$

- $2Al + 3/2O_2 \text{ -----> } Al_2O_3 \qquad \Delta H = -1675.7 \text{ KJ}$

- $Fe_2O_3 \text{ -----> } 2Fe + 3/2O_2 \qquad \Delta H = 825.5 \text{ KJ}$

- $2Al + Fe_2O_3 \text{ -------> } Al_2O_3 + 2Fe \quad \Delta H = -850.2 \text{ KJ}$

A thermite mystery:

http://www.youtube.com/watch?v=BnHR4cMXiyM